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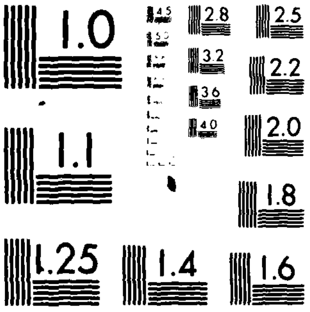

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EVALUATION OF HYDROCRACKING CATALYSTS FOR CONVERSION OF WHOLE SHALE OIL INTO HIGH YIELDS OF JET FUELS

Amoco Oil Company
Research and Development Department
P. O. Box 400
Naperville, Illinois 60566

OCTOBER 1981

FINAL REPORT FOR PERIOD DECEMBER 1979 - OCTOBER 1981

AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEM COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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A catalyst development and screening program has led to a formulation capable of upgrading whole shale oil into high yields of military jet fuel in a single operation. The catalyst is multifaceted in its functionality in that it sequentially saturates, denitrogenates, and hydrocracks the feedstock in the presence of high levels of contaminants, such as organic nitrogen compounds and ammonia, while maintaining a high selectivity towards jet-fuel, boiling range material. The catalyst, developed by optimization of both chemical and

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20. ABSTRACT (continued)

physical properties, consists of 1.5% cobalt oxide, 10% chromium oxide, and 15% molybdenum oxide on a support of 50% ultrastable molecular sieve in alumina. The effectiveness of the catalyst for the direct upgrading of an Occidental whole shale oil was demonstrated in a 100-day test. The feed, containing approximately 15 weight percent material boiling within the range for JP-4 and containing 13,000 ppm nitrogen, was upgraded to a water-white product containing 1 to 3 ppm nitrogen and approximately 75% JP-4 material. The hydrogen consumption required for this level of upgrading and conversion was approximately 1800 SCFB. The catalyst developed represents an advance in shale oil upgrading technology over more conventional petroleum-based technology.

FOREWORD

This report describes work performed by the Catalysis Research Division, Amoco Oil Company, Naperville, Illinois, under Contract No. F33615-79-C-2095 for the United States Department of the Air Force, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio.

Under the contract, the following specific tasks were performed in order to evaluate novel hydrocracking catalysts for the conversion of a whole shale oil into high yields of jet fuel boiling-range material.

A Process Variable Study on Existing Catalysts
A Catalyst Composition Study
A Catalyst Physical Properties Study
and An Activity Maintenance Test

A Catalyst Support Optimization Study was added, by contract modification, after the completion of the composition study, and allowed for additional testing of catalyst types developed during that study.

This final report covers the period from December 1979 to June 1981 and was released by Amoco Oil in August, 1981. The work was performed under the initial direction of A. L. Hensley and later under the direction of A. M. Tait, project managers.

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SUMMARY

Extensive screening of novel catalysts has led to the development of a single catalyst capable of the direct upgrading of whole shale oil into saleable jet fuels on a once-through basis. To maximize jet fuels a catalyst must have the ability to sequentially saturate, denitrogenate, and hydrocrack the feedstock in the presence of high levels of contaminants such as organic nitrogen compounds and ammonia, while maintaining high selectivity towards jet fuel boiling-range material.

An initial brief process variable study indicated that a catalyst consisting of cobalt, chromium, and molybdenum salts on an alumina support could effectively reduce product nitrogen to very low levels at moderate process conditions. The removal of nitrogen is a prerequisite for hydrocracking since cracking sites are effectively poisoned by nitrogen compounds. The required cracking activity was achieved by incorporating an acidic function, in the form of a molecular sieve, into the support.

The final catalyst, developed by optimization of both the chemical and physical properties, consists of 1.5% cobalt oxide, 10% chromium oxide, and 15% molybdenum oxide on a support of 50% ultrastable molecular sieve in alumina. The effectiveness of the catalyst for the direct upgrading of an Occidental whole shale oil was demonstrated in a 100-day test. The feed, containing approximately 15 weight percent JP-4 material and 13,000 ppm nitrogen, was upgraded to a water-white product containing approximately 75% JP-4 material and 1 to 3 ppm nitrogen. The hydrogen consumption required for this level of conversion was approximately 1800 to 1900 SCFB.

The catalyst developed is novel and represents an advance in shale oil upgrading. The screening studies indicate that catalysts can be prepared for the direct conversion of an Occidental shale oil into military fuels at moderate processing conditions. These results could serve as a basis for developing more active catalysts and should be used in a thorough process development and design study to support evaluation of specific commercial projects.

I. INTRODUCTION

In December, 1979, Amoco Oil Company began a 19-month study to evaluate catalysts for the direct upgrading of a whole shale into JP-4 boiling-range jet fuel. The basis of the contract with the Air Force was a proprietary alumina-based catalyst containing cobalt, chromia, and molybdena. The catalyst had previously been developed for processing petroleum feedstocks and was known to have excellent thermal stability. Amoco proposed to use this catalyst for shale oil upgrading initially in a brief process variable study to define broad operating conditions. These results were the basis for a logical and stepwise catalyst development program to maximize jet fuel production from a whole shale oil.

It should be emphasized that this work involved development of catalysts and was not directed towards process development. However, in order to test catalysts, a processing scheme was required and we chose to use a catalyst system capable of direct conversion of a whole shale oil into jet fuel boiling-range material in a single-stage reactor.

The key to successful shale oil upgrading is effective removal of nitrogen contaminants. The key to the development of a single catalyst to maximize jet fuel production is multifaceted in that the catalyst must be capable of sustaining high denitrogenation and desulfurization activities as well as high cracking activity in the presence of large quantities of ammonia. Sufficient saturation activity is required (for contaminants removal, particularly nitrogen) as well as a high selectivity towards jet fuel boiling-range material.

To our knowledge, this study represents the first major work directed specifically at the development of new catalysts for shale oil upgrading. Other major studies have been directed primarily toward process development using conventional catalysts. Chevron (1) used advanced commercial petroleum processing technology to produce gasoline, jet fuels, and diesel from an above-ground-retorted Paraho shale oil. Three likely processing routes were identified and investigated, namely:

Hydrotreating followed by hydrocracking.
Hydrotreating followed by catalytic cracking.
Coking followed by hydrotreating.

Of the three, the hydrotreating/hydrocracking case offered the most flexibility and was the only scheme to efficiently maximize jet fuel production. The initial hydrotreating step at 0.6 LHSV, 2200 psig and 767°F produced product nitrogens of ~500 to 1000 ppm with a hydrogen consumption of ~2000 SCFB. Recycle hydrocracking of the 650°F+ vacuum gas oil from the hydrotreated product required an additional 1300 SCFB hydrogen.

More recently, UOP Incorporated (2) studied the upgrading of an in-situ generated Occidental whole shale oil and concluded that the preferred processing scheme also involved hydrotreating followed by hydrocracking. Preliminary results are also available for the more complex upgrading schemes developed by Ashland (3) and Suntech Incorporated (4).

II. CONTRACT OBJECTIVES AND SCOPE OF WORK

The work performed under this contract was concerned with an evaluation and subsequent optimization of a catalyst, previously developed by Amoco Oil Company, for upgrading a whole shale oil. The objective was to identify the combination of catalyst physical and chemical properties which would maximize:

(a) Conversion of raw crude shale oil to material in the jet fuel boiling range.

(b) Desulfurization and denitrogenation.

(c) Catalyst activity and activity maintenance in order to reduce the cost of processing whole shale oils.

To achieve the overall objective, four specific tasks were originally defined. These were:

(1) A Process Variable Study on Existing Catalysts

(2) A Catalyst Composition Study

(3) A Catalyst Physical Properties Study

(4) An Activity Maintenance Test

The Catalyst Composition Study involved the preparation and testing of catalysts with the active metals systematically varied and of catalysts on different types of supports. Results for the latter indicated a promising advance in catalyst activity for both jet fuel production and nitrogen removal could be achieved by changes in the support type. Subsequently, Amoco Oil requested and received approval to modify the original contract to more thoroughly investigate this aspect. The added task was defined as Catalyst Support Optimization Study.

III. CATALYST AND PILOT PLANT STUDIES

1. General

The feed used throughout this study was an Occidental shale oil. Two barrels, dewatered and deashed, were received from UOP Incorporated, and the contents transferred to five-gallon storage containers. No special precautions were taken except that the containers were sealed and stored in a cold room at 40°F. Each container, once opened, was kept at room temperature without nitrogen blanketing.

Properties of the feed as received are shown in Table 1. The major organic components were analyzed in triplicate with each set being normalized. The average values of the three sets are shown in the right-hand column and were used in all data manipulations. The feed consisted of mainly distillate (360°-650°F) and heavy gas oil (650°F+) with approximately 13 weight percent resid (1000°F+) and approximately 2 weight percent naphtha (360°F-). Simulated distillation data are shown in Figure 1.

The nitrogen content of 1.32% is low for shale oils, but still significantly higher than that found in petroleum crudes. The oxygen content is also high, but the sulfur content is similar to that of petroleum light crudes. The nitrogen and sulfur contents of the feed, as a function of the various fractions, are shown in Figure 2. As expected, nitrogen content increases with boiling point, whereas the sulfur distribution indicates highest sulfur content in the 360°F- and 1000°F+ fractions.

The major metal contaminants were arsenic, 26 ppm, and iron, 61 ppm, with approximately 10 to 12 ppm nickel, sodium, and calcium. Other minor contaminants, all in the <5 ppm range, were Al, Co, Cu, Mg, Mn, Mo, Si, V, Zn, Pb and Cu.

All processing schemes for upgrading whole shale oils normally incorporate an arsenic removal step. Arsenic is known to be detrimental to catalyst performance either by poisoning of active sites or by plugging catalyst pores or catalyst beds. However, for this work the feed was not pretreated to remove arsenic nor was a guard chamber used in the catalyst screening runs. The short time period and the low feed rates used were not expected to result in a significant accumultion of arsenic on the catalyst. For the three longer runs of over 40 days, there was no indication of catalyst bed plugging or activity loss due to arsenic deposition.

Operating conditions and data for all catalyst screening runs and the activity maintenance test are detailed in Tables 2 through 35. Comparative data are highlighted throughout the text. For the tables, metal oxide loadings on catalyst have been designated in an abbreviated form. For example, the notation 1.5/10/15 implies metal oxide loadings, in order, of approximately 1.5% CoO, 10% Cr_2O_3, and 15% MoO_3 for the fresh, unsulfided catalyst. The support, in this example, would constitute the remaining 73.5 weight percent of the total catalyst.

Several appendices contain information on the Research Technical Plan, Work Schedule, Process Unit Operations and Procedures, Analytical Methods, Catalyst Preparations and Properties, Activity Maintenance Test Process Highlights, Simulated and Bulk Distillation Data, Catalyst Digisorb Plots and on Catalysts Containing Nickel.

2. Task 1. Process Variable Study

"The contractor shall determine separately the effects of feed rate (liquid hourly space velocity, LHSV), pressure, and temperature. This shall be done by changing one variable while keeping the others constant. Material balances shall be measured at each set of conditions after the catalyst has been lined out. Samples shall be analyzed. A minimum of ten runs shall be done."

This task, as just defined, was based on the original proposal to use a previously developed catalyst, 1.5% CoO, 10% Cr_2O_3, 10% MoO_3 on alumina* (3609-162), as a basis for the catalyst development program to upgrade an Occidental shale oil into jet fuel boiling-range material. The actual catalyst used was from an experimental batch prepared by a commercial catalyst manufacturer.

One requirement for the direct hydrocracking of the whole shale oil was effective removal of nitrogen. Since the activity of the CoO, Cr_2O_3, MoO_3 catalyst (Co/Cr/Mo) for nitrogen removal was not known, Task 1 was modified in order to test a two-catalyst system. Equal volumes of a NiO, MoO_3, P on alumina catalyst (3.8% NiO, 15.2% MoO_3, 1.5% P, Ni/Mo/P) and the Co/Cr/Mo on alumina catalyst were used. Previous proprietary results had indicated that the former catalyst had excellent denitrogenation activity for shale oils.

Data for these two process variable studies are detailed in Tables 2 and 3. Base conditions for the single-catalyst system were 790°F, 1800 psig, and 0.55 LHSV. The processing extremes were 1400 and 2400 psig for pressure, 770°F and 810°F for temperature, and 0.27 and 0.97 for space velocity. The conditions for the two-catalyst system were similar to those just given except that the first bed containing the Ni/Mo/P catalyst was always held at 735°F, with only the second bed temperature varied and, because of compressor limitations for the screening unit used for the two-catalyst system study, only two pressures, 1400 and 1800 psig, were investigated.

Comparison of the data indicates that for each set of process conditions studied, the performance of the single-catalyst system was superior. Product gravities were one to two units higher, product nitrogen, sulfur, and viscosities were lower, and conversion to 650°F- fraction was higher. The superior product qualities resulted in a slightly higher consumption of hydrogen.

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*For convenience, catalysts are discussed in terms of the metal oxides. The active species are primarily the metal sulfides.

The data summarized below illustrates these differences for mass balance periods at base conditions at the beginning and end of each run.

	NiMoP+ CoCrMo		CoCrMo	
Temperature, °F	735/790		790	
Pressure, psig	1800		1800	
LHSV, Vo/Vc/Hr	0.5		0.55	
Period	10	48	5	43
API°	37.2	36.2	39.4	39.1
Nitrogen, ppm	261	775	87	376
Sulfur, ppm	229	280	334	100
Pour Point, °F	75	70	80	75
Viscosity (104°F), cst	5.03	4.70	3.61	3.28
650°F-, Wt%	66.1	69.2	73.5	78.3
JP-4, Wt%	31	32	37	43
SCFBH	1220	1130	1395	1320

Although both catalyst systems maintained high levels of nitrogen and sulfur removal (approximately 95% or better) over the run periods, some deactivation for nitrogen removal occurred. Despite this deactivation, both systems maintained high conversion to 650°F- fraction and constant levels of JP-4 boiling-range material. Values for product sulfur, pour point, viscosity, and API gravity all remained steady.

The poorer product qualities for the two-catalyst system are a reflection of the low temperature, 735°F, maintained for half of the total catalyst system, i.e., the Ni/Mo/P section. As indicated previously, the Ni/Mo/P catalyst had excellent denitrogenation activity and this is indicated in the run data for the first four days in Table 3. For this period, the Co/Cr/Mo part of the bed was held at 300°F with the Ni/Mo/P catalyst used to process the feed at 735°F, 1800 psig and 0.5 LHSV. Product nitrogen at 65 ppm was roughly equivalent to the single-catalyst Co/Cr/Mo system operating at 1800 psig, 0.55 LHSV but at a much higher temperature of 790°F (Table 2, days 1 through 5).

Kinetic results for the single-catalyst Co/Cr/Mo system are shown in Figures 3 and 4. Using data for the first fourteen days on stream, the results show good first-order kinetics for nitrogen removal. Above approximately 99% nitrogen removal (approximately 100 ppm N), some deviation from first-order kinetics was apparent. Nitrogen removal was also found to be dependent upon total pressure to the first power. For this plot, the data were corrected for catalyst activity loss as determined at base conditions, according to Figure 5. Kinetic data for the two-catalyst system were not obtained because of the constant lower temperature maintained for half of the catalyst system.

Relative activities for nitrogen removal for both systems are shown in Figure 5. The plots are based on first-order kinetics with data points at base conditions being plotted. The single-catalyst system was assigned an activity of 100 for the averaged product nitrogen for days 2 through 5. The comparison shows that both systems deactivated rapidly and smoothly and that the single-catalyst Co/Cr/Mo system maintained the higher activity for nitrogen removal over the 40- to 50-day run periods. These high deactivation rates are typical of tests with extreme and rapid changes in process conditions. The smoothness of both curves suggests, however, that no particular combination of process variables was directly responsible for the deactivation for nitrogen removal.

Figure 6 shows the correlation between product nitrogen and hydrogen consumption for both systems for mass balance periods under all process conditions. Although the dual-catalyst system was less active for nitrogen removal, hydrogen consumption for equivalent product nitrogen was 60 to 100 SCFB lower than for the more active single-catalyst system. This is due to less saturation activity as a result of the lower average temperature used for the dual-catalyst system.
From Figure 6, an estimate can be made for the hydrogen consumption required for saturation and cracking of olefins and aromatics only, excluding the hydrogen consumed in saturation/cracking reactions required to remove nitrogen and produce ammonia. This value is about 1050 SCFB for both systems.

3. Task 2. Catalyst Composition Study

"The contractor shall use the data generated in the Process Variable Study to select conditions (LHSV, pressure, and temperature) for catalyst screening. A minimum of eight runs shall be done.

"The contractor shall prepare catalysts with each hydrogenation metal systematically varied. Each catalyst shall be analyzed for metal content, surface area, pore volume, and pore size distribution.

"The contractor shall test each catalyst to determine its operating performance as follows: After line-out to obtain constant operating conditions, a material balance shall be performed. Samples shall be analyzed. Hydrogen balance shall be calculated based on analysis of feed and products.

"The contractor shall use the data from the previous runs to determine the optimum concentration of each of the hydrogenation components. Catalysts shall be prepared at these optimum concentrations on supports varied to evaluate the effects of support on activity. These shall be tested as above."

Results from the Process Variable Study indicated that by itself the Co/Cr/Mo catalyst was capable of upgrading a high nitrogen feedstock to a product of very low nitrogen content at reasonable process conditions. This previously untested ability and the other advantages mentioned previously over the two-catalyst system dictated that the remainder of the work be based upon the single-catalyst system.

For the metals optimization study, a commercially available alumina extrudate was chosen for the catalyst support. Physical properties of this alumina were similar to those of the support for the Co/Cr/Mo catalyst used in the process variable study. A series of catalysts were prepared in which the metal concentrations, calculated as oxides, were varied in accordance with the nominal compositions as follows:

Weight Percent Metal Oxide		
CoO	Cr_2O_3	MoO_3
1.5, 3.0, 5.0	10.0	10.0
1.5	5.0, 10.0, 15.0	10.0
1.5	10.0	5.0, 10.0, 15.0

These catalysts were tested in short screening runs at 780°F, 0.5 LHSV, and 1800 psig. Tables 4 through 10 give the data for these studies.

The effect of molybdenum oxide concentration on initial product nitrogen is shown in Figure 7 using the results from day three of each run. At constant CoO and Cr_2O_3 concentrations of nominally 1.5 and 10.0 weight percent respectively, the effect of increasing MoO_3 concentration from approximately 5 to 15 weight percent was to decrease product nitrogen from approximately 430 ppm to less than 100 ppm. The curve suggests that MoO_3 loadings greater than about 15 weight percent would not result in a significant improvement in initial denitrogenation activity.

Relative activities for nitrogen removal for the three catalysts with different MoO_3 loadings are shown in Figure 8 for each run period. For this and the other activity curves discussed subsequently, the 1.5% CoO/10% Cr_2O_3/10% MoO_3 (1.5/10/10) system was considered the base case and was assigned an activity of 100 (corresponds to 145 ppm product nitrogen as average lined-out activity, run AU-27-127, Table 5). The catalyst with the lowest MoO_3 loading was decidedly less active and had a high activity decline rate, whereas the highest MoO_3 loading led to increased activity and good activity maintenance.

Similar plots for variation in CoO concentration at constant Cr_2O_3 and MoO_3 loadings are shown in Figures 9 and 10 which indicate that both the high and low CoO loadings (approximately 5 and 1.5 weight percent) resulted in similar activities. The catalyst containing 1.5% CoO maintained better activity for the test period.

Figures 11 and 12 show comparable results for variation in Cr_2O_3 concentration at constant CoO and MoO_3 loadings. While a loading of approximately 5 weight percent Cr_2O_3 resulted in highest activity, the decline rate was rapid. Figure 11 indicates that even lower product nitrogens could be obtained by eliminating the chromium active species. However, past experience has indicated that the high temperature stability of the resultant CoMo catalyst might be suspect with the catalyst possibly undergoing rapid deactivation.

These results indicated that for nitrogen removal, the most effective metals loading on an alumina support was 1.5% CoO, 10% Cr_2O_3 and 15% MoO_3. The second phase of this composition study was to determine the most effective support. Because of time limitations, catalysts on various supports were prepared and some tested prior to complete evaluation of the metals optimizaton studies. Consequently, these catalysts were prepared to contain 1.5% CoO, 10% Cr_2O_3 and 10% MoO_3, i.e., a lower-than-optimum molybdenum oxide concentration.

Catalysts were prepared on silica, alumina/alumina phosphate, silica/alumina (20% silica), and sieve/alumina (30% Ultrastable Y sieve) supports. The silica and silica/alumina supports were available from commercial manufacturers. The alumina/alumina phosphate support was a proprietary Amoco support prepared by a manufacturer, whereas the 30% US sieve/alumina support was formulated at Amoco.

Data for these screening studies are given in Tables 11 through 14. Plots of relative activities for nitrogen removal versus days on oil are shown in Figure 13. The alumina-supported catalyst was assigned an activity of 100 as the base case The effect of support type on denitrogenation activity was dramatic and appeared to parallel the relative support acidities. Thus the nonacidic silica system had only 30 activity with a rapid decline rate, the alumina/alumina phosphate system had an activity comparable to the alumina system but with a greater decline rate, whereas the two more acidic catalysts displayed activities greater than 150.

Pertinent data from mass balance periods for each system are summarized as follows for comparison.

Product Qualities

Catalyst Support*	Nitrogen, ppm	Pour Point, °F	650°F-, Wt%	JP-4, Wt%	SCFBH
Alumina	145	75	75.5	38	1390
Alumina/ Alumina Phosphate	164	70	70.4	36	1365
Silica	3330	80	67.5	29	1080
20% Silica/Alumina	20	70	72.0	37	1340
30% US Sieve/ Alumina	12	55	84.2	58	1560

The sieve/alumina supported catalyst gave the first indication of the required high cracking activity for JP-4 production. The product, by simulated distillation, contained approximately 84 weight percent naphtha and distillate or 650°F- fraction, and a significant 58 weight percent JP-4 jet fuel boiling-range material (90% distilled at not more than 470°F and 20% distilled at not more than 290°F). By comparison, the feed contained approximately 48 weight percent 650°F- fraction, but only approximately 15 weight percent of a heavy JP-4 fraction. The chemical hydrogen consumed for the sieve/alumina system was calculated as a moderate 1560 SCFB for the high-quality "water-white" product.

Because these catalysts on different types of supports were prepared and tested while the metals optimization studies were in progress, they did not contain the optimum concentration of 15 weight percent molybdenum oxide. To verify the increased activity for the 20% silica/alumina and 30% US sieve/alumina supported catalysts, additional tests were conducted on these two supports with the optimum metals loadings.

Data for these tests are given in Tables 15 and 16. Relative activities, plotted versus days on oil, are shown in Figure 14. For comparison, results for the optimum metals loading on alumina are also shown, all three curves being relative to the base case 1.5/10/10 alumina catalyst with 100 activity. The plots verify the increase in denitrogenation activity expected for higher MoO_3 loadings. As well, the 1.5/10/15 sieve/alumina system maintained high conversion activity, yielding 82 weight percent 650°F- fraction after twelve days on oil.

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*Metals loadings were nominally 1.5% CoO, 10% Cr_2O_3 and 10% MoO_3.

4. Task 3. Catalyst Support Optimization Study

"The contractor shall use the data generated in the Composition Study to select conditions and catalysts for support optimization. A minimum of eight catalyst-support combinations shall be prepared.

"The contractor shall prepare catalysts on not less than three different types of molecular sieve dispersed-on-alumina supports. The contractor shall prepare catalysts on not less than three silica-alumina supports, each support with a different silica-to-alumina ratio.

"The contractor shall test each catalyst to determine its operation performance as follows. After line-out to obtain constant operating conditions, a material balance shall be performed. Samples shall be analyzed. Hydrogen balance shall be calculated based on analysis of feed and products.

"Analysis, data collection and evaluation to be performed as in previous tasks. Research samples to be provided."

In view of the significant improvements in nitrogen removal obtained with the silica/alumina and sieve/alumina supported catalysts, Amoco requested a contract modification to more thoroughly investigate the effects noted. Task 3 reflects this modification.

Initially, catalysts with the optimized metal loadings (1.5/10/15) were prepared on supports containing 10, 30, 50, and 70 weight percent silica. Data for the catalyst screening runs at 780°F, 1800 psig and 0.5 LHSV are detailed in Tables 17 through 20. Product nitrogens versus days on oil are shown in Figure 15 for these silica/alumina catalysts along with the pure silica 1.5/10/10 catalyst. As indicated previously, activities for nitrogen removal were 30 for the silica based catalyst (Figure 13) and approximately 160 for the 20% silica/alumina catalyst (Figure 14) relative to 100 for the 1.5/10/10 alumina base case catalyst.

As summarized in the following table, for the mass balance periods, silica contents in the 20 to 50 weight percent range resulted in product nitrogens lower than the comparable alumina system, whereas the 70 weight percent silica/alumina catalyst gave product nitrogens tending towards those obtained with the pure silica based catalysts. This trend for the mass balance periods is shown in Figure 16.

Product Qualities

Support[1]	Nitrogen, ppm	Pour Point, °F	650°F-, Wt%	JP-4, Wt%	SCFBH
Alumina	83	80	76	38	1400
10% Silica[2]	100	--	--	--	--
20% Silica	8	65	76	38	1400
30% Silica	30	65	72	36	1435
50% Silica	20	75	72	36	1360
70% Silica	770	70	68	32	1260
100% Silica[3]	3330	80	60	29	1030

The overall product qualities indicated that the 20% silica/alumina system was the most active of these catalysts with denitrogenation activity better than, and cracking activity comparable to, the 1.5/10/15 alumina supported catalyst. Hydrogen consumption required to reduce nitrogen in the product to <30 ppm was a moderate 1400 SCFB or approximately 300 SCFB above that required for pure olefins/aromatics saturation.

For the second phase of the Support Optimization Study, catalysts with optimized metals loadings were prepared on supports containing 20 weight percent molecular sieve. The sieves used were: H-ZSM-5, RE-Y (a rare-earth-exchanged Y-type sieve), H-Zeolon, and a proprietary Amoco borosilicate molecular sieve, H-AMS. Screening data at 780°F, 1800 psig and 0.5 LHSV are detailed in Tables 21 through 24.

Product nitrogens versus days on oil are plotted in Figure 17 for these catalysts along with the data for the previously tested 30% US

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[1] Nominal metals loadings of 1.5% CoO, 10% Cr_2O_3 and 15% MoO_3.

[2] Unit upset during mass balance periods.

[3] Contained 10% MoO_3 instead of 15% MoO_3.

sieve/alumina system. Of the catalysts containing 20% sieve, only the 20% H-AMS system showed high activity for nitrogen removal with good activity maintenance (excluding a unit upset) over the test period.

Comparative data are summarized in the following table for the mass balance periods.

Product Qualities

Support*	Nitrogen, ppm	Pour Point, ^{o}F	$650^{o}F-$, Wt%	JP-4, Wt%	SCFBH
30% US	<10	30	87	60	1660
20% H-AMS	5	-60	83	48	1610
20% H-Zeolon	57	65	72	36	1450
20% RE-Y	31	75	71	35	1410
20% H-ZSM-5	34	-10	80	46	1500

Use of the shape-selective sieves, H-AMS and H-ZSM-5, resulted in significant pour point reductions due to selective long-chain paraffin cracking. These latter two systems gave highest $650^{o}F-$ fraction and highest yields of JP-4 boiling-range material of approximately 46 to 48 weight percent.

However, as indicated in the summary table, the US sieve-containing catalyst, albeit at the 30 weight percent level, gave the best yield of $650^{o}F-$ fraction and a significantly higher yield, 60 weight percent, of JP-4 material. Although a 20% US sieve-containing catalyst had not been tested in the time frame of this study for strict comparison, the superior performance of the US sieve-containing catalyst combined with the greater cost of the next best system, i.e., 20% H-AMS in alumina, dictated that the US sieve be used to optimize the sieve content in the next phase of Task 3.

Additional catalysts were prepared on supports containing 20 and 50 weight percent US sieve in alumina with the optimum metals loadings. Screening data at $780^{o}F$, 1800 psig, and 0.5 LHSV are detailed in Tables 25 and 26. Figure 18 compares product nitrogen versus days on oil for

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*Balance of support was alumina.

the 20%, 30%, and 50% US sieve/alumina catalysts. For nitrogen removal, the 20% US sieve system had lowest activity and deactivated to a level equivalent to the previously discussed nonsieve-containing 1.5/10/15 alumina based catalyst (Table 6). Sieve loadings of 30% and 50% resulted in lower product nitrogens, although the values were somewhat scattered for the 50% sieve system.

Data for initial catalyst performance, taken from the mass balance periods, are summarized in the following table.

	Product Qualities					
Support*	Nitrogen, ppm	Pour Point, °F	650°F-, Wt%	JP-4, Wt%	C_1-C_4, Wt%	SCFBH
20% US Sieve	28	65	76	42	3.7	1490
30% US Sieve	<10	30	87	60	3.6	1660
50% US Sieve	3	-15	95	77	6.0	1870

All product qualities improved significantly with increasing sieve content with hydrogen consumptions reflecting the increasing activity.

Figure 19 plots the effect of sieve content in the support on fractional distillate yields. The fraction designated "diesel" was taken as the difference between the JP-4 fraction (90% distilled at 470°F) and the 650°F+ gas oil. For comparison, the results for the nonsieve-containing alumina based 1.5/10/15 system are also shown. The curves indicate that the addition of up to 20% sieve to an alumina support had little effect on distillate yields (and on product nitrogen, as previously indicated, or hydrogen consumption, Figure 20). Above a 20% sieve content, JP-4 yields increased significantly whereas the diesel and gas oil fractions decreased in a parallel manner. At the 50% sieve level, approximately 95% of the product boiled below 650°F. The C_1-C_4 gas-make increased slightly with sieve content.

A correlation between JP-4 yields and hydrogen consumption is given in Figure 20. The four data points represent 1.5/10/15 catalysts containing

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*Balance of support was alumina.

0%, 20%, 30%, and 50% US sieve. At the highest conversion, the hydrogen consumed begins to increase at the expense of JP-4 yields and the curvature suggests a limit of approximately 80% JP-4 boiling-range material could be produced on a once-through basis before recracking would reduce JP-4 yields.

Activities for cracking for the three sieve/alumina supported catalysts are illustrated in Figure 21 which plots estimated JP-4 yields for each system on a daily basis. The 20% and 30% sieve-containing catalyst both lost cracking activity over the first eight days on oil to give lined-out JP-4 yields of approximately 50 and 33 weight percent respectively. For comparison, the nonsieve-containing alumina based catalyst, Table 6, gave a constant yield of approximately 37 weight percent for the same period of time. The 50% US sieve catalyst maintained a higher activity for JP-4 production and appeared to undergo a less severe loss in activity.

The estimated JP-4 yields used in Figure 21 were obtained from Figure 22, which represents a correlation between JP-4 yields from simulated distillation data and whole product API gravities both for mass balance periods. The solid data points represent all previously tested US sieve-containing catalysts whereas the open points represent all other catalysts previously tested, independent of support type or metals loading, and all 50% US sieve alumina catalysts tested subsequently. The correlation can be represented by:

$$\text{JP-4, Wt\%} = 3.46\ \text{API}^{\circ} - 98$$

Simulated distillation data agreed within one to two percentage points with actual distillation data for all mass balance samples so that Figures 21 and 22 represent actual yields of JP-4 to a high degree of accuracy.*

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*Figure 22 also proved valuable for monitoring catalyst activities on a daily basis for subsequent tasks in view of the delays in obtaining simulated distillation data.

5. Task 4. Catalyst Physical Properties Study

"The contractor shall use the data from the previous runs to select a support composition and the concentration of each hydrogenation metal to give optimum denitrogenation and boiling-range conversion. The contractor shall prepare not less than eight catalysts, each having the selected support composition and concentration of hydrogenation metals, but each with different physical properties. The physical properties to be varied are surface area per unit mass, pore volume per unit mass, and pore size distribution. Each catalyst shall be characterized and tested as in previous tasks. Data from these runs shall be analyzed to identify correlations between catalyst physical properties and performance. A minimum of eight runs shall be done."

Results from the previous task indicated that the 1.5/10/15 catalyst on a 50% US sieve/alumina support was the system of choice for further investigation. The catalyst resulted in low product nitrogens and gave highest yields of JP-4 material with the lowest cracking activity decline rate.

For the previous three tasks, catalyst physical properties, as detailed in Appendix E, were kept within fairly narrow ranges for sets of catalysts within each task except for the various silica/alumina based systems. With the metals optimized, and the support type and composition determined, Task 4 was designed to optimize the support physical properties.

Eight supports, consisting of 50% US sieve in aluminas were prepared to give a range for each of three physical properties as detailed in the following table for the finished catalyst.

Catalyst ID 3838-	Surface Area m^2/g	Pore Volume cc/g	Avg Pore Diameter (4 V/A), °A
023	280.5	0.477	68.0
028	255.2	0.545	85.5
030	222.4	0.505	90.8
031	312.5	0.824	105.4
034	305.0	0.589	77.2
035	276.3	0.784	113.4
037	280.4	0.710	101.3
039	234.0	0.417	71.4

These variations were achieved by modification of the alumina component, since modification of the sieves themselves would destroy their original nature and their inherent activity for cracking. Pore size distributions as a function of pore diameters are detailed in Appendix E for these eight catalysts. Digisorb plots are detailed in Appendix I.

Data for the screening runs at 780°F and 1800 psig are given in Tables 27 through 34. Since the previous tasks had demonstrated that high sieve-containing catalysts could reduce the nitrogen content to less than 10 ppm at 0.5 LHSV, the possibility existed that all eight of the above-detailed catalysts could exhibit similar high nitrogen removal at that space velocity and hence negate the purpose of the task. To avoid that possibility, each catalyst was additionally tested at a higher space velocity. Pertinent data are summarized in the following tables for mass balance periods.

0.5 LHSV

Catalyst ID 3838-	Nitrogen, ppm	Pour Point, °F	650°F-, Wt%	JP-4, Wt%	SCFBH
023	1	-50	92.5	79.5	1930
028	4	35	86.5	62.7	1670
030	600	75	65.6	29.6	1190
031	76	70	72.5	36.8	1390
034	5	55	71.2	50.6	1520
035	46	65	75.6	43.9	1380
037	77	70	74.0	39.9	1360
039	1	40	79.5	57.1	1660

0.75 LHSV

Catalyst ID 3838-	Nitrogen, ppm	Pour Point, °F	650°F-, Wt%	JP-4, Wt%	SCFBH
023	44	75	67.5	33.8	1310
028	1510	75	63.0	30.1	1300
030	1240	75	65.5	29.4	1190
031	985	75	62.6	30.1	1200
034	--	--	--	--	--
035	1950	75	64.5	29.3	1120
037	1560	--	66.4	28.8	1150
039	289	75	60.4	33.3	1260

At constant sieve content, the relationship between JP-4 yield and hydrogen consumption for these eight catalysts is shown in Figure 23 for all mass balance periods. Hydrogen consumption appears to increase linearly with JP-4 yields in the range of approximately 40 to 70 weight percent. (See also Figure 20.) Below approximately 40 weight percent JP-4, hydrogen consumption increased with little increase in product JP-4 probably as a result of saturation reactions required prior to cracking reactions. Above approximately 70 weight percent JP-4, hydrogen usage appears to increase more rapidly than JP-4 content probably as a result of additional long-chain paraffin cracking which in addition reduces product pour point. A relationship between pour point and JP-4 yield for these eight US sieve-containing catalysts is given in Figure 24 which indicates a rapid drop in JP-4 yield for whole products with pour points greater than about 40°F. Data for the 20%, 30% and 50% US sieve catalysts tested previously can also be represented by Figure 24.

The effect of product nitrogen on JP-4 yield is shown in Figure 25. The results indicate that JP-4 yield remained at approximately 30 weight percent for product nitrogen above 600 ppm and increased with decreasing nitrogen content. To produce a product with approximately 50 weight percent JP-4, product nitrogen must be reduced to approximately 10 ppm. Product nitrogen must be virtually eliminated to produce JP-4 yields of approximately 70 weight percent or more. Hydrogen usage to achieve these levels of product nitrogens is shown in Figure 26. About 1550 SCFB of hydrogen was required for 10 ppm product nitrogen (50% JP-4 yield). About 400 SCFB additional hydrogen was required to decrease product nitrogen to near zero and to increase JP-4 yields to 80%. These results are instructive in that correlations important to the overall hydrocracking scheme have been developed within this set of catalysts.

Nitrogen removal kinetic plots for these catalysts are shown in Figure 27. Of the eight catalysts tested, only one, 3838-023, performed well at both 0.5 and 0.75 LHSV with respect to nitrogen removal in particular, conversion, and activity maintenance at the lower throughput. Nitrogen removal for this catalyst appears to be first order as shown in Figure 27, whereas all other catalysts display less than first-order (or mixed-order) kinetics. This type of kinetic behavior is perhaps a reflection upon nitrogen removal efficiency and suggests an axial dependence on nitrogen content, or an accelerating nitrogen removal reaction promoted by the sieve itself.

In general, it is difficult to obtain correlations between the physical properties of catalysts containing molecular sieves and catalyst performance because of the complexity of the systems. Figure 28, however, does reflect a correlation between catalyst average pore diameters (calculated as $4V \times 10^4/A$) and product nitrogen. At 0.75 LHSV, the correlation is reasonable, but is somewhat less so at 0.5 LHSV. Both sets of results indicate that greatest nitrogen removal occurs with the catalysts of smallest average pore diameters. The two best catalysts in the series, 3838-023 and 3838-039, have APD's close to 70°A, but only the former is "efficient" at both space velocities and has the highest cracking activity and best activity maintenance. Comparison of the pore size distributions for these two catalysts indicates a sharper distribution of pores for catalyst 3838-023 when compared to catalyst 3838-039. All other catalysts in this series, with one exception, have broader pore size distributions (Appendix I, Figures I-3 to I-10).

Other catalyst physical properties, namely surface area and pore volumes, did not show any correlation with product nitrogens.

6. Task 5. Activity Maintenance Test

"The contractor shall conduct an activity maintenance test to predict catalyst life and performance.

"The contractor shall use the data from the previous runs to select an optimum combination of catalyst chemical composition and physical properties. Compromises may be made between interrelated optimum properties as necessary in selecting the optimum combination of properties.

"The contractor shall prepare catalysts with the selected optimum combination of chemical and physical properties.

"The optimum catalyst system shall be tested in a two-month run on shale oil at operating LHSV, pressure, and temperature conditions selected to give high yields of material in the jet-fuel boiling range. A complete material balance and elemental analysis of the products shall be performed at intervals not to exceed ten days.

"Products from the run shall be composited, analyzed, and distilled to produce experimental samples of 200 to 500 milliliters in size. The experimental samples shall be analyzed to determine composition and physical properties."

Results from the catalyst physical properties study indicated that for high denitrogenation and cracking activity the preferred support of 50% US sieve in alumina should have pores of average pore diameters near 70°A combined with a high surface area and a sharp pore size distribution. These properties were exemplified in catalyst 3838-023 and also in catalyst 3862-003, tested in the Sieve Concentration Optimization Study. The latter catalyst was prepared by blending the US sieve with an unmodified alumina sol. This method was also used to prepare catalyst 3838-043 used for the activity maintenance test.

Data for this test are detailed in Table 35 and are summarized below for mass balance periods.

Day	3	9	17	19	27	32	39	46	53
Temperature, °F	770.1	770.3	775.6	774.5	777.2	777.1	777.5	777.0	786.0
API°	52.4	48.0	51.2	47.0	48.8	49.2	48.9	42.4	50.3
Nitrogen, ppm	2	1	1	2	1	2	6	11	3
Sulfur, ppm	18	133	728	36	64	92	234	22	60
Pour Point, °F	-30	5	-10	20	-15	-15	20	60	-15
650°F-, Wt%	96.7	87.7	94.4	--	91.1	91.7	88.6	88.6	94.4
JP-4, Wt%	84	68	79	--	72	79	67	49	77
SCFBH	1980	1770	1740	1740	1850	1800	1800	1515	1920

Day	60	67	73	80	87	93	96	101
Temperature, °F	785.5	785.4	786.0	786.0	785.8	785.5	789.7	779.9
API°	48.6	47.4	48.4	48.9	48.1	47.4	50.3	43.8
Nitrogen, ppm	2	15	1	1	30	1	1	10
Sulfur, ppm	36	229	76	70	121	20	85	100
Pour Point, °F	5	10	10	-5	-10	5	-10	55
650°F-, Wt%	89.4	89.3	90.9	91.7	90.2	89.4	93.2	84.5
JP-4, Wt%	70	68	73	73	70	67	76	57
SCFBH	1890	1740	1810	1850	1850	1720	1940	1400

Start-of-run conditions were 0.4 LHSV, 2000 psig hydrogen, and 770°F and were chosen to maximize hydrogenation and hydrocracking reactions while allowing for an increase in reactor temperature in case catalyst deactivation occurred.

In contrast to all other previous tests, the activity maintenance test was subjected to numerous unit upsets during the first 50 days on stream. As a result of some of these upsets catalyst activity was seriously reduced. To compensate, reactor temperature was raised 15°F over the first 48 days on stream to maintain high yields of JP-4 material. The details of the upsets, the compensatory temperature increases, and other actions are detailed in Appendix F.

As a result of these unit upsets, the test was extended to 103 days with processing conditions held constant at approximately 786°F, 0.4 LHSV, and 2000 psig for the periods 49 through 93. For the last ten days, reactor temperature was deliberately raised to 790°F and then lowered to 780°F in order to obtain the cracking temperature response.

Figure 29 shows product nitrogens as a function of days on oil. With the exception of those upsets which affected product nitrogens (shown as solid points), product nitrogens were maintained generally in the 1 to 3 ppm range throughout the test. As indicated previously (Figure 25), 10 ppm product nitrogen would reduce JP-4 yields to approximately 50 weight percent or less whereas a JP-4 yield of $\geq$70 weight percent would require <2 ppm nitrogen in the product. High cracking activity to produce JP-4 is critically dependent upon very low product nitrogen levels.

Daily JP-4 yields, estimated from product API gravities and Figure 22, are shown in Figure 30. The solid points represent upsets affecting JP-4 yields or cracking activity. The following points can be drawn from Figure 30.

(i) For the first ten days on oil at 770°F, cracking activity declined as reflected in the drop in JP-4 yields from approximately 82 weight percent to approximately 68 weight percent.

(ii) The unit upset of day 19 (unit depressurized, subjecting catalyst to high temperature without hydrogen) seriously affected catalyst cracking activity at 775°F as reflected in the drop in JP-4 yields from approximately 80 weight percent to approximately 67 weight percent. This loss in activity was also reflected in the JP-4 yields at 777°F being lower than initially achieved at 775°F.

(iii) The unit upset on day 43 (very little hydrogen flow for 16 hours) also seriously affected cracking activity as evidenced by the poor temperature response upon raising temperatures from 777°F to 786°F.

(iv) At 786°F, over approximately a 50-day period, cracking activity declined steadily as indicated by the drop in JP-4 yields from about 80 to 67 weight percent. This decline may have been affected by the upset on day 65.

In order to calculate catalyst life at a specified JP-4 yield, temperature response factors need to be calculated. This was done by using the data in Figure 31 and the following equation:

$$\Delta E_{1,2} = \ln \frac{A1/LHSV_1}{A2/LHSV_2} \cdot R \cdot \frac{T_1 T_2}{\Delta T}$$

where: $\Delta E_{1,2}$ = temperature response factor difference for temperatures T_1 and T_2

A_1, A_2 = cracking activities for each temperature (°K)

R = gas constant = 1.9872 cal deg^{-1} mole^{-1}

ΔT = temperature range, °K

$LHSV_1$, $LHSV_2$ = space velocities corresponding to constant JP-4 yields

Figure 31 was generated using the data at the end of the test at 785°F (period 93), 790°F (period 96) and 780°F (period 101) assuming zero-order kinetics, no nitrogen inhibition in the actual cracking zone, and constant activity. Hydrocracking reactions in the presence of nitrogen are generally zero order over the total catalyst system and in this case all samples contained <10 ppm nitrogen.

Using a constant JP-4 yield of 50 weight percent, temperature response factors of 62.5, 67.9, and 65.6 Kcal mole^{-1} were calculated for the three temperature couples, the average being 65.4 Kcal mole^{-1}. This value is not unusual for full-range, high-boiling feedstocks containing large amounts of nitrogen.

Based upon the temperature response factor, a catalyst life of approximately four and one-half months can be calculated for a constant JP-4 yield of 75 weight percent by increasing reactor temperature from 775°F to 800°F at 2000 psig and 0.4 LHSV. However, due to the operational problems encountered in the test, this should be considered a minimum life and six months is probable. The deactivation rate of approximately 0.18°F/day was calculated from the data for periods 53 and 93 using zero-order kinetics according to the equation:

$$\frac{E}{R} = \frac{\ln (1-JP_4)_{53} - \ln (1 - JP_4)_{93}}{(1/T_{53} - 1/T_2)}$$

where: $(1-JP_4)_{53}$ corresponds to 75% JP-4 taken for period 53
$(1-JP_4)_{93}$ corresponds to 67% JP-4 observed for period 93

T_{53} *corresponds to the temperature*, $^{\circ}K$, *for period* 53

T_2 corresponds to the temperature required to maintain 75% JP-4 after the 40 days

Within the same constraints, catalyst life would be longer for lower JP-4 yields. As discussed previously, several unit upsets seriously affected catalyst activity and one of these upsets occurred during the period used to calculate the temperature decline rate. Thus, the projected life for constant 75% JP-4 yields should be viewed as a rough estimate. Detailed process variable studies which were not part of this contract would be needed to more accurately define a deactivation rate.

Throughout this activity test, it was noted that the once-through gas rate affected JP-4 yields. Figure 32 shows variations in daily gas rates. Comparison with JP-4 yields, Figure 30, indicates a qualitative correlation between the gas rate and JP-4 yields. Thus, if the gas rate was changed significantly from the prior period, JP-4 yields increased or decreased by up to 10% relative to the prior period. With the small-scale unit used for this study it was extremely difficult to maintain a constant gas rate. The high gas rate of 12 to 16 SCFB was required to ensure stability of unit operation and to act as an effective sweep to remove ammonia.

The data for the distillations of the products from the activity test to produce JP-4 and JP-8 jet fuel fractions are given in Table 36. All samples for periods 1 through 73, with the exception of those samples containing more than 10 ppm nitrogen or having an API gravity less than 45°, were combined to yield approximately four gallons of product. The composite was washed with water and then dried. Two distillations to yield JP-4 and JP-8 fractions were completed. The JP-4 yield was 76 weight percent on the composite product with a JP-8 yield of 61 weight percent. The analytical data indicates that the samples would meet all specifications with perhaps one exception. The pour point of -40°F for the JP-8 fraction is low in view of the freeze point specification of -58°F. However, the simulated distillation data indicates an end point very close to the specified limit. A slightly lower temperature cut point, and perhaps a slightly lower initial point, would lower the pour point and hence bring the freeze point to the specified value.

Based on the qualities measured, with the one exception, saleable jet fuels were produced in high yields by the single-catalyst process.

SECTION IV

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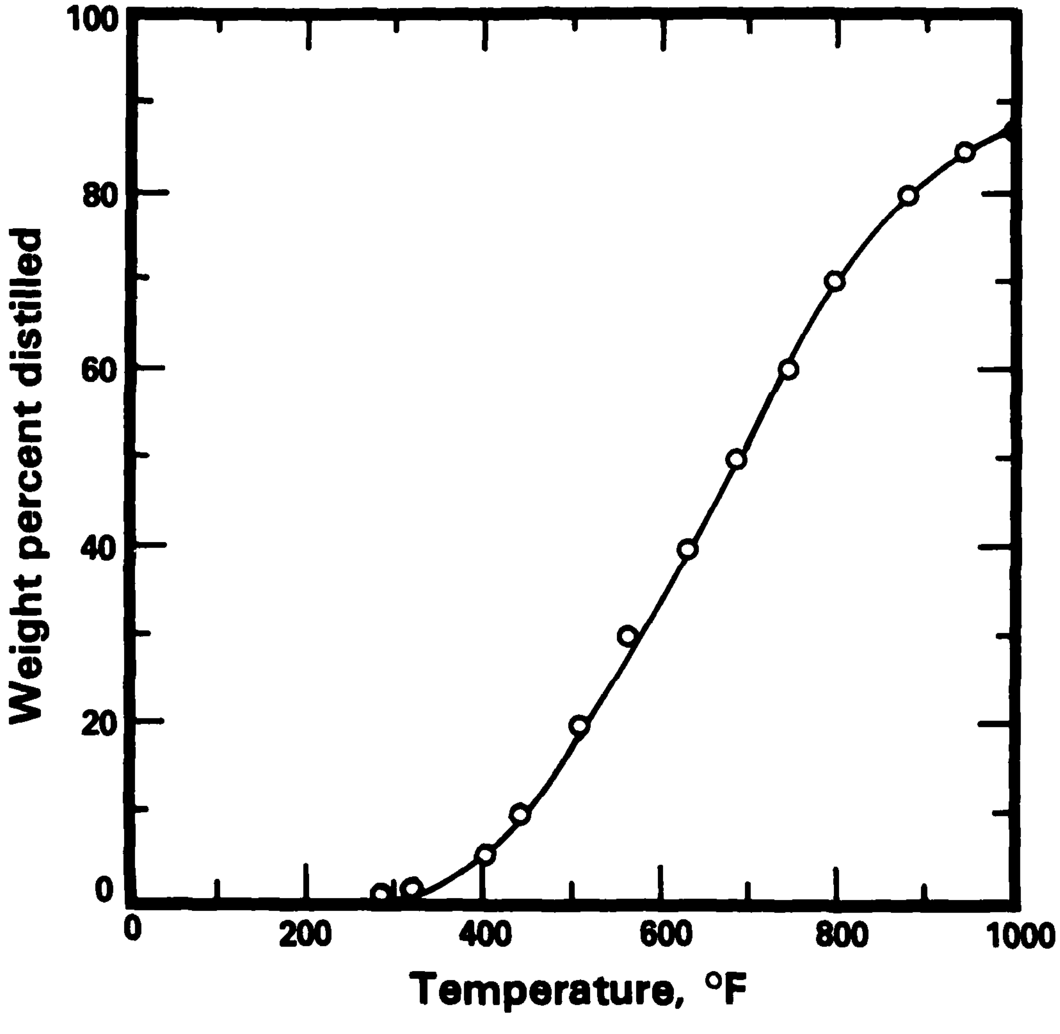

Figure 1 — Simulated Distillation Boiling Point Distribution for Occidental Whole Shale Oil

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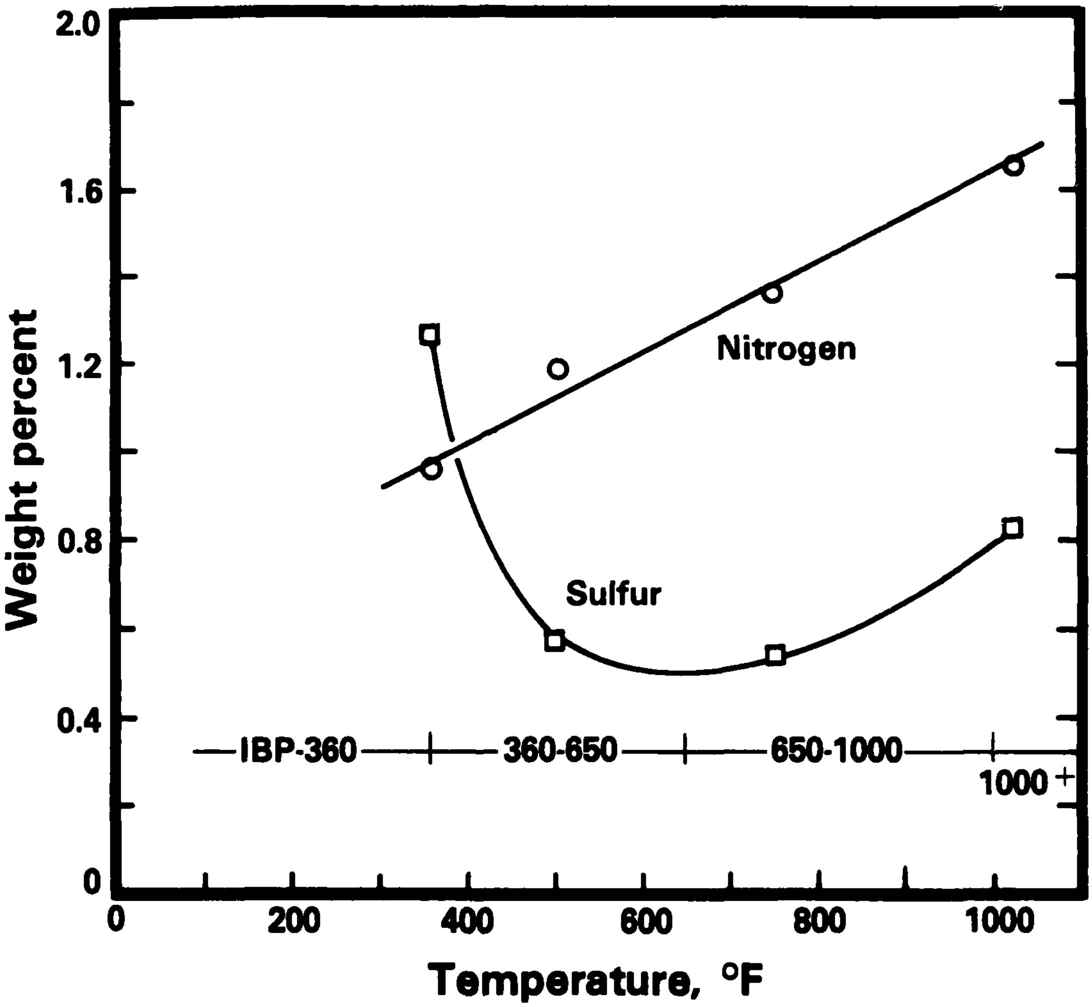

Figure 2 — Distribution of Sulfur and Nitrogen in Shale Oil Fractions

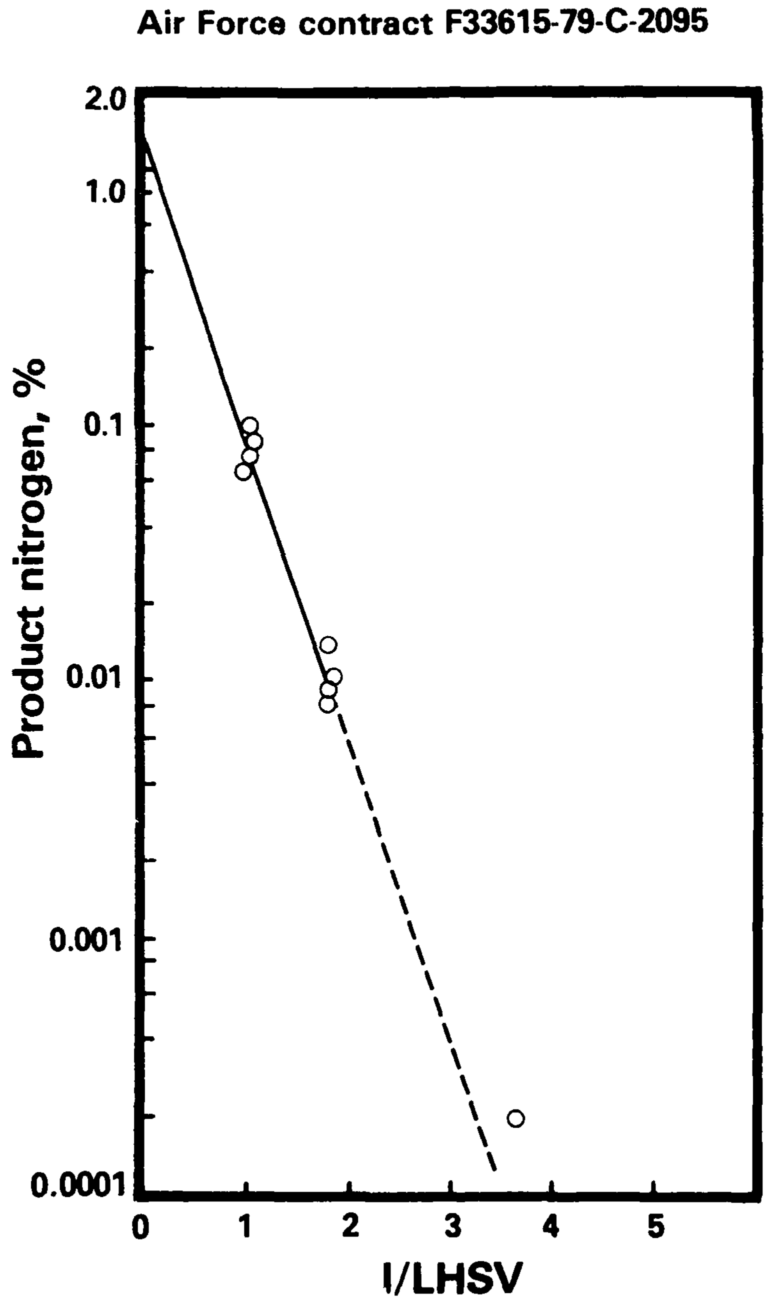

Figure 3 — Effect of Space Velocity on Product Nitrogen for CoCrMo at 790°F and 1800 psig

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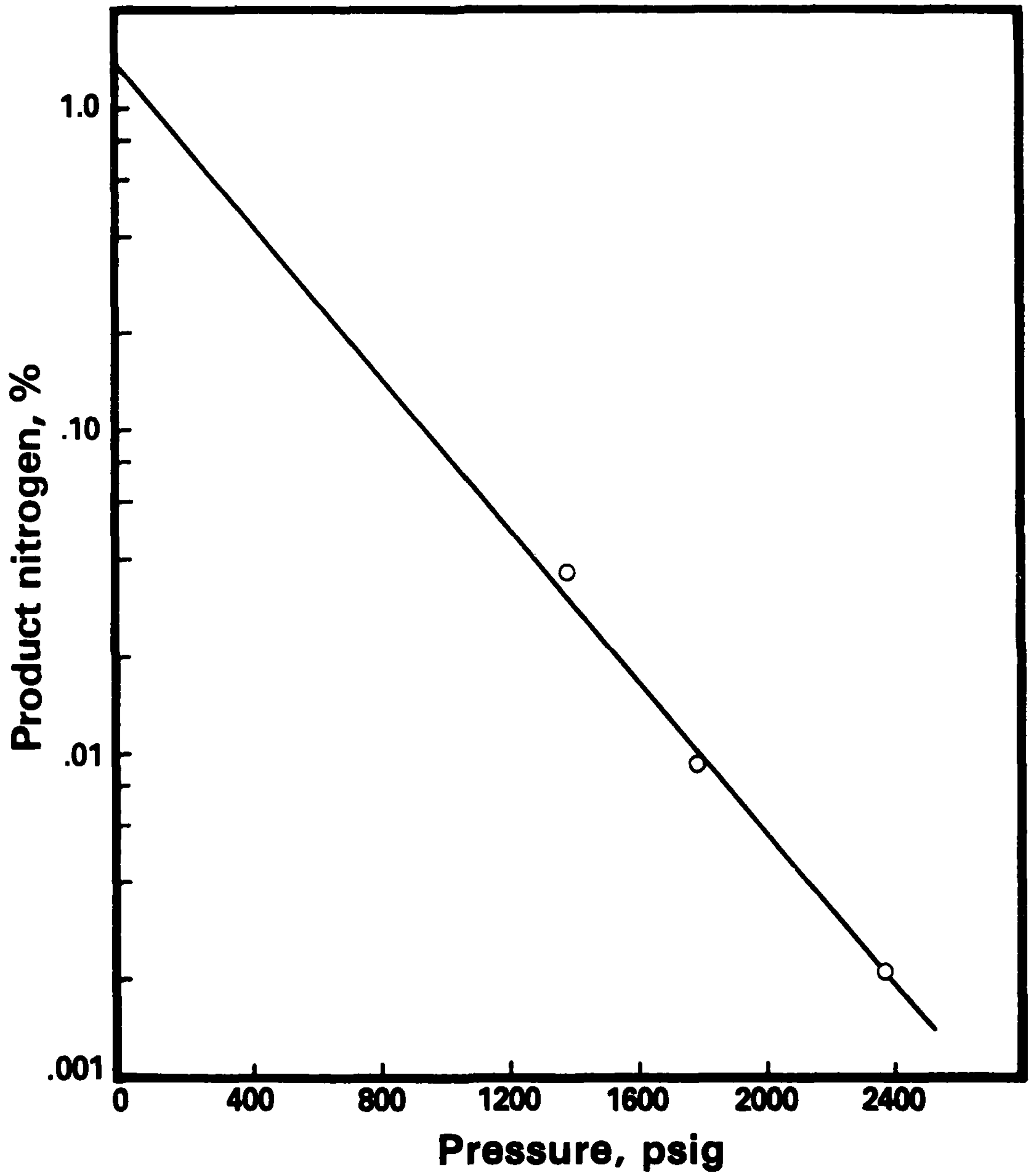

Figure 4 — Effect of Pressure on Product Nitrogen for CoCrMo at 790°F and 0.5 LHSV

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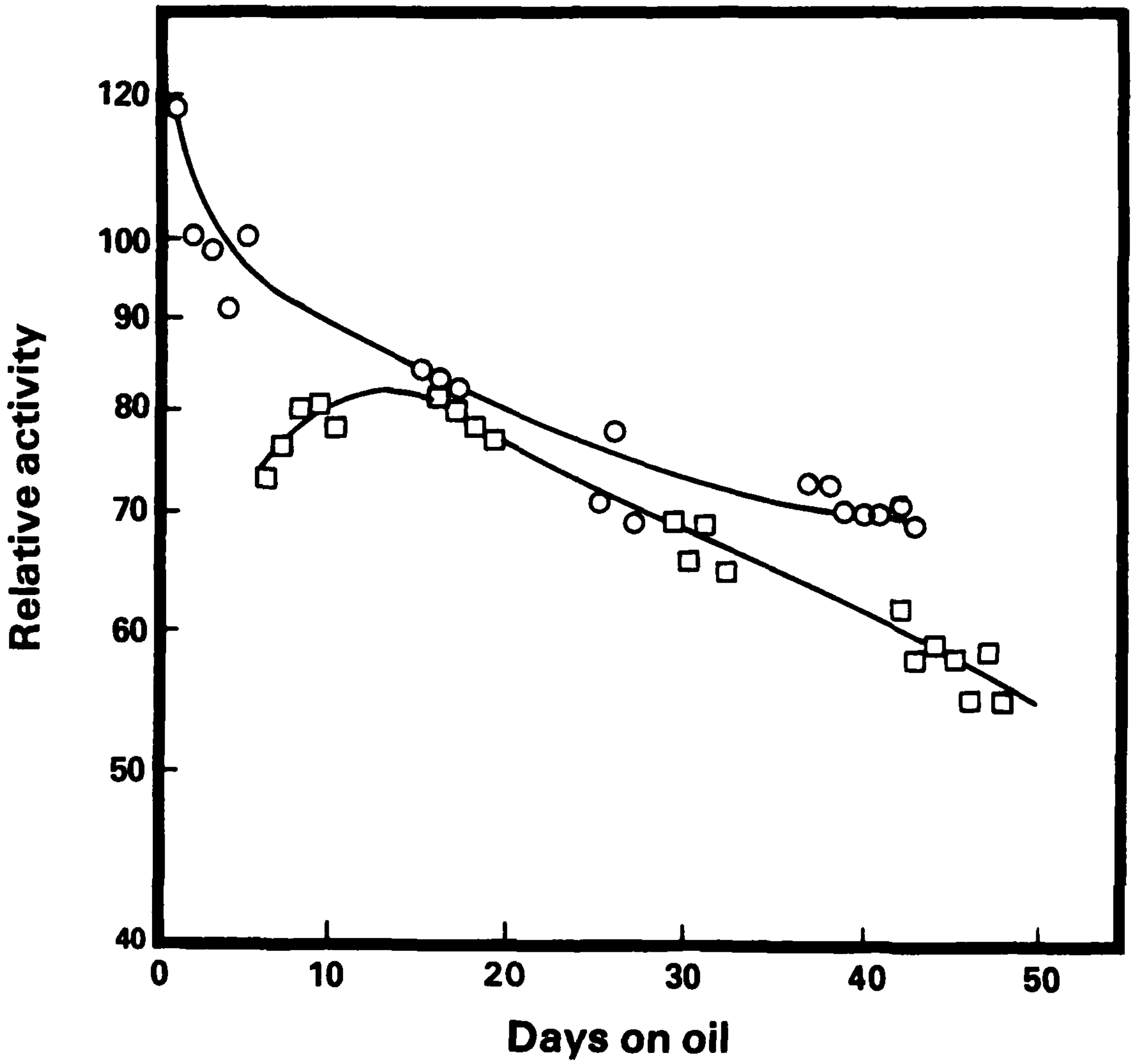

Figure 5 — Relative Dentrogenation Activities at Base Conditions for CoCrMo (○) and NiMoP + CoCrMo (□)

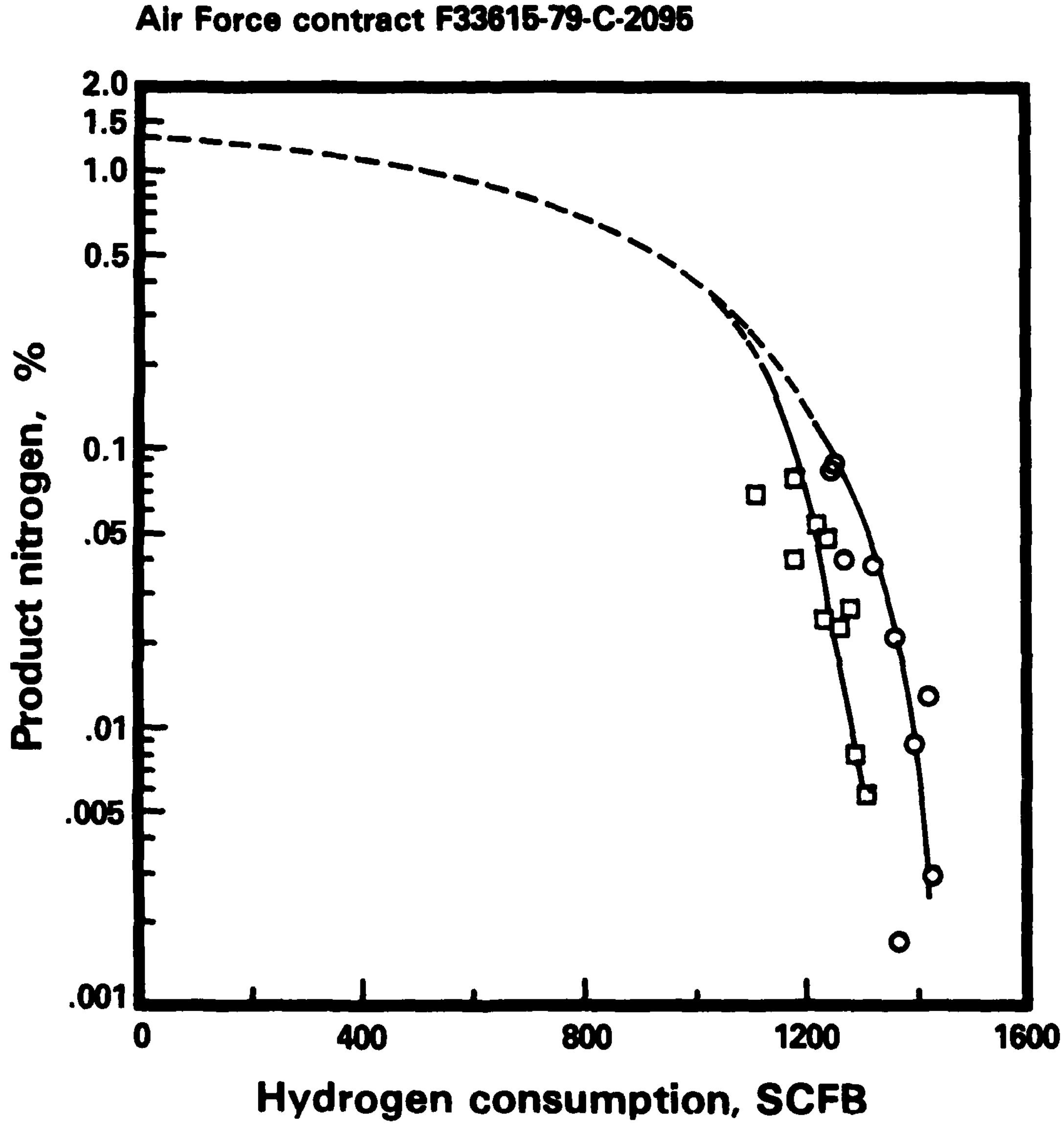

Figure 6 — Correlation Between Product Nitrogen and Hydrogen Consumption for CoCrMo (○) and NiMoP + CoCrMo (□)

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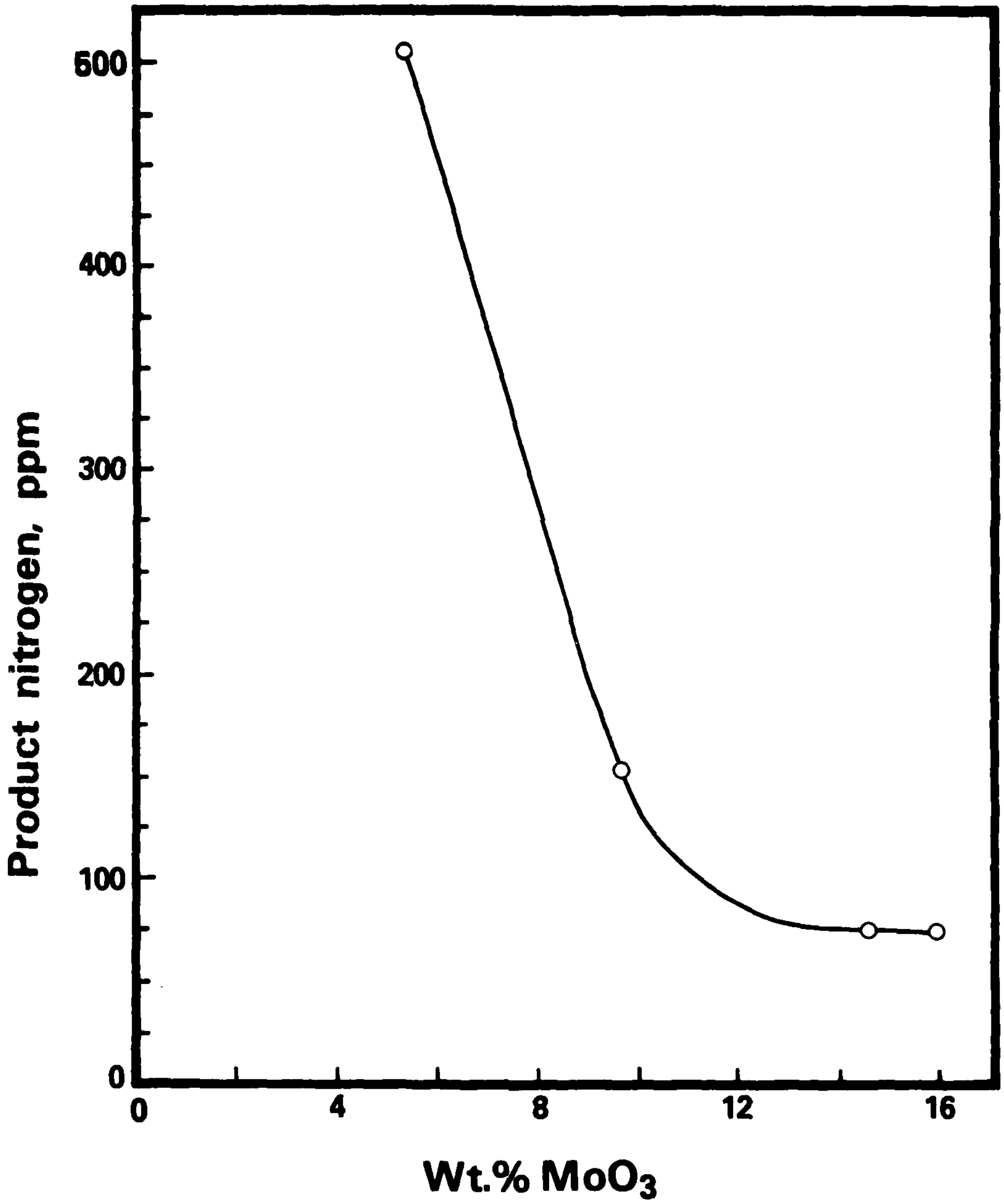

Figure 7 — Effect of MoO_3 Concentration at Constant CoO and Cr_2O_3 Contents on Product Nitrogen

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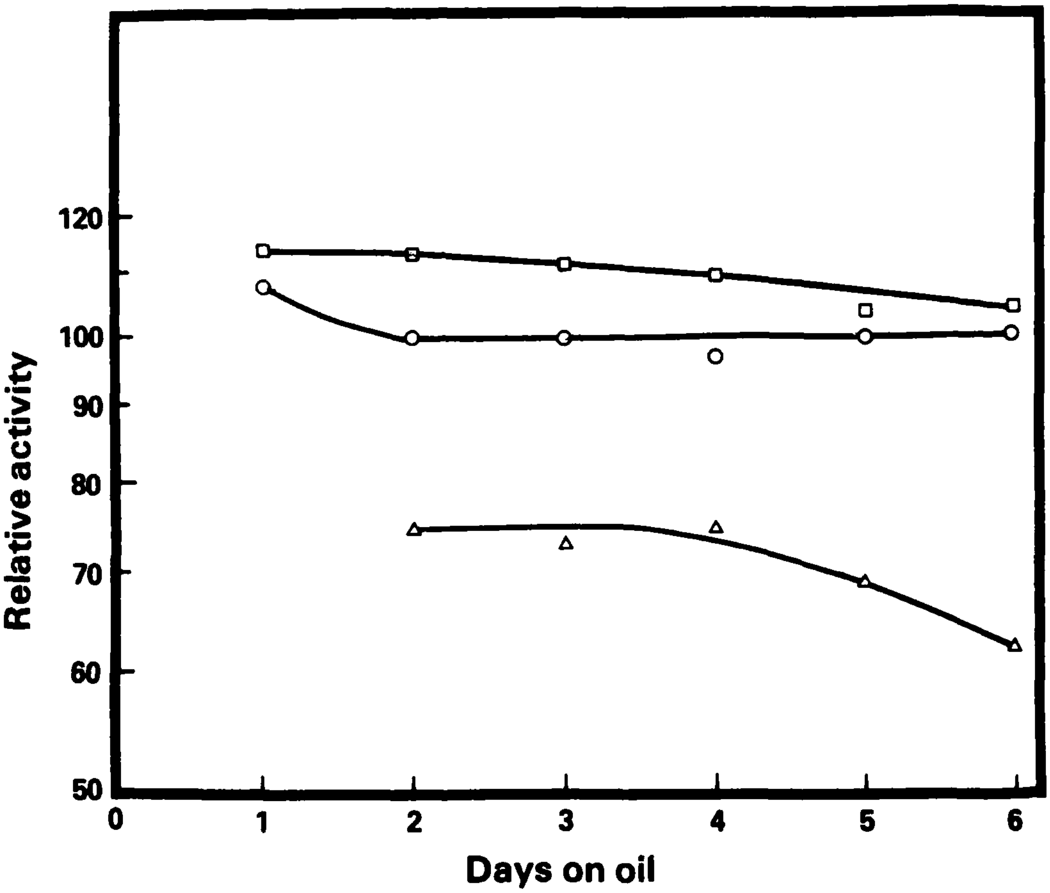

Figure 8 — Effect of MoO_3 Concentration on Activity for Nitrogen Removal, □, 16.0%; ○, 9.6%; △, 5.3% MoO_3

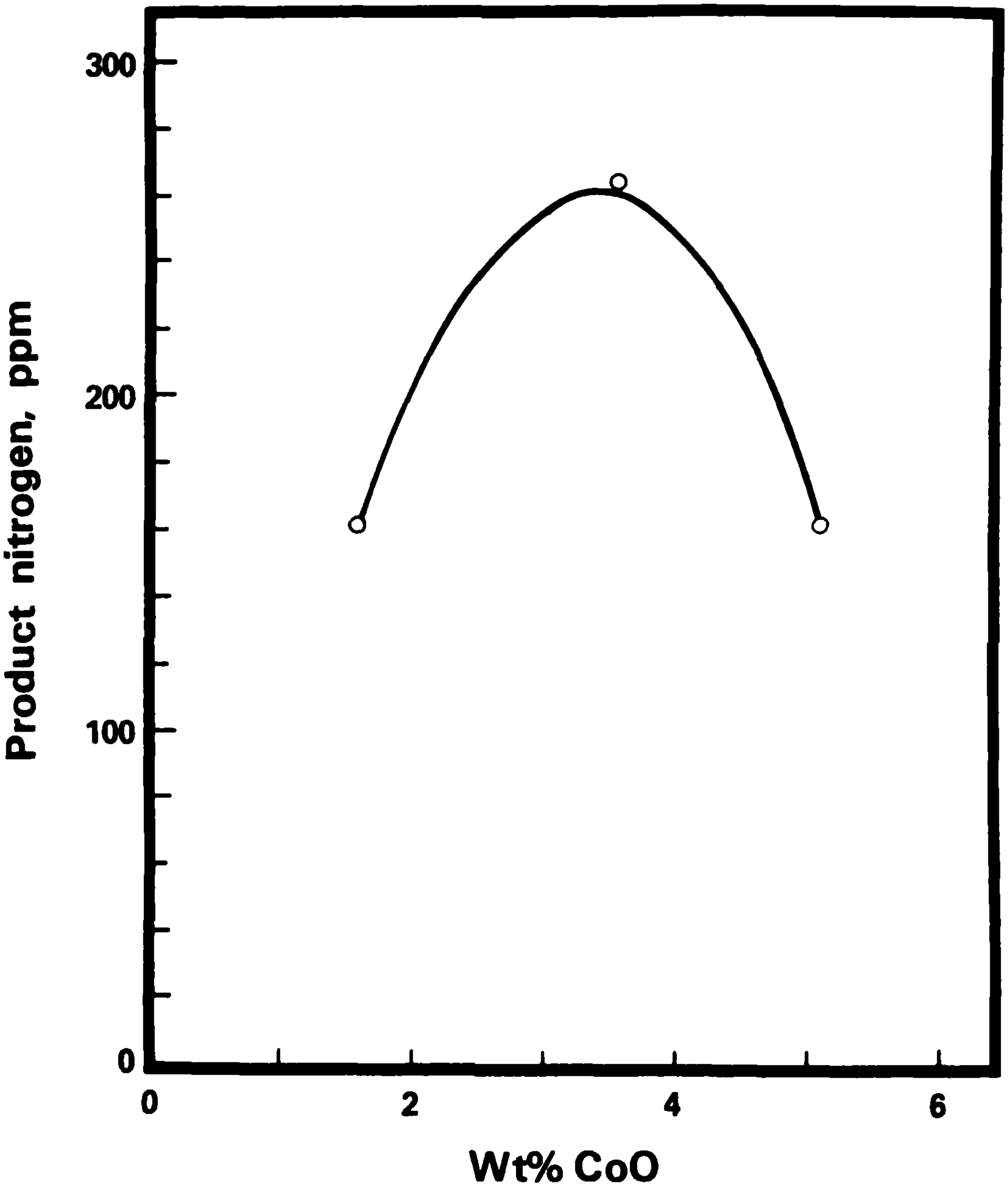

Figure 9 — Effect of CoO Concentration at Constant MoO_3 and Cr_2O_3 Content on Product Nitrogen

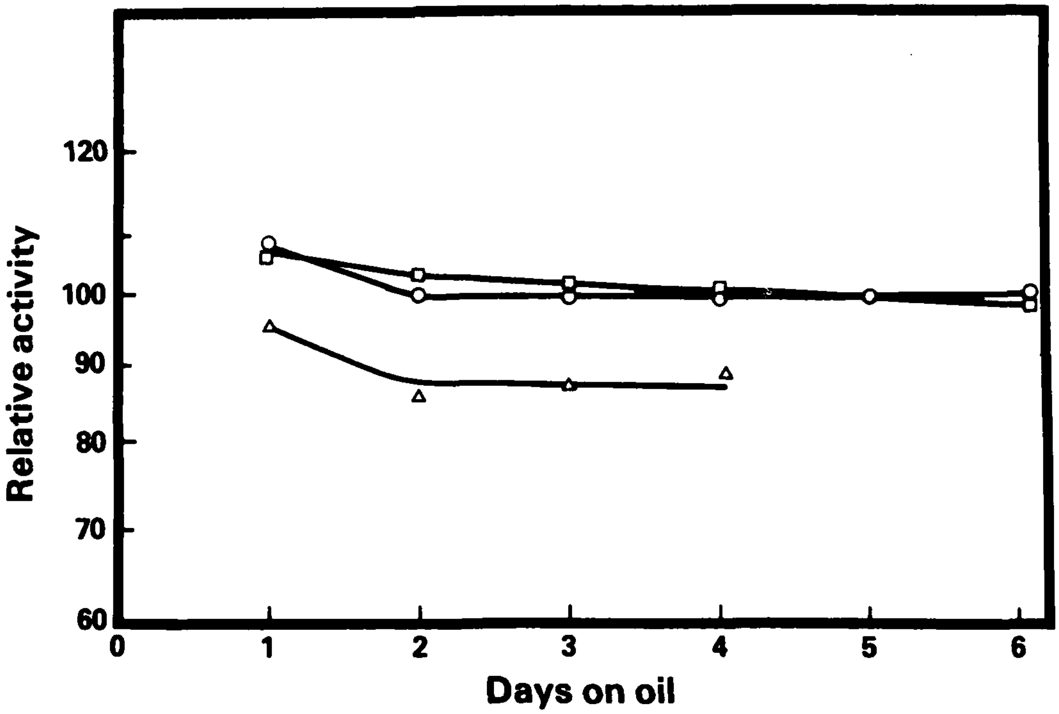

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Figure 10 — Effect of CoO Concentration on Activity for Nitrogen Removal, □, 5.1%; △, 3.6%; ○, 1.6% CoO

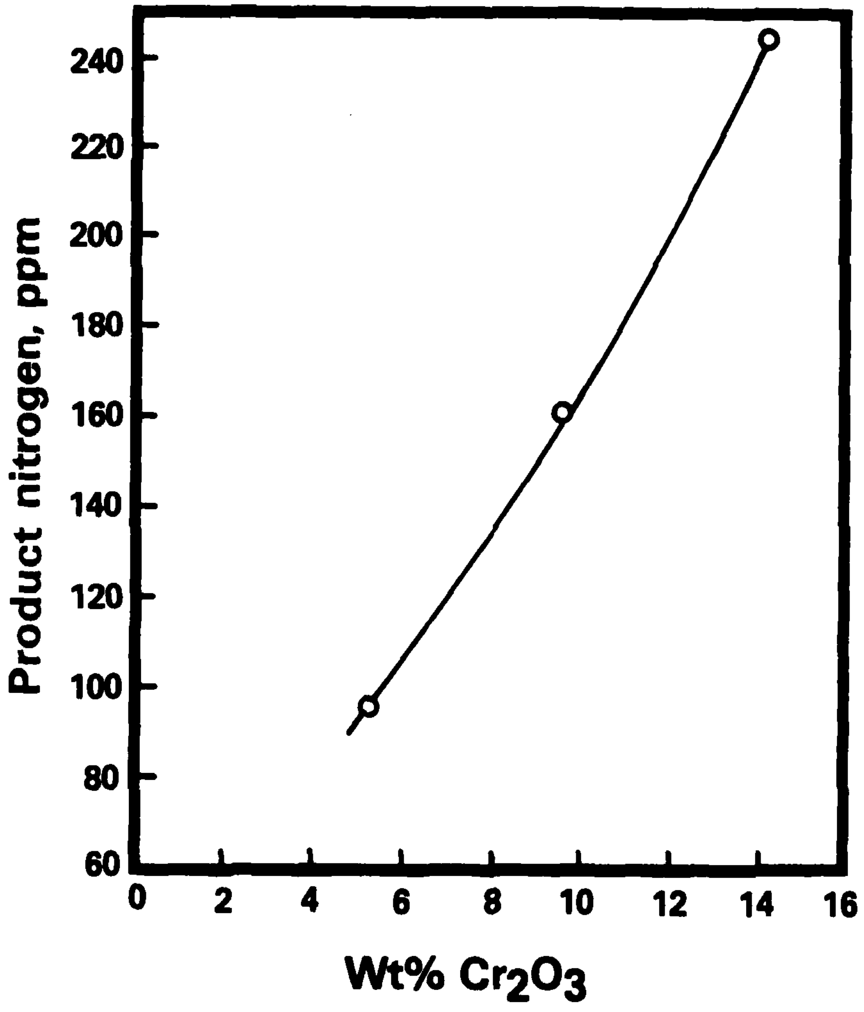

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Figure 11 — Effect of Cr_2O_3 Concentration at Constant MoO_3 and CoO Content on Product Nitrogen

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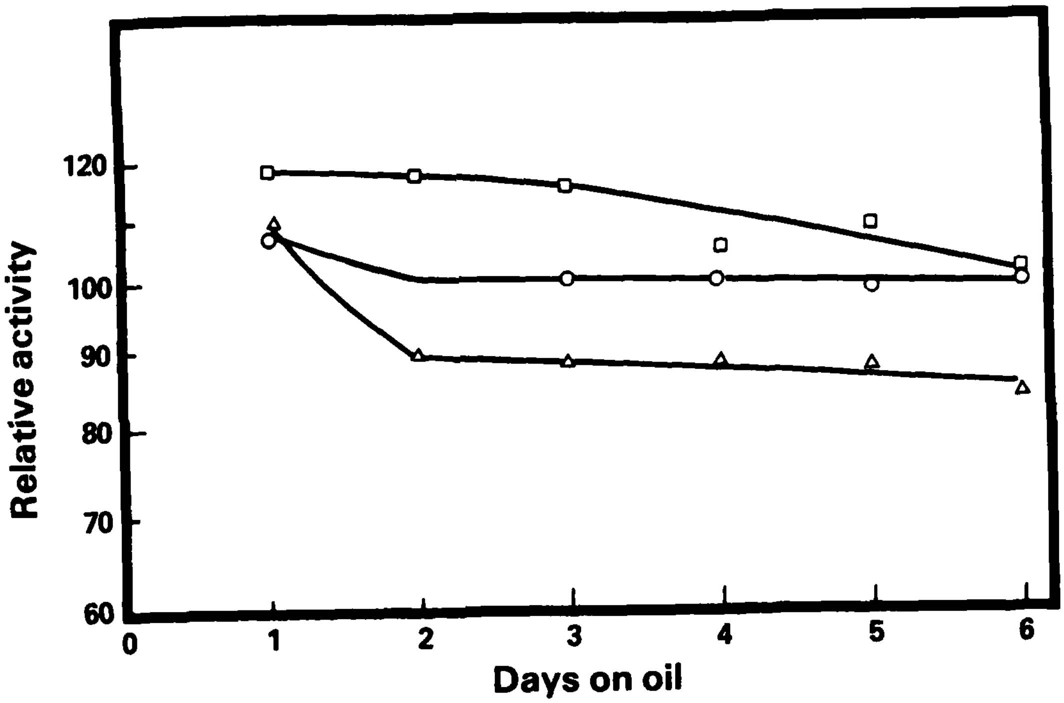

Figure 12 — Effect of Cr_2O_3 Concentration on Activity for Nitrogen Removal, △, 14.2%; ○, 9.6%; □, 5.3% Cr_2O_3

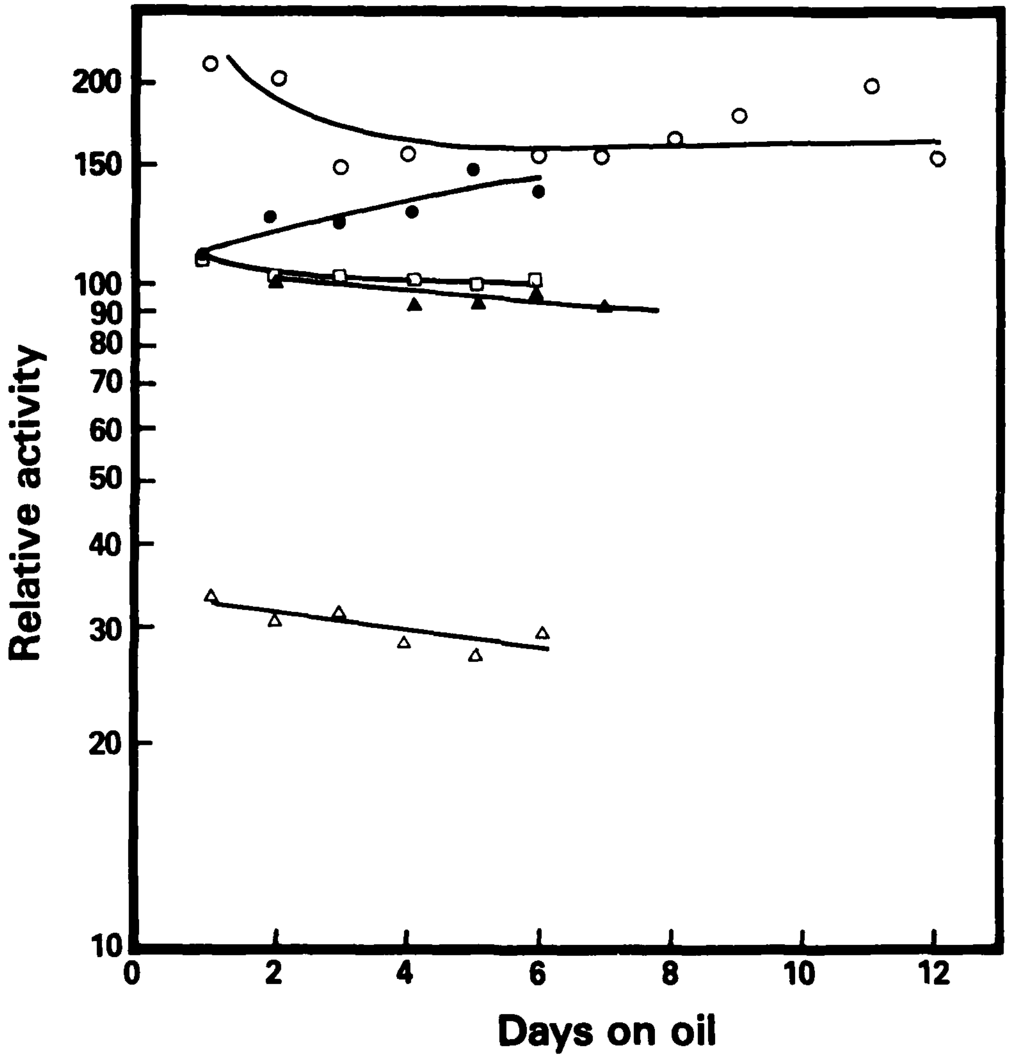

Figure 13 — Effect of Support Type on Relative Denitrogenation Activity for 1.5/10/10 Catalysts, △ Silica; ▲, Alumina/Alumina Phosphate; □, Alumina; ● 20% Silica Alumina; ○ 30% US Sieve Alumina

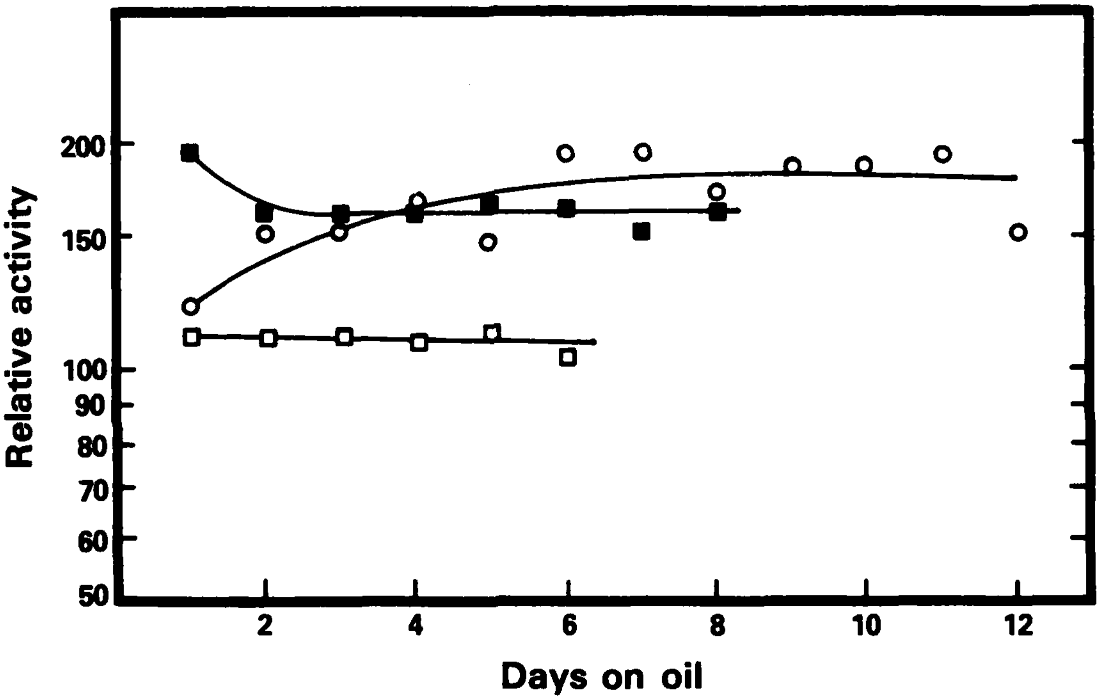

Figure 14 — Effect of Support Type on Relative Denitrogenation Activity for 1.5/10/15 Catalysts, □, Alumina; ○, 30% US Sieve Alumina; ■, 20% Silica Alumina

Air Force contract F33615-79-C-2095

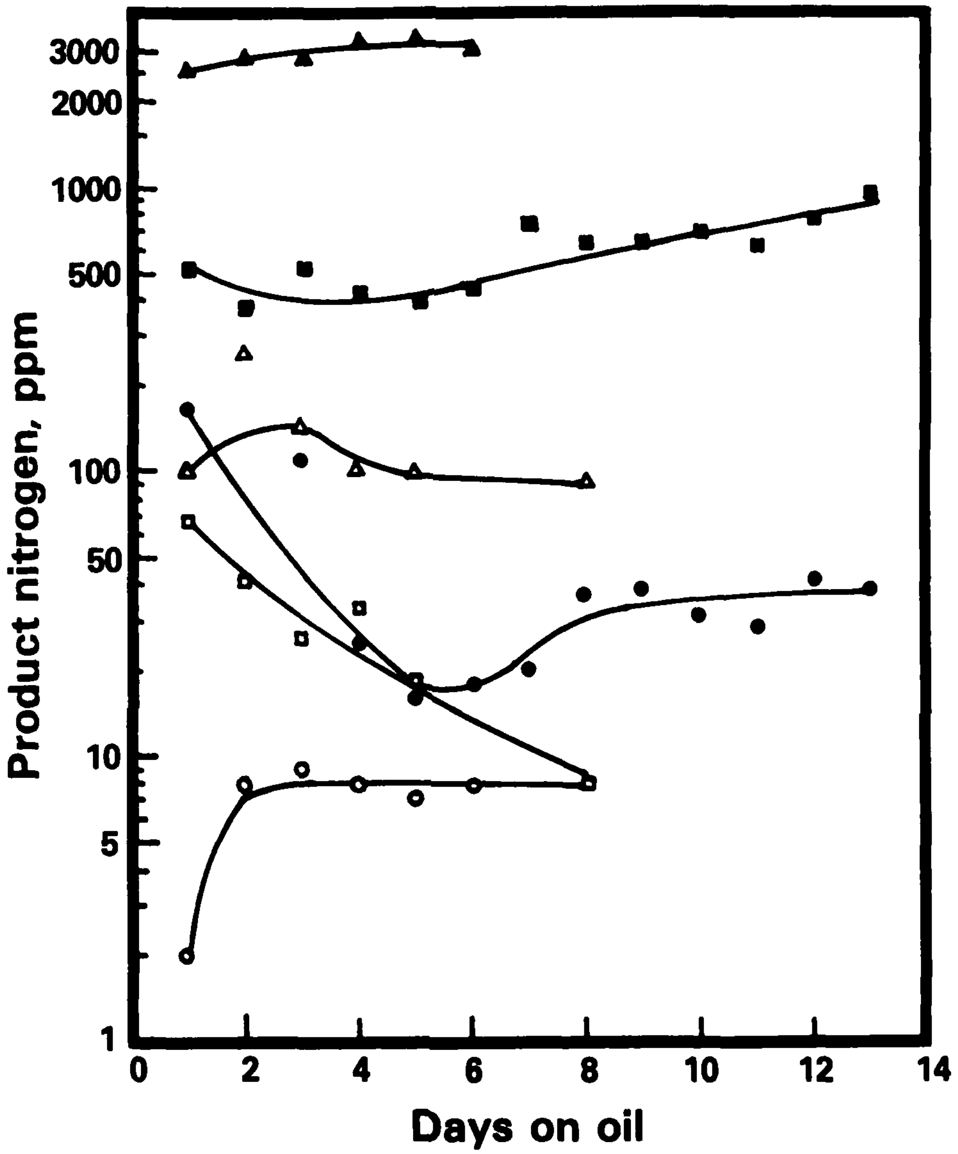

Figure 15 — Effect of Silica Concentration in the Support on Product Nitrogen, ○, 20%; □, 30%; ●, 50%; △, 10%; ■,70%; ▲, 100% Silica

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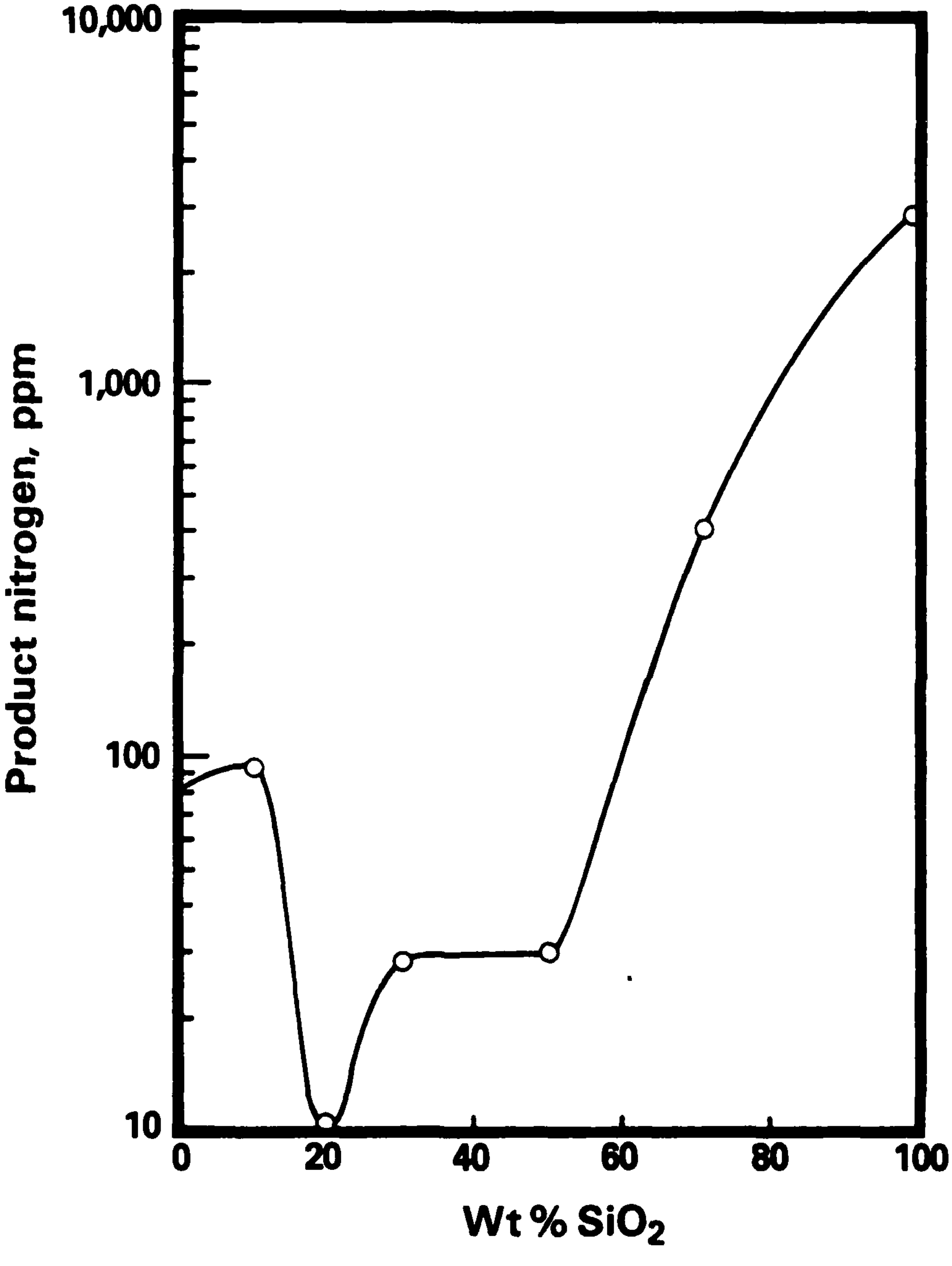

Figure 16 — Variation of Product Nitrogen as a Function of Support Silica Content

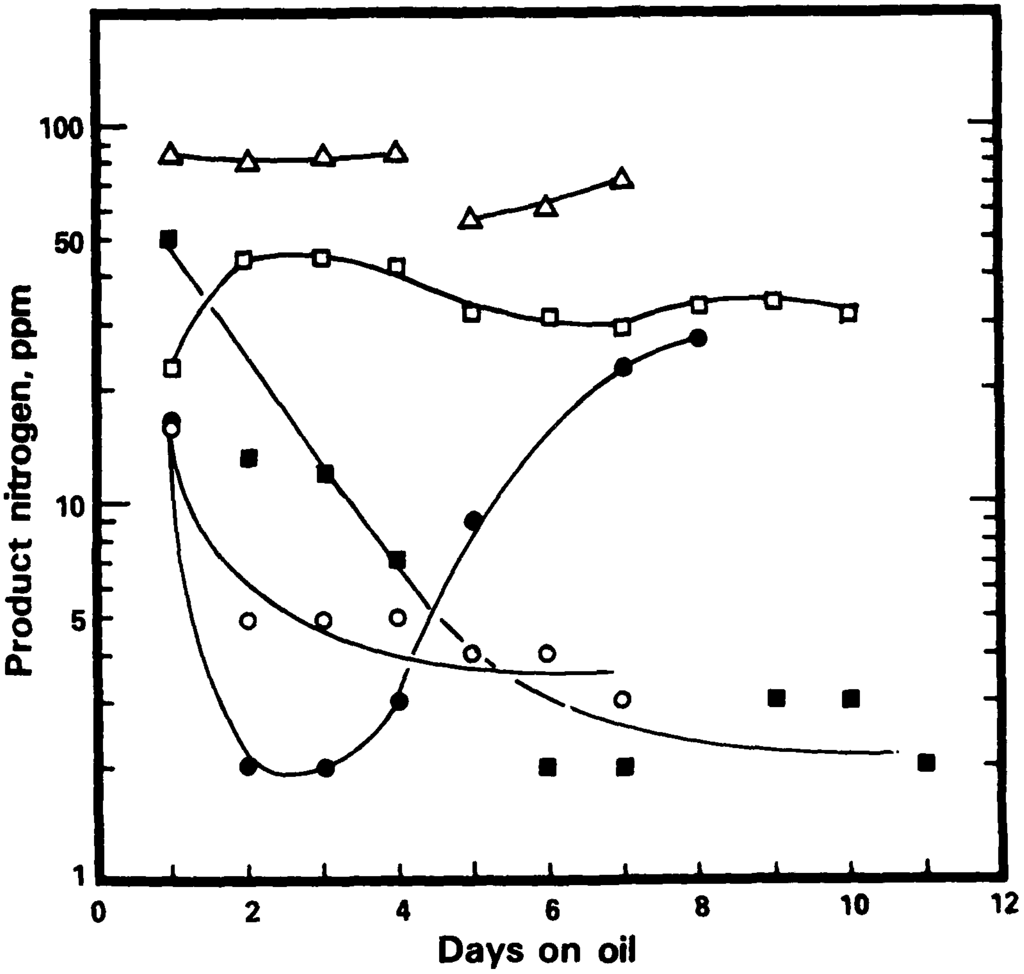

Figure 17 — Product Nitrogens as a Function of Sieve Type in the Support, ■, 30% US; ●, 20% Re-Y; ○, 20% H-AMS; □, 20% H-ZSM5; △, 20% H-Zeolon Sieve

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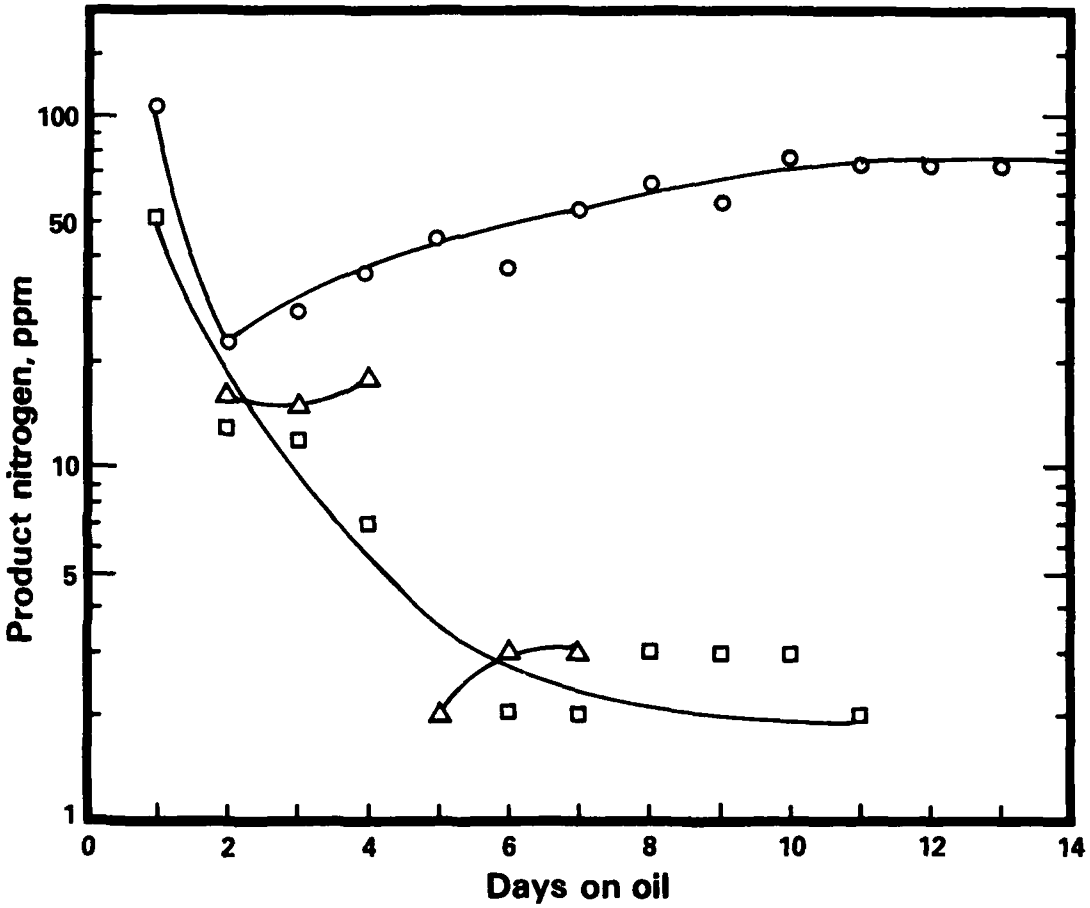

Figure 18 — Effect of US Sieve Concentration in the Support on Product Nitrogens, □, 30%; △, 50%; ○, 20% Sieve

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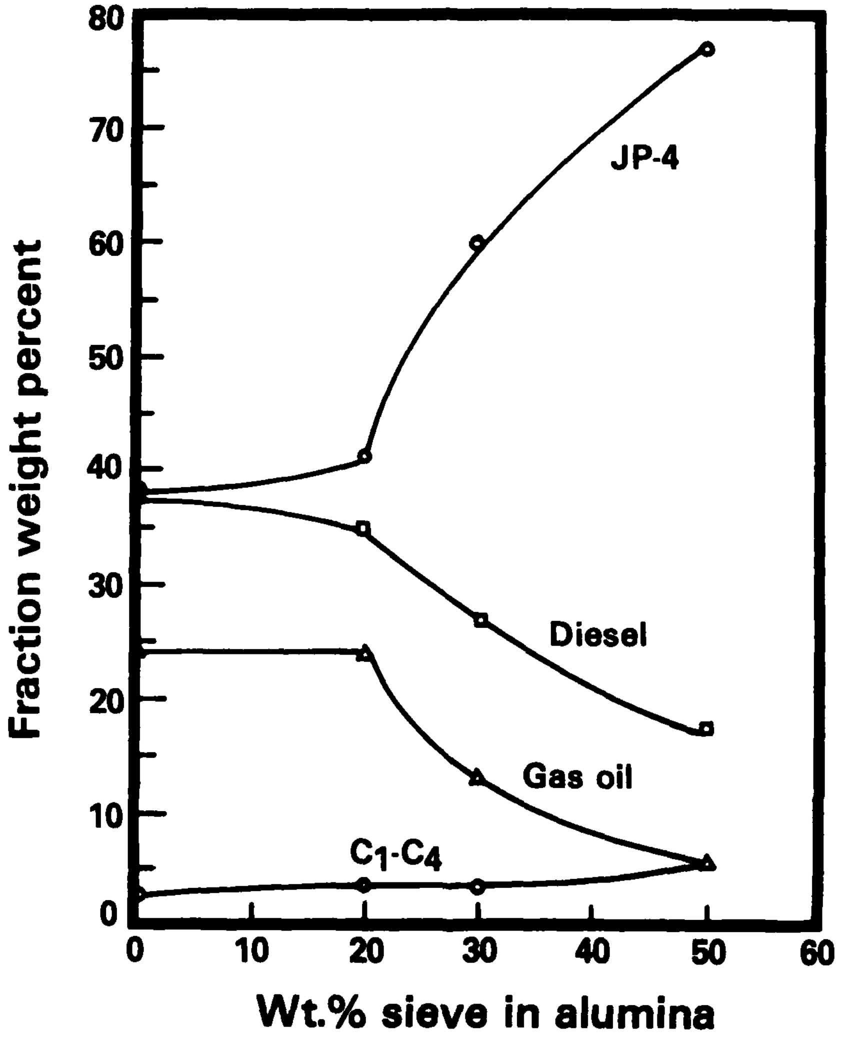

Figure 19 — Product Yield Structures as a Function of US Sieve Content in the Support

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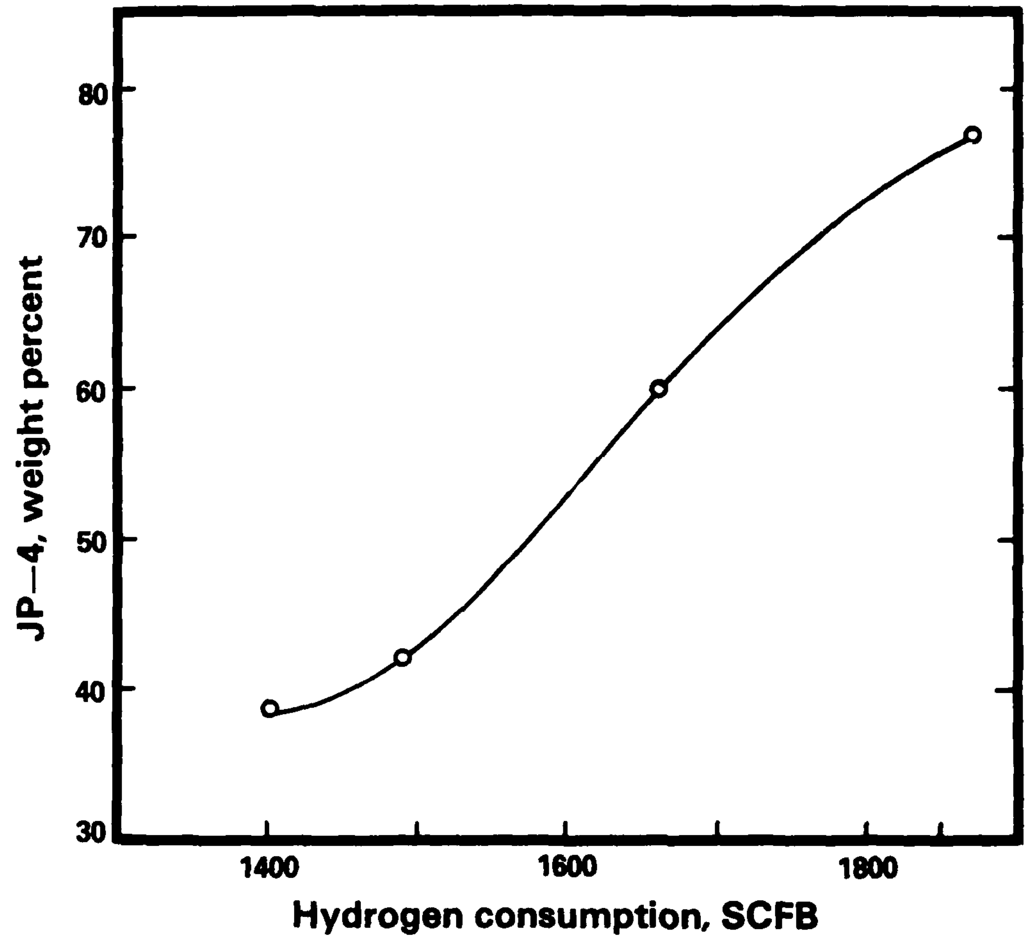


Figure 20 — Correlation Between JP-4 Yields and Hydrogen Consumption for Catalysts Containing 0, 20, 30, and 50% US Sieve

Air Force contract F33615-79-C-2095

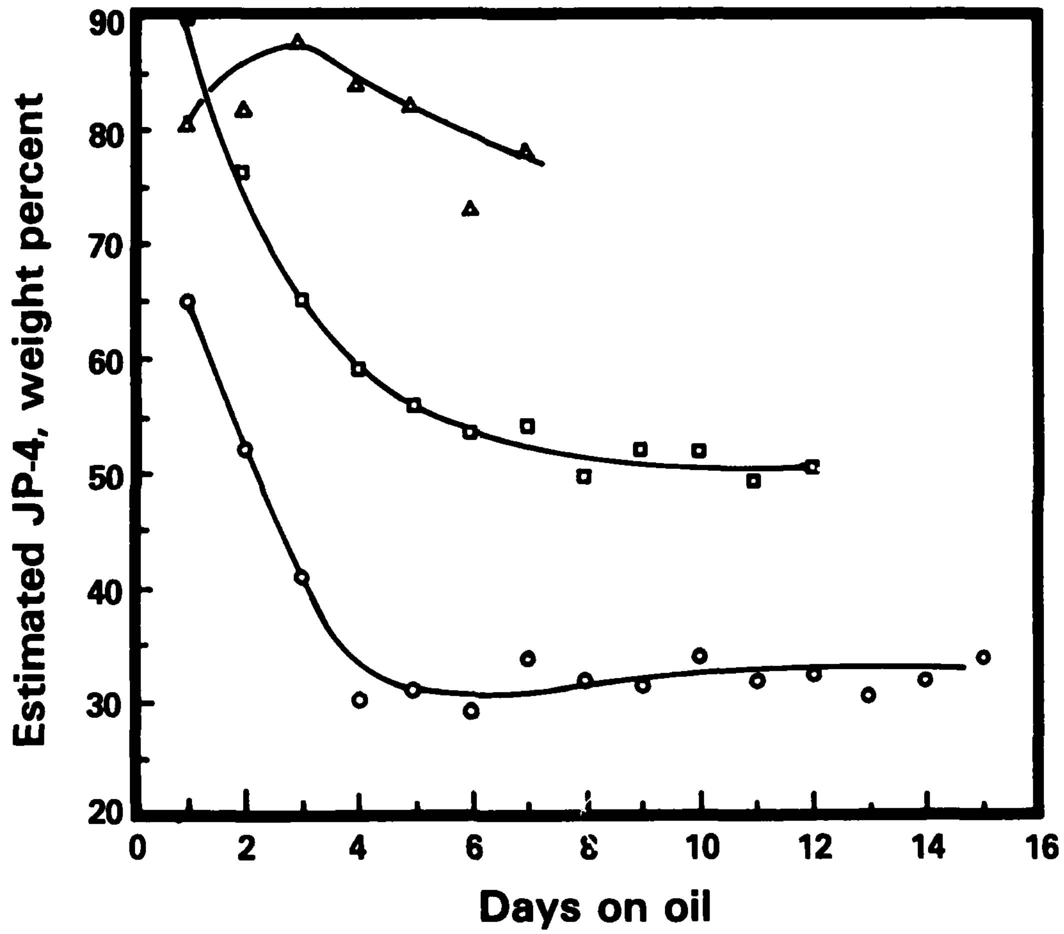


Figure 21 — Estimated Daily Yields of JP-4 for Catalyst of Different Sieve Content, ○, 20%; □, 30%; and △, 50% US Sieve

Air Force contract F33615-79-C-2095

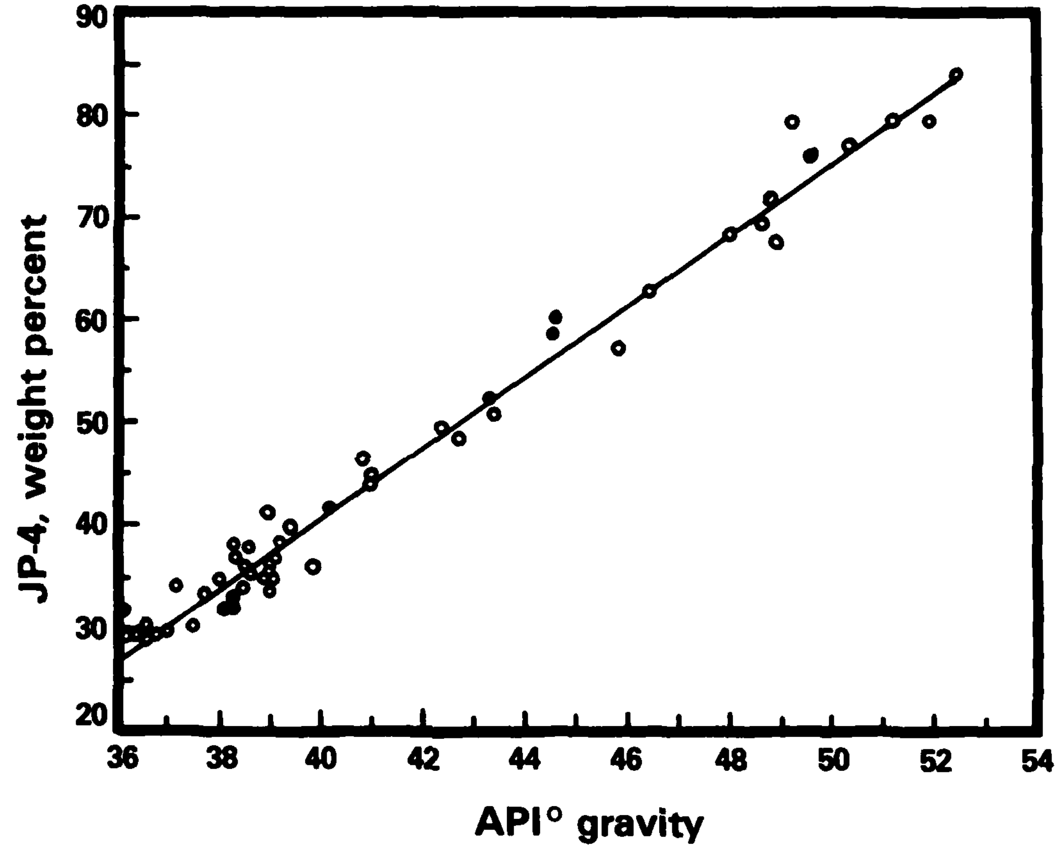


Figure 22 — Correlation Between Product API° Gravities and JP-4 Yields

Air Force contract F33615-79-C-2095

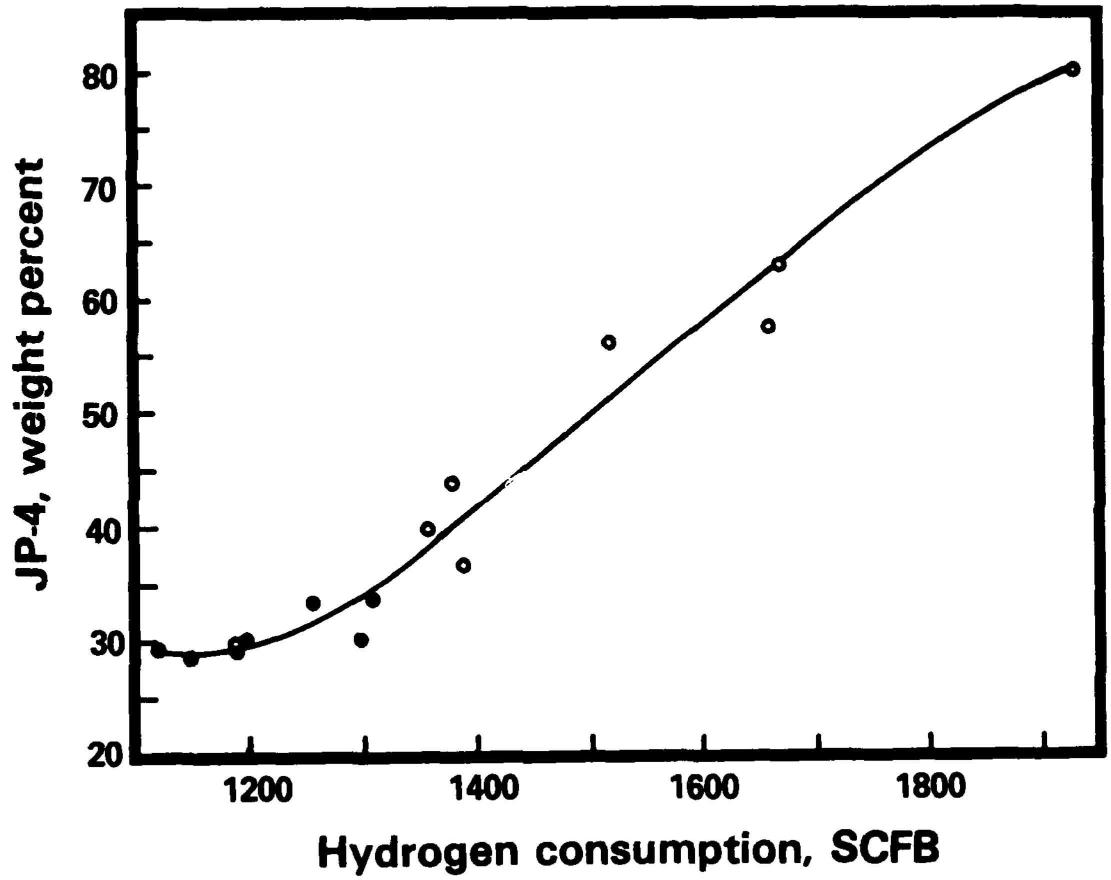


Figure 23 — Correlation Between JP-4 Yields and Hydrogen Consumption for Catalysts Containing 50% US Sieve, •, 0.75 LHSV; ○, 0.5 LHSV

Air Force contract F33615-79-C-2095

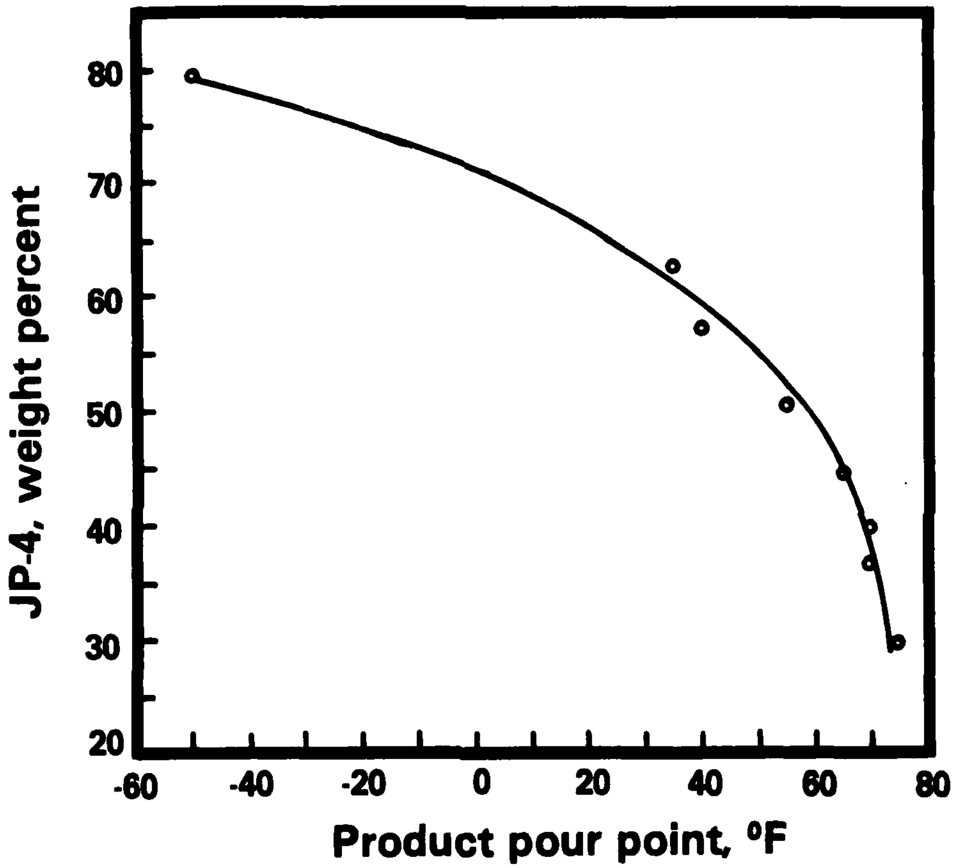


Figure 24 — Correlation Between Product Pour Point and JP-4 Yields for Catalysts Containing 50 % US Sieve

Air Force contract F33615-79-C-2095

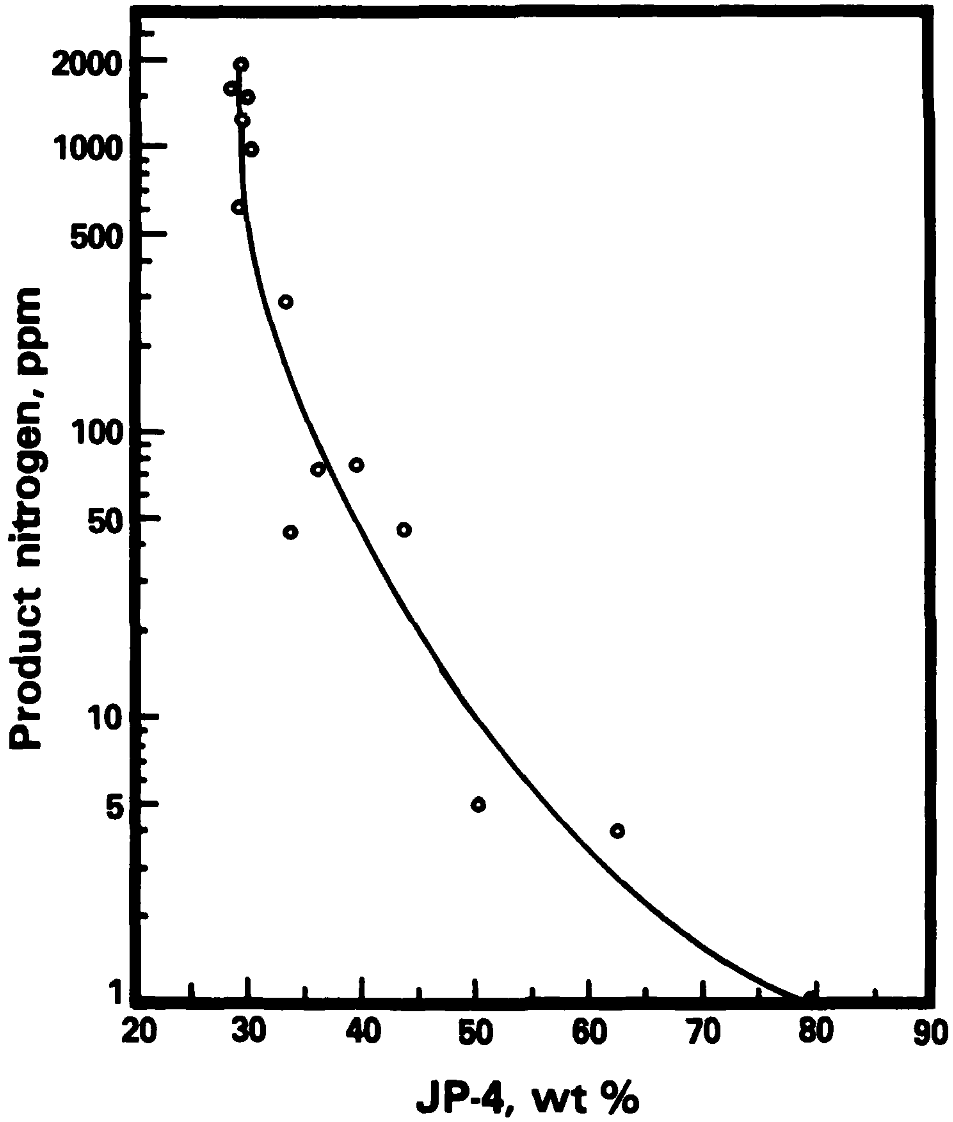


Figure 25 — JP-4 Yields as a Function of Product Nitrogen for Catalysts Containing 50% US Sieve

Air Force contract F33615-79-C-2095

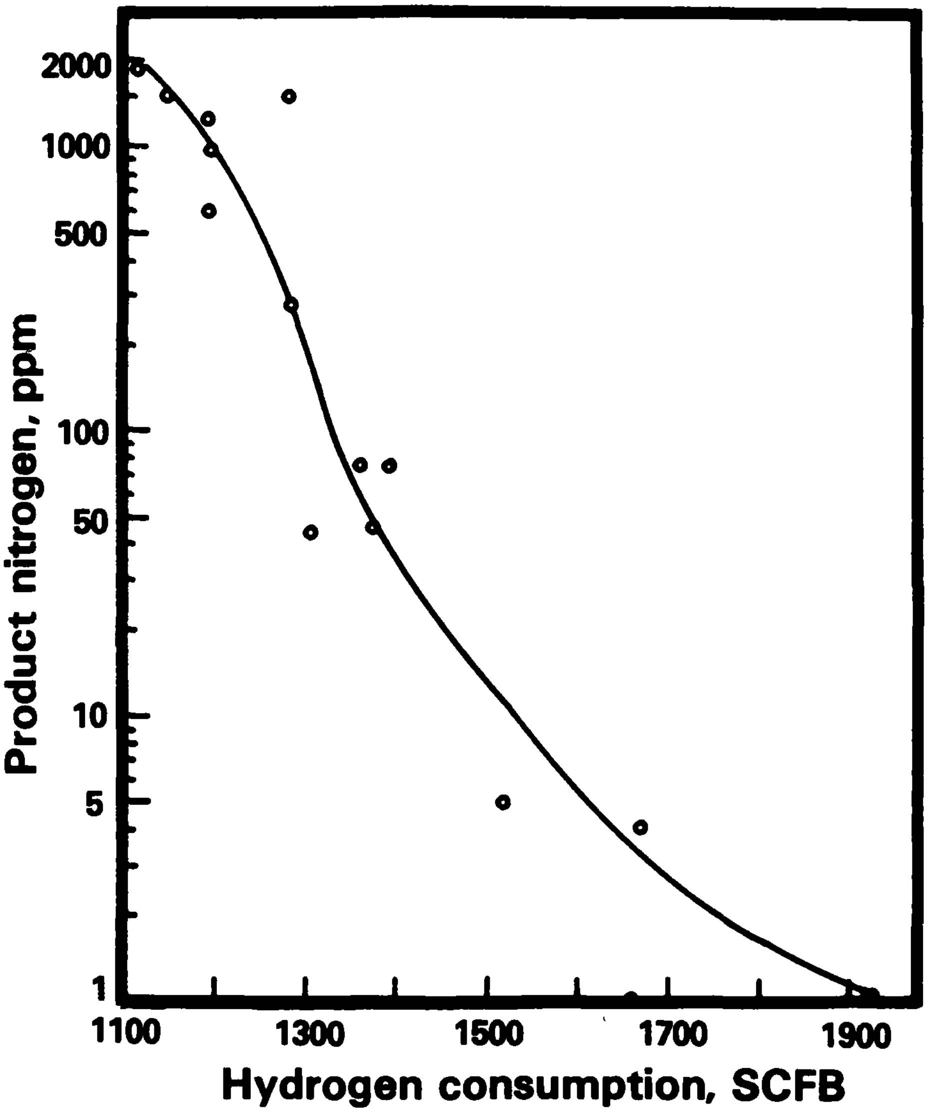


Figure 26 — Hydrogen Consumption as a Function of Product Nitrogen for Catalyst Containing 50% US Sieve

Air Force contract F33615-79-C-2095

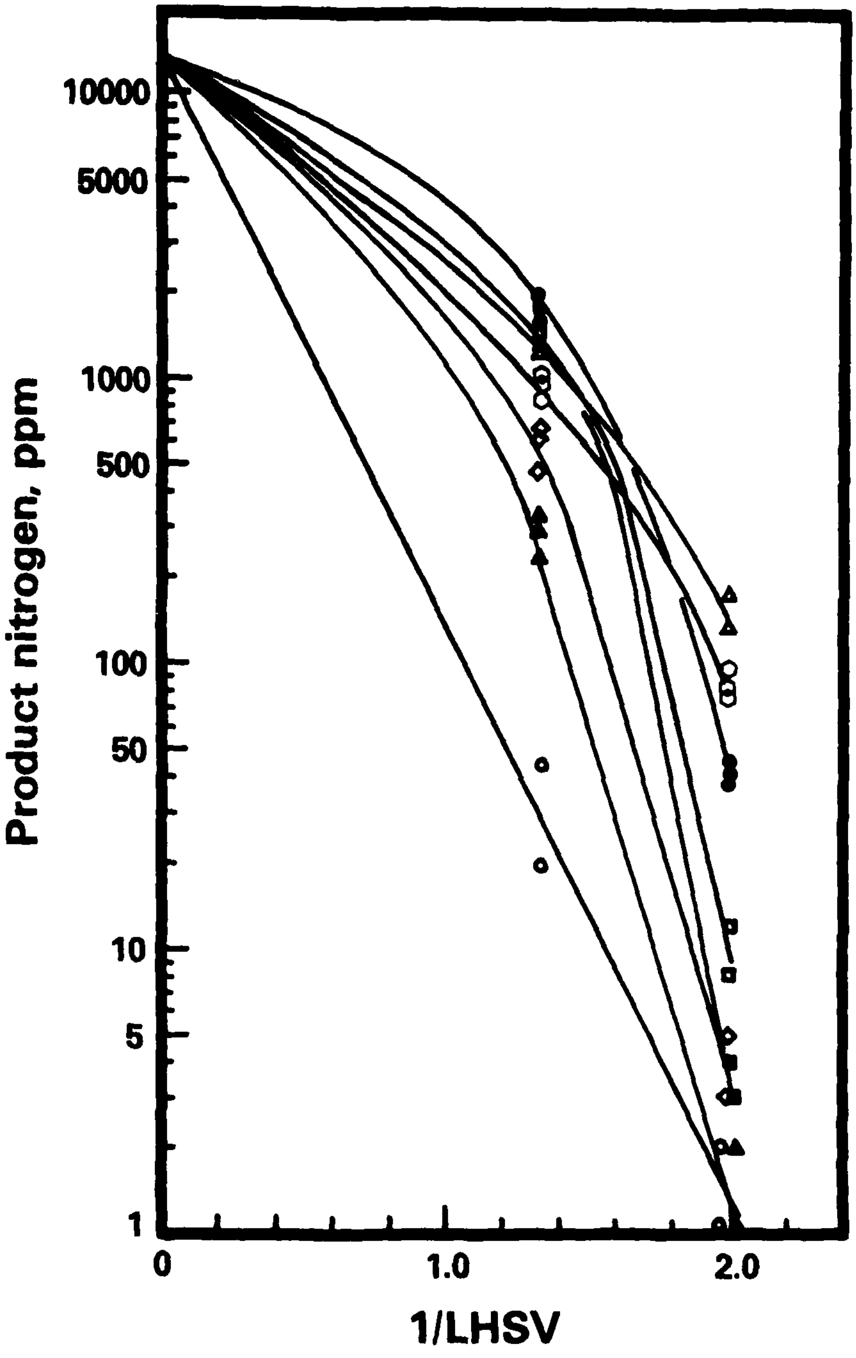
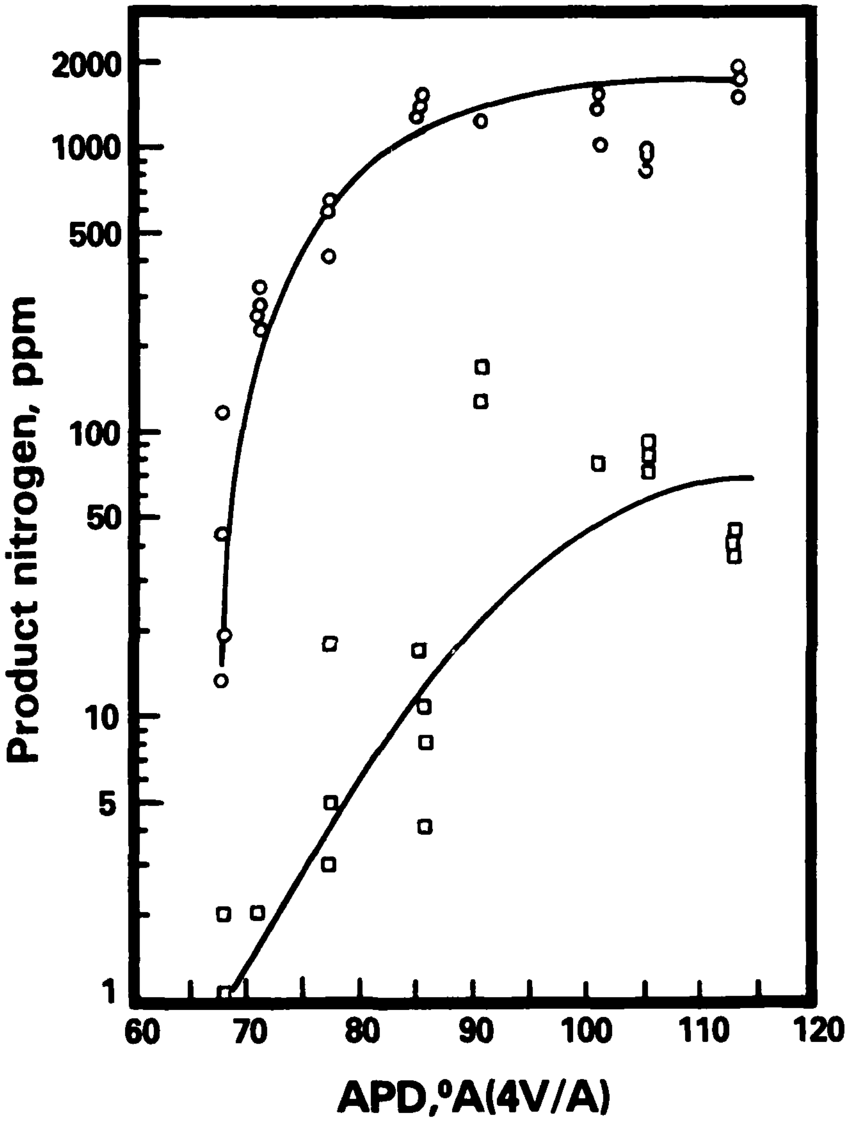
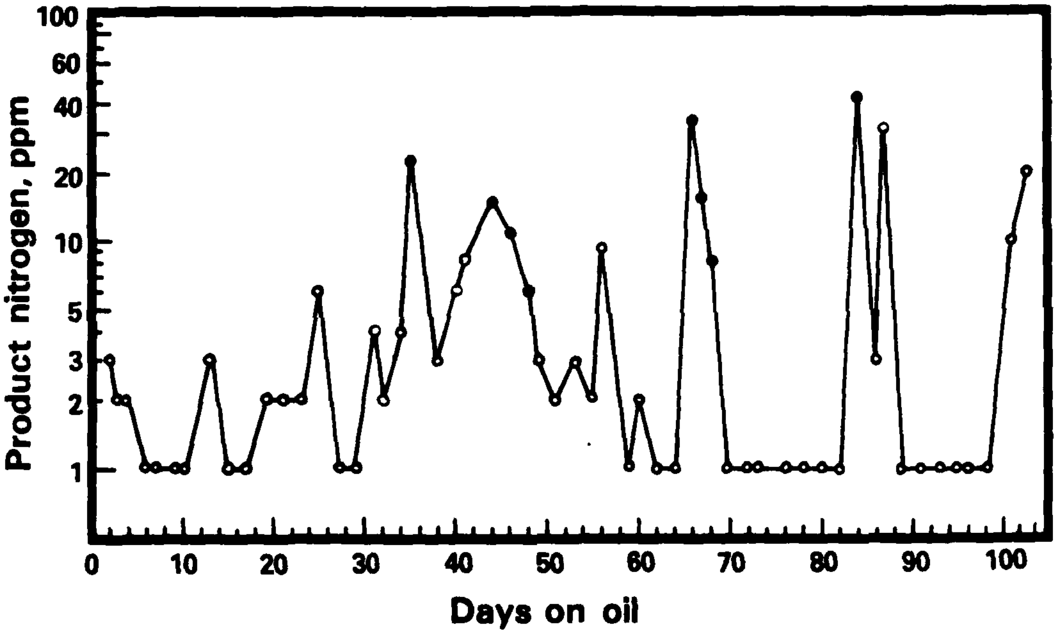


Figure 27 — Effect of Space Velocity on Product Nitrogens for Catalyst with Different Physical Properties,
Catalysts 3838-023 (○); -028 (□); -030 (△); -031 (⬡);
-034 (◇); -035 (●); -037 (■); -039 (▲).



Air Force contract F33615-79-C-2095

Figure 28 — Correlation Between Catalyst Average Pore Diameters and Product Nitrogen for 50% US Sieve Alumina Catalysts, ○, 0.75 LHSV; □, 0.5 LHSV.



Air Force contract F33615-79-C-2095

Figure 29 — Product Nitrogen as a Function of Days on Oil for the Activity Maintenance Test

Air Force contract F33615-79-C-2095

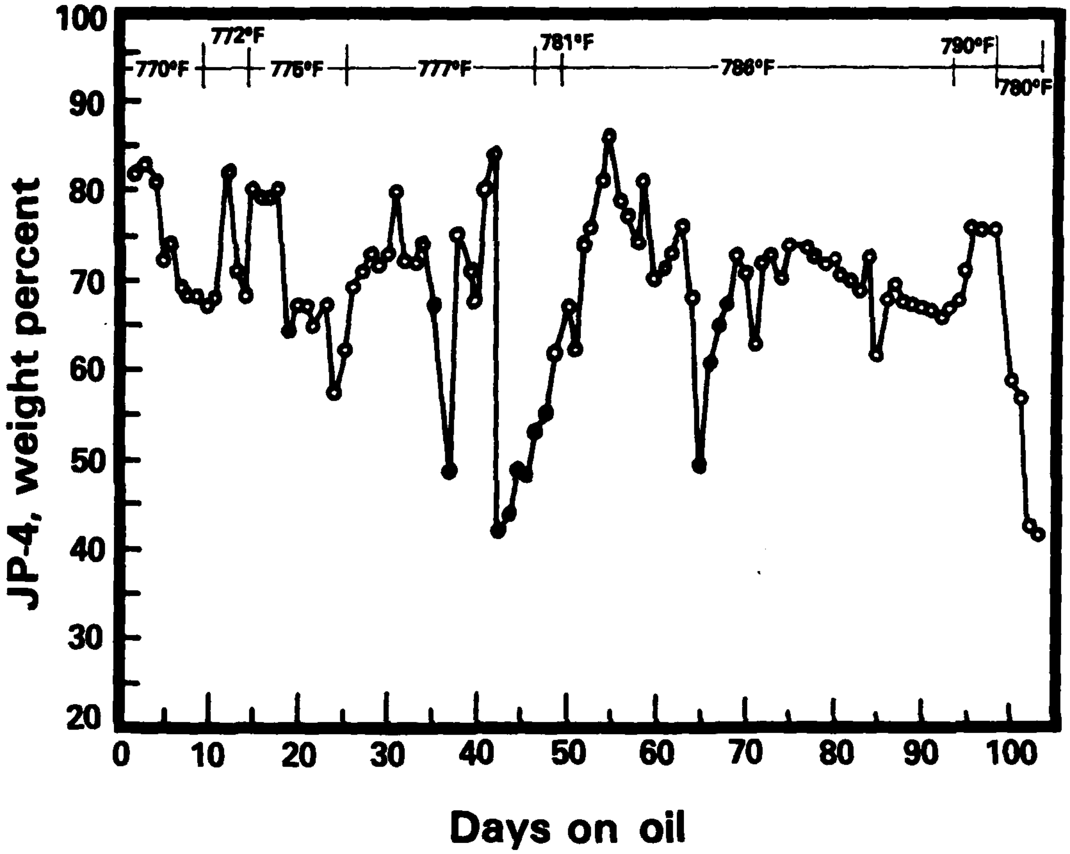


Figure 30 — Daily JP-4 Yields for the Activity Maintenance Test

Air Force contract F33615-79-C-2095

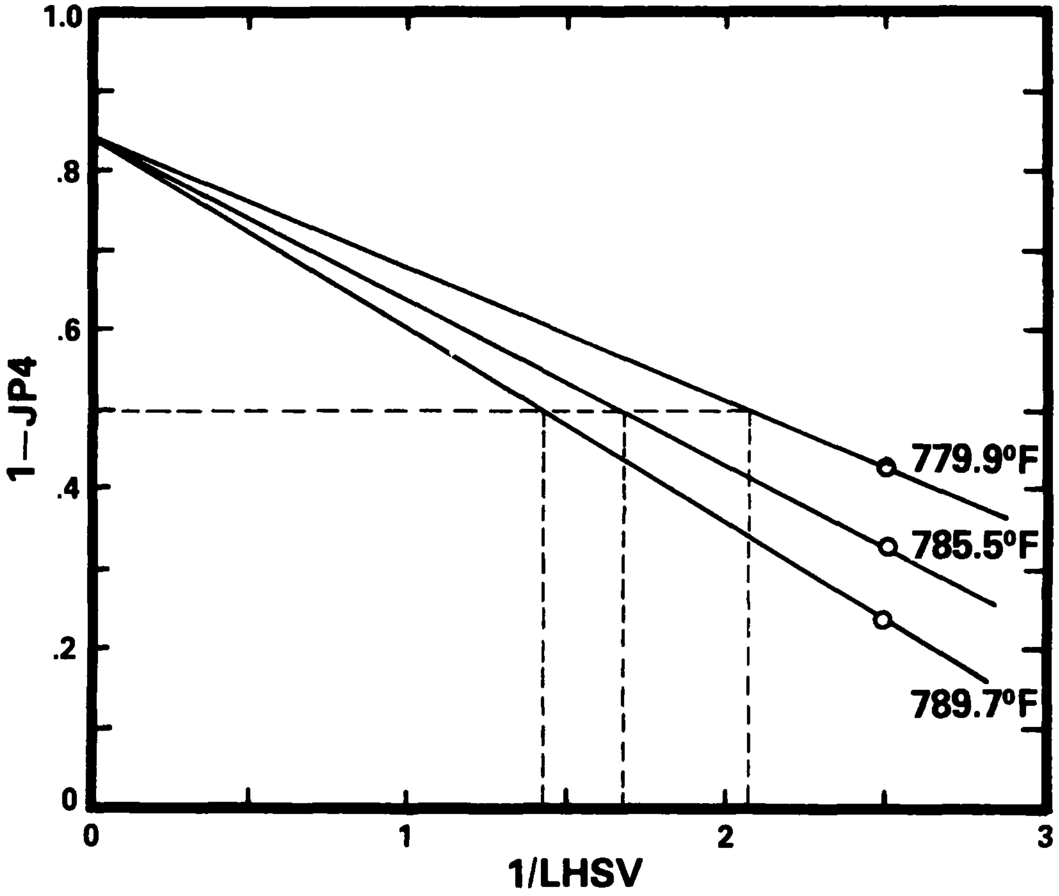


Figure 31 — Kinetic Data for Temperature Response Factors for Hydrocracking

Air Force contract F33615-79-C-2095

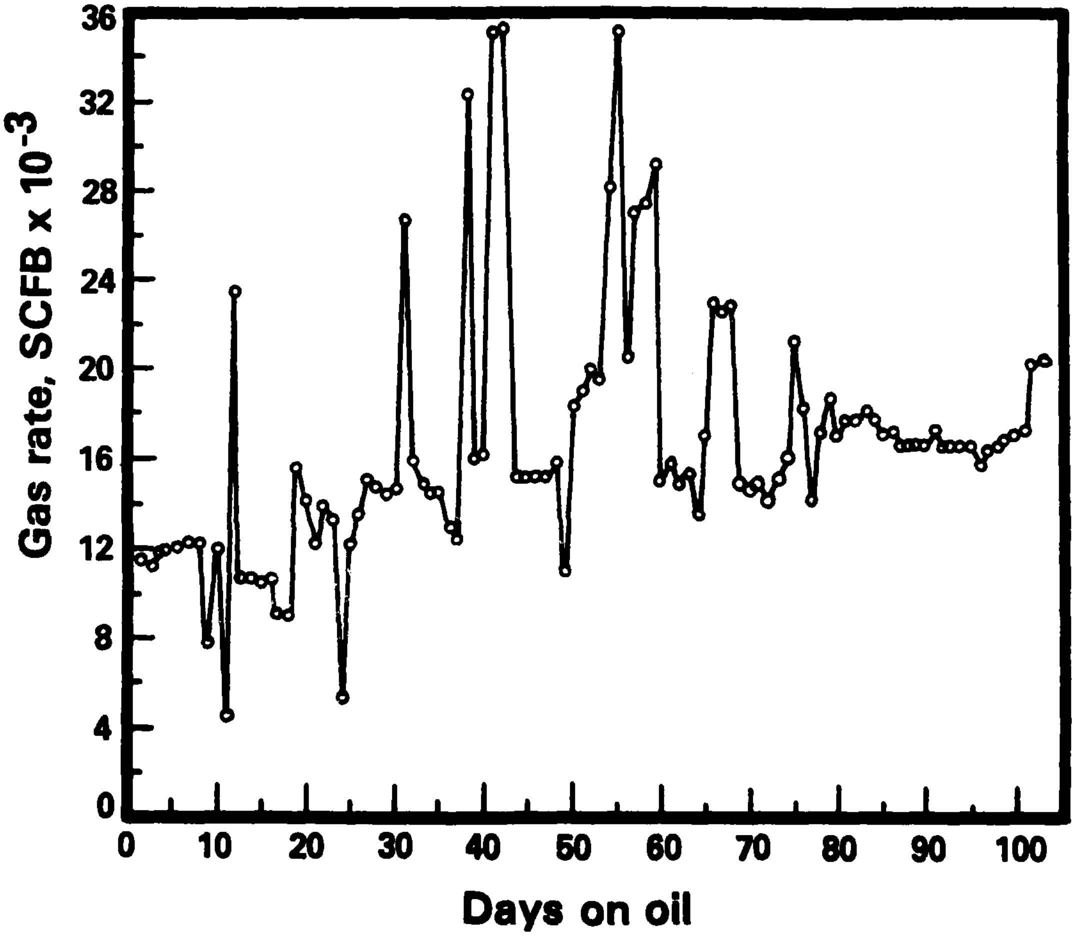


Figure 32 — Daily Gas Throughput for the Activity Maintenance Test

SECTION V

TABLE I

AIR FORCE CONTRACT F33615-79-C-2095
PROPERTIES OF DEWATERED AND DEASHED OCCIDENTAL SHALE OIL

Amoco ID		FHC-337
Gravity, API°		23.8
Carbon, Wt%	84.89, 84.86, 84.71	84.82
Hydrogen, Wt%	11.89, 11.78, 11.81	11.83
Nitrogen, Wt%	1.27, 1.37, 1.32	1.32
Sulfur, Wt%	0.65, 0.64, 0.62	0.64
Oxygen, Wt%	1.31, 1.35, 1.54	1.40
Pour Point, °F		60
Viscosity, cst, 104°F		32.9
212°F		5.1
Ramsbottom Carbon, Wt%		1.22
Trace Metals[a]		
Arsenic, ppm		26
Nickel, ppm		11
Iron, ppm		61
		41
Sodium, ppm		10
Calcium, ppm		12
Simulated Distillation[b]		
IBP, °F		290
IBP-360°F, Wt%		2.0
360-650°F, Wt%		42.5
650°F+, Wt%		55.5
% at 1000°F		87.2
JP-4, Wt%[c]		15.5
Bulk Distillation		
IBP-360°F, Wt%		1.1
360-650°F, Wt%		45.8
650°F+, Wt%		53.1
1000°F+, Wt%		14.3

a. Arsenic by wet chemical methods, nickel by X-ray fluorescence and emission spectrograph, iron by X-ray fluorescence (61 ppm) and emission spectrograph (41 ppm), sodium by atomic absorption and emission spectrograph.

b. ASTM method 2887, see Appendix G.

c. Heavy JP-4 fraction, IBP of 290°F, 90% at 470°F, by simulated distillation.

TABLE 2

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 1
PROCESS VARIABLE STUDY, SINGLE-CATALYST SYSTEM

Catalyst: 3609-162, Co/Cr/Mo on Alumina
Run ID: AU-75-35

Days on Oil	1	2	3	4	5A	6	7	8A	9
Avg Cat Temperature, °F	788.9	--	--	790.9	791.0	792.3	790.9	790.8	790.7
Pressure, psig	1800	—	—	—	—	—	—	—	→
LHSV, Vo/Vc/hr	0.55	—	—	—	—	0.97	—	—	→
Gravity, API°	38.1	38.5	38.5	38.5	39.4	36.6	37.4	37.8	37.2
Liquid Product, g	63	221	182	220	162	156	346	297	178
Carbon, Wt%					86.36			86.47	
Hydrogen, Wt%					13.60			13.43	
Nitrogen, ppm	38	94	97	140	87	737	743	860	963
Sulfur, ppm	329	243	224	282	334	98	200	61	126
Pour Point, °F					80			75	
Viscosity, cst (104°F)					3.61			4.36	
Simulated Distillation									
IBP, °F					68			82	
IBP-360°F, Wt%					15.5			12.6	
360-650°F, Wt%					58.0			56.6	
650°F+, Wt%					26.5			30.8	
FBP, °F					925			984	
JP-4, Wt%					37.3			32.0	
Gas Rate, SCFB x 10^{-3}					6.2			7.0	
Hydrogen Consumption, SCFB					1395			1250	
Wt%, C_1-C_4 on Feed					3.3			2.4	
Volume Expansion, %					105			103	

TABLE 2 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 1
PROCESS VARIABLE STUDY, SINGLE-CATALYST SYSTEM

Catalyst: 3609-162, Co/Cr/Mo on Alumina
Run ID: AU-75-35

Days on Oil	10[a]	11	12	13	14A	15	16	17A	18
Avg Cat Temperature, °F	--	--	789.8	789.8	789.4	791.2	790.7	791.1	791.3
Pressure, psig	1800	→	→	→	→	→	→	→	2400
LHSV, Vo/Vc/hr	0.27	→	→	→	→	0.55	→	→	→
Gravity, API°	--	39.0	38.7	39.0	39.8	38.5	38.3	38.9	38.7
Liquid Product, g		110	94	101	106	94	219	212	305
Carbon, Wt%					86.32			86.39	
Hydrogen, Wt%					13.65			13.57	
Nitrogen, ppm	--	36	2	15	14	195	206	209	18
Sulfur, ppm	--	600	504	820	231	245	284	193	110
Pour Point, °F					70			65	
Viscosity, cst (104°F)					3.59			3.56	
Simulated Distillation									
IBP, °F					114			182	
IBP-360°F, Wt%					15.2			12.6	
360-650°F, Wt%					60.2			60.6	
650°F+, Wt%					24.6			26.8	
FBP, °F					912			905	
JP-4, Wt%					38.4			39.3	
Gas Rate, SCFB x 10^{-3}					29.4			14.7	
Hydrogen Consumption, SCFB					1370			1360	
Wt%, C_1-C_4 on Feed					2.3			3.1	
Volume Expansion, %					106			105	

a. Sample slopped for 24 hours due to change to lower liquid hourly space velocity.

TABLE 2 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 1
PROCESS VARIABLE STUDY, SINGLE-CATALYST SYSTEM

Catalyst: 3609-162, Co/Cr/Mo on Alumina
Run ID: AU-75-35

Days on Oil	19	20A	21	22A	23	24	25	26	27A
Avg Cat Temperature, °F	790.2	790.2	790.1	790.0	790.2	--	--	790.5	790.3
Pressure, psig	2400	→	1400	→	→	→	1800	→	→
LHSV, Vo/Vc/hr	0.55	→	→	→	→	→	→	→	→
Gravity, API°	38.4	39.3	38.3	38.3	38.3	37.4	39.0	39.1	39.1
Liquid Product, g	144	162	146	151	208	163	203	205	150
Carbon, Wt%		86.29		87.07					86.54
Hydrogen, Wt%		13.71		12.85					13.40
Nitrogen, ppm	--	29	557	702	--	948	357	253	395
Sulfur, ppm	82	50	40	70	87	261	163	114	153
Pour Point, °F		70		70					75
Viscosity, cst (104°F)		3.78		3.26					3.25
Simulated Distillation									
IBP, °F		75		170					142
IBP-360°F, Wt%		14.6		13.4					9.1
360-650°F, Wt%		59.4		60.6					65.9
650°F+, Wt%		26.0		26.0					25.0
FBP, °F		914		915					805
JP-4, Wt%		37.8		36.2					32.7
Gas Rate, SCFB x 10^{-3}		17.4		7.6					13.4
Hydrogen Consumption, SCFB		1430		910					1265
Wt%, C_1-C_4 on Feed		2.8		3.4					3.0
Volume Expansion, %		105		103					106

TABLE 2 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK I
PROCESS VARIABLE STUDY, SINGLE-CATALYST SYSTEM

Catalyst: 3609-162, Co/Cr/Mo on Alumina
Run ID: AU-75-35

Days on Oil	28	29	30A	31	32[a]	33[b]	34	35	36A
Avg Cat Temperature, °F	769.7	769.7	770.0	770.9	--	--	809.5	809.4	809.4
Pressure, psig	1800	→	→	→	→	→	→	→	→
LHSV, Vo/Vc/hr	0.55	→	→	→	→	→	→	→	→
Gravity, API°	36.1	37.0	39.8	37.0	--	--	39.4	40.4	40.2
Liquid Product, g	94	219	171	222	--	--	200	213	174
Carbon, Wt%			86.45						86.39
Hydrogen, Wt%			13.46						13.58
Nitrogen, ppm	875	1000	837	885	--	--	145	98	130
Sulfur, ppm	130	140	90	110	--	--	150	120	210
Pour Point, °F			70						70
Viscosity, cst (104°F)			4.64						2.58
Simulated Distillation									
IBP, °F			183						74
IBP-360°F, Wt%			9.9						14.9
360-650°F, Wt%			58.6						62.1
650°F+, Wt%			31.5						23.0
FBP, °F			922						866
JP-4, Wt%			29.9						38.3
Gas Rate, SCFB x 10^{-3}			13.0						12.9
Hydrogen Consumption, SCFB			1245						1420
Wt%, C_1-C_4 on Feed			2.2						4.0
Volume Expansion, %			106						105

a. Sample slopped for 24 hours due to change in temperature from 770°F to 810°F.
b. Sample accidentally slopped.

TABLE 2 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK I
PROCESS VARIABLE STUDY, SINGLE-CATALYST SYSTEM

Catalyst: 3609-162, Co/Cr/Mo on Alumina
Run ID: AU-75-35

Days on Oil	37	38	39	40	41	42	43A
Avg Cat Temperature, °F	789.3	--	--	790.0	790.0	790.1	789.9
Pressure, psig	1800	→	→	→	→	→	→
LHSV, Vo/Vc/hr	0.55	→	→	→	→	→	→
Gravity, API°	38.1	38.4	38.2	38.2	38.4	38.2	39.1
Liquid Product, g	94	206	204	204	216	208	162
Carbon, Wt%							86.44
Hydrogen, Wt%							13.50
Nitrogen, ppm	327	335	380	380	368	365	376
Sulfur, ppm	81	340	160	190	90	60	100
Pour Point, °F							75
Viscosity, cst (104°F)							3.28
Simulated Distillation							
IBP, °F							131
IBP-360°F, Wt%							15.9
360-650°F, Wt%							62.4
650°F+, Wt%							21.7
FBP, °F							1000+
JP-4, Wt%							42.6
Gas Rate, SCFB x 10^{-3}							12.9
Hydrogen Consumption, SCFB							1320
Wt%, C_1-C_4 on Feed							3.1
Volume Expansion, %							105

TABLE 3

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 1
PROCESS VARIABLE STUDY, DUAL-CATALYST SYSTEM

Catalyst: (1) 3609-161, Ni/Mo/P on Alumina
(2) 3609-162, Co/Cr/Mo on Alumina
Run ID: AU-27-125

Days on Oil	1	2[a]	3	4A	5[b]	6	7	8
Avg Cat (1) Temperature, ^{o}F	733.8	--	734.8	734.7	735.4	--	--	735.2
Avg Cat (2) Temperature, ^{o}F	300.0	--	300.0	300.0	790.9	--	--	791.0
Pressure, psig	1800	→						
LHSV, Vo/Vc/hr[c]	0.5	→						
Gravity, API^{o}	36.8	--	36.8	36.8	--	37.0	37.2	37.2
Liquid Product, g	119	--	75	79	--	208	207	178
Carbon, Wt%				86.30				
Hydrogen, Wt%				6.17				
Nitrogen, ppm	229	--	138	65	--	324	282	235
Sulfur, ppm	1070	--	1190	550	--	600	4600	560
Pour Point, ^{o}F				80				
Viscosity, cst (104^{o}F)				6.17				
Simulated Distillation								
IBP, ^{o}F				182				
IBP-360^{o}F, Wt%				7.9				
360-650^{o}F, Wt%				52.3				
650^{o}F+, Wt%				39.8				
FBP, ^{o}F				1000+				
JP-4, Wt%				24.0				
Gas Rate, SCFB x 10^{-3}				5.2				
Hydrogen Consumption, SCFB				1290				
Wt%, C_1-C_4 on Feed				1.0				
Volume Expansion, %				105				

a. Pump off for unit repairs. Hydrogen flow maintained.
b. Sample slopped after bringing second reactor on stream.
c. Overall space velocity. 10.3 cc of each catalyst used.

TABLE 3 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 1
PROCESS VARIABLE STUDY, DUAL-CATALYST SYSTEM

Catalyst: (1) 3609-161, Ni/Mo/P on Alumina
(2) 3609-162, Co/Cr/Mo on Alumina
Run ID: AU-27-125

Days on Oil	9	10A	11	12	13A	14	15A	16
Avg Cat (1) Temperature, °F	735.2	735.2	735.1	735.3	735.7	735.2	735.9	--
Avg Cat (2) Temperature, °F	791.0	791.0	787.6	790.2	790.9	791.9	790.3	--
Pressure, psig	1800	→	1400	→	→	→	→	1800
LHSV, Vo/Vc/hr	0.5	→	→	→	→	→	→	→
Gravity, API°	37.2	37.2	37.6	37.8	36.4	36.8	36.1	34.8
Liquid Product, g	222	193	113	139	166	193	172	106
Carbon, Wt%		86.41			86.45		86.63	
Hydrogen, Wt%		13.54			13.48		13.26	
Nitrogen, ppm	230	261	407	500	533	673	686	218
Sulfur, ppm	570	229	342	680	199	530	391	400
Pour Point, °F		75			75		75	
Viscosity, cst (104°F)		5.03			4.65		5.28	
Simulated Distillation								
IBP, °F		124			127		66	
IBP-360°F, Wt%		10.9			10.8		14.9	
360-650°F, Wt%		55.2			53.3		52.3	
650°F+, Wt%		33.9			35.9		32.8	
FBP, °F		1000+			1000+		1014	
JP-4, Wt%		31.1			29.5		31.5	
Gas Rate, SCFB x 10^{-3}		10.1			5.0		7.1	
Hydrogen Consumption, SCFB		1280			1220		1110	
Wt%, C_1-C_4 on Feed		1.7			1.5		2.3	
Volume Expansion, %		105			105		10[illegible]	

TABLE 3 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 1
PROCESS VARIABLE STUDY, DUAL-CATALYST SYSTEM

Catalyst: (1) 3609-161, Ni/Mo/P on Alumina
(2) 3609-162, Co/Cr/Mo on Alumina
Run ID: AU-27-125

Days on Oil	17	18A	19	20	21	22A	23	24
Avg Cat (1) Temperature, °F	--	735.8	735.3	735.9	735.6	735.9	--	735.5
Avg Cat (2) Temperature, °F	--	791.9	789.2	770.4	770.0	772.3	--	811.4
Pressure, psig	1800	→						
LHSV, Vo/Vc/hr	0.5	→						
Gravity, API°	37.0	37.2	36.4	36.1	36.4	36.2	36.1	37.9
Liquid Product, g	200	200	169	100	225	160	176	--
Carbon, Wt%		86.47				86.28		
Hydrogen, Wt%		13.48				13.51		
Nitrogen, ppm	219	234	260	293	287	398	311	47
Sulfur, ppm	94	290	580	1670	118	1670	1720	46
Pour Point, °F		75				75		
Viscosity, cst (104°F)		4.99				5.86		
Simulated Distillation								
IBP, °F		76				81		
IBP-360°F, Wt%		14.2				12.2		
360-650°F, Wt%		52.0				49.3		
650°F+, Wt%		33.8				38.5		
FBP, °F		1000+				1000+		
JP-4, Wt%		31.0				27.1		
Gas Rate, SCFB x 10^{-3}		16.5				3.6		
Hydrogen Consumption, SCFB		1240				1180		
Wt%, C_1-C_4 on Feed		2.0				0.4		
Volume Expansion, %		105				106		

TABLE 3 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 1
PROCESS VARIABLE STUDY, DUAL-CATALYST SYSTEM

Catalyst: (1) 3609-161, Ni/Mo/P on Alumina
(2) 3609-162, Co/Cr/Mo on Alumina
Run ID: AU-27-125

Days on Oil	25	26A	27	28	29	30	31	32A
Avg Cat (1) Temperature, °F	736.2	735.9	736.2	736.0	--	--	736.9	736.2
Avg Cat (2) Temperature, °F	811.8	810.2	811.0	789.8	--	--	790.8	791.8
Pressure, psig	1800	→						
LHSV, Vo/Vc/hr	0.5	→						
Gravity, API°	37.9	38.1	37.2	37.0	36.4	35.6	35.8	36.6
Liquid Product, g	268	161	186	112	216	202	210	185
Carbon, Wt%		86.43						86.45
Hydrogen, Wt%		13.51						13.48
Nitrogen, ppm	251	229	205	--	393	443	398	475
Sulfur, ppm	380	380	570	371	560	320	182	180
Pour Point, °F		70						75
Viscosity, cst (104°F)		3.84						4.56
Simulated Distillation								
IBP, °F		116						126
IBP-360°F, Wt%		12.5						6.8
360-650°F, Wt%		57.2						56.2
650°F+, Wt%		30.3						37.0
FBP, °F		1000+						939
JP-4, Wt%		33.3						24.4
Gas Rate, SCFB x 10^{-3}		18.0						28.4
Hydrogen Consumption, SCFB		1260						1240
Wt%, C_1-C_4 on Feed		2.0						1.7
Volume Expansion, %		105						104

TABLE 3 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 1
PROCESS VARIABLE STUDY, DUAL-CATALYST SYSTEM

Catalyst: (1) 3609-161, Ni/Mo/P on Alumina
(2) 3609-162, Co/Cr/Mo on Alumina
Run ID: AU-27-125

Days on Oil	33	34	35A	36	37[a]	38	39	40
Avg Cat (1) Temperature, °F	337.7	737.4	738.4	735.6	735.0	--	--	733.6
Avg Cat (2) Temperature, °F	791.2	793.1	790.9	790.1	790.0	--	--	787.5
Pressure, psig	1800	→	→	→	→	→	→	→
LHSV, Vo/Vc/hr	1.0	→	→	→	0.25	→	→	→
Gravity, API°	34.6	35.0	35.0	34.4	--	37.8	37.6	38.0
Liquid Product, g	177	434	391	387	--	108	102	117
Carbon, Wt%			86.39					
Hydrogen, Wt%			13.39					
Nitrogen, ppm	2170	2290	1920	2280	--	144	83	20
Sulfur, ppm	410	510	270	650	--	370	410	300
Pour Point, °F			75					
Viscosity, cst (104°F)			5.74					
Simulated Distillation								
IBP, °F			144					
IBP-360°F, Wt%			7.4					
360-650°F, Wt%			52.6					
650°F+, Wt%			40.0					
FBP, °F			962					
JP-4, Wt%			23.3					
Gas Rate, SCFB x 10^{-3}			54.8					
Hydrogen Consumption, SCFB			1140					
Wt%, C_1-C_4 on Feed			1.4					
Volume Expansion, %			104					

a. Sample slopped due to change to low space velocity.

TABLE 3 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 1
PROCESS VARIABLE STUDY, DUAL-CATALYST SYSTEM

Catalyst: (1) 3609-161, Ni/Mo/P on Alumina
(2) 3609-162, Co/Cr/Mo on Alumina
Run ID: AU-27-125

Days on Oil	41A	42	43	44	45	46	47	48A
Avg Cat (1) Temperature, °F	733.8	735.8	--	--	735.2	735.0	735.6	735.3
Avg Cat (2) Temperature, °F	787.7	788.2	--	--	787.9	789.0	788.8	790.8
Pressure, psig	1800							
LHSV, Vo/Vc/hr	0.25	0.5						
Gravity, API°	37.8	36.6	36.6	36.6	36.4	36.2	36.4	36.2
Liquid Product, g	96	122	182	240	199	228	218	199
Carbon, Wt%	86.40							86.49
Hydrogen, Wt%	13.58							13.41
Nitrogen, ppm	56	553	691	632	668	779	642	775
Sulfur, ppm	120	260	490	360	200	370	370	280
Pour Point, °F	70							70
Viscosity, cst (104°F)	3.69							4.70
Simulated Distillation								
IBP, °F	161							99
IBP-360°F, Wt%	8.4							11.7
360-650°F, Wt%	58.6							57.5
650°F+, Wt%	32.5							40.8
FBP, °F	916							909
JP-4, Wt%	27.9							31.5
Gas Rate, SCFB x 10^{-3}	27.9							26.7
Hydrogen Consumption, SCFB	1310							1180
Wt%, C_1-C_4 on Feed	2.0							2.0
Volume Expansion, %	105							106

TABLE 4

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, METALS OPTIMIZATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-175, 1.5/10/5 on Alumina
Run ID: AU-27-130

Days on Oil	1[a]	2	3	4	5	6A
Avg Cat Temperature, °F	--	--	780.4	781.0	780.3	780.2
Gravity, API°		38.0	38.0	37.6	38.0	38.3
Liquid Product, g		207	220	207	201	164
Carbon, Wt%						86.43
Hydrogen, Wt%						13.51
Nitrogen, ppm		437	451	395	509	678
Sulfur, ppm		410	191	286	115	87
Pour Point, °F						80
Viscosity, cst (104°F)						3.57
Simulated Distillation						
IBP, °F						-1
IBP-360°F, Wt%						14.4
360-650°F, Wt%						60.0
650°F+, Wt%						25.6
FBP, °F						919
JP-4, Wt%						36.7
Gas Rate, SCFB x 10^{-3}						11.9
Hydrogen Consumption, SCFB						1290
Wt%, C_1-C_4 on Feed						2.7
Volume Expansion, %						105

a. Sample slopped.

TABLE 5

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, METALS OPTIMIZATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-165, 1.5/10/10 on Alumina
Run ID: AU-27-127

Days on Oil	1	2	3	4	5A	6
Avg Cat Temperature, °F	779.6	--	779.4	779.9	779.7	779.9
Gravity, API°	39.0	38.7	39.0	38.6	38.6	38.5
Liquid Product, g	162	239	204	73	161	221
Carbon, Wt%					86.33	
Hydrogen, Wt%					13.64	
Nitrogen, ppm	99	144	155	153	161	143
Sulfur, ppm	430	96	147	378	112	211
Pour Point, °F					75	
Viscosity, cst (104°F)					3.46	
Simulated Distillation						
IBP, °F					123	
IBP-360°F, Wt%					14.1	
360-650°F, Wt%					61.4	
650°F+, Wt%					24.5	
FBP, °F					929	
JP-4, Wt%					37.7	
Gas Rate, SCFB x 10^{-3}					10.5	
Hydrogen Consumption, SCFB					1390	
Wt%, C_1-C_4 on Feed					2.8	
Volume Expansion, %					105	

TABLE 6

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, METALS OPTIMIZATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-174, 1.5/10/15 on Alumina
Run ID: AU-75-40

Days on Oil	1	2	3	4	5	6	7A
Avg Cat Temperature, °F	779.2	--	--	779.8	780.0	780.0	780.0
Gravity, API°	39.9	39.0	39.1	39.1	39.0	39.2	39.2
Liquid Product, g	98	207	209	208	170	197	169
Carbon, Wt%							86.32
Hydrogen, Wt%							13.65
Nitrogen, ppm	78	82	83	88	82	116	110
Sulfur, ppm	358	120	293	122	183	--	117
Pour Point, °F							80
Viscosity, cst (104°F)							3.24
Simulated Distillation							
IBP, °F							5
IBP-360°F, Wt%							15.1
360-650°F, Wt%							60.9
650°F+, Wt%							24.0
FBP, °F							915
JP-4, Wt%							38.4
Gas Rate, SCFB x 10^{-3}							10.0
Hydrogen Consumption, SCFB							1400
Wt%, C_1-C_4 on Feed							2.8
Volume Expansion, %							105

TABLE 7

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, METALS OPTIMIZATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-171, 3.5/10/10 on Alumina
Run ID: AU-27-129

Days on Oil	1	2	3	4A
Avg Cat Temperature, °F	780.4	--	779.5	779.5
Gravity, API°	38.5	38.4	38.6	38.6
Liquid Product, g	105	87	171	182
Carbon, Wt%				86.42
Hydrogen, Wt%				13.55
Nitrogen, ppm	165	281	270	264
Sulfur, ppm	279	102	87	35
Pour Point, °F				75
Viscosity, cst (104°F)				3.50
Simulated Distillation				
IBP, °F				-6
IBP-360°F, Wt%				16.2
360-650°F, Wt%				57.3
650°F+, Wt%				26.5
FBP, °F				930
JP-4, Wt%				35.0
Gas Rate, SCFB x 10^{-3}				14.2
Hydrogen Consumption, SCFB				1320
Wt%, C_1-C_4 on Feed				2.6
Volume Expansion, %				105

TABLE 8

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, METALS OPTIMIZATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-166, 5/10/10 on Alumina
Run ID: AU-75-37

Days on Oil	1	2	3	4	5A	6
Avg Cat Temperature, °F	780.3	--	780.7	780.0	779.9	779.9
Gravity, API°	83.5	38.6	38.2	38.4	38.3	39.1
Liquid Product, g	168	228	185	207	177	192
Carbon, Wt%					86.34	
Hydrogen, Wt%					13.63	
Nitrogen, ppm	104	119	125	142	159	160
Sulfur, ppm	192	96	98	185	121	89
Pour Point, °F					75	
Viscosity, cst (104°F)					3.49	
Simulated Distillation						
IBP, °F					117	
IBP-360°F, Wt%					14.5	
360-650°F, Wt%					59.5	
650°F+, Wt%					26.0	
FBP, °F					928	
JP-4, Wt%					37.8	
Gas Rate, SCFB x 10^{-3}					11.6	
Hydrogen Consumption, SCFB					1380	
Wt%, C_1-C_4 on Feed					2.7	
Volume Expansion, %					105	

TABLE 9

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, METALS OPTIMIZATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-173, 1.5/5/10 on Alumina
Run ID: AU-75-39

Days on Oil	1	2	3	4	5A	6
Avg Cat Temperature, °F	780.9	--	780.3	779.9	779.9	780.3
Gravity, API°	39.1	39.5	39.3	38.9	39.0	38.9
Liquid Product, g	204	218	203	202	168	197
Carbon, Wt%					86.29	
Hydrogen, Wt%					13.67	
Nitrogen, ppm	66	68	80	120	96	134
Sulfur, ppm	258	189	410	151	228	152
Pour Point, °F					75	
Viscosity, cst (104°F)					3.24	
Simulated Distillation						
IBP, °F					74	
IBP-360°F, Wt%					16.7	
360-650°F, Wt%					61.1	
650°F+, Wt%					22.2	
FBP, °F					928	
JP-4, Wt%					41.1	
Gas Rate, SCFB x 10^{-3}					11.3	
Hydrogen Consumption, SCFB					1415	
Wt%, C_1-C_4 on Feed					2.8	
Volume Expansion, %					105	

TABLE 10

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, METALS OPTIMIZATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-170, 1.5/15/10 on Alumina
Run ID: AU-27-128

Days on Oil	1	2	3	4	5A	6
Avg Cat Temperature, °F	779.1	--	779.9	779.9	780.0	780.0
Gravity, API°	38.0	37.5	37.5	38.4	39.0	38.8
Liquid Product, g	217	216	204	194	162	208
Carbon, Wt%					86.33	
Hydrogen, Wt%					13.56	
Nitrogen, ppm	93	224	250	246	244	288
Sulfur, ppm	115	620	134	222	810	258
Pour Point, °F					75	
Viscosity, cst (104°F)					3.39	
Simulated Distillation						
IBP, °F					130	
IBP-360°F, Wt%					13.0	
360-650°F, Wt%					59.4	
650°F+, Wt%					27.6	
FBP, °F					941	
JP-4, Wt%					33.9	
Gas Rate, SCFB x 10^{-3}					12.6	
Hydrogen Consumption, SCFB					1310	
Wt%, C_1-C_4 on Feed					2.2	
Volume Expansion, %					106	

TABLE 11

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, SUPPORT TYPE

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-176, 1.5/10/10 on Alumina/Alumina Phosphate
Run ID: AU-75-41

Days on Oil	1	2	3	4	5	6	7A
Avg Cat Temperature, °F	779.7	--	--	779.9	780.0	780.2	780.2
Gravity, API°	38.2	38.2	38.4	38.6	38.1	38.9	38.9
Liquid Product, g	145	163	206	215	243	178	180
Carbon, Wt%							86.36
Hydrogen, Wt%							13.60
Nitrogen, ppm	--	142	132	148	187	164	193
Sulfur, ppm	--	195	--	81	108	148	164
Pour Point, °F							70
Viscosity, cst (104°F)							3.40
Simulated Distillation							
IBP, °F							71
IBP-360°F, Wt%							14.7
360-650°F, Wt%							55.7
650°F+, Wt%							29.6
FBP, °F							1000+
JP-4, Wt%							34.9
Gas Rate, SCFB x 10^{-3}							10.7
Hydrogen Consumption, SCFB							1365
Wt%, C_1-C_4 on Feed							2.8
Volume Expansion, %							105

TABLE 12

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, SUPPORT TYPE

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-177, 1.5/10/10 on Silica
Run ID: AU-27-131

Days on Oil	1	2	3	4	5A	6
Avg Cat Temperature, ^{o}F	780.2	--	780.3	779.9	780.1	779.6
Gravity, API^{o}	36.1	36.1	36.5	36.1	36.2	36.3
Liquid Product, g	221	201	215	212	206	208
Carbon, Wt%					86.40	
Hydrogen, Wt%					13.25	
Nitrogen, ppm	2530	2790	2800	3260	3330	3000
Sulfur, ppm	259	220	217	217	150	121
Pour Point, ^{o}F					80	
Viscosity, cst (104^{o}F)					4.80	
Simulated Distillation						
IBP, ^{o}F					192	
IBP-360^{o}F, Wt%					9.7	
360-650^{o}F, Wt%					57.8	
650^{o}F+, Wt%					32.5	
FBP, ^{o}F					945	
JP-4, Wt%					29.1	
Gas Rate, SCFB x 10^{-3}					12.9	
Hydrogen Consumption, SCFB					1080	
Wt%, C_1-C_4 on Feed					2.1	
Volume Expansion, %					104	

TABLE 13

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, SUPPORT TYPE

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-178, 1.5/10/10 on 20% Silica Alumina
Run ID: AU-27-132

Days on Oil	1	2	3	4	5A	6
Avg Cat Temperature, °F	--	--	780.0	780.6	780.2	780.7
Gravity, API°	39.2	39.2	39.1	39.2	39.2	39.3
Liquid Product, g	195	229	194	226	202	191
Carbon, Wt%					86.40	
Hydrogen, Wt%					13.55	
Nitrogen, ppm	93	50	54	42	20	29
Sulfur, ppm	343	237	379	278	393	289
Pour Point, °F					70	
Viscosity, cst (104°F)					3.16	
Simulated Distillation						
IBP, °F					62	
IBP-360°F, Wt%					15.3	
360-650°F, Wt%					56.7	
650°F+, Wt%					28.0	
FBP, °F					1000+	
JP-4, Wt%					37.1	
Gas Rate, SCFB x 10^{-3}					12.1	
Hydrogen Consumption, SCFB					1340	
Wt%, C_1-C_4 on Feed					3.0	
Volume Expansion, %					105	

TABLE 14

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, SUPPORT TYPE

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-179, 1.5/10/10 on 30% US Sieve Alumina
Run ID: AU-75-42

Days on Oil	1	2	3	4	5	6A
Avg Cat Temperature, °F	781.0	--	--	779.6	781.0	780.8
Gravity, API°	50.7	49.8	47.3	44.9	42.7	44.5
Liquid Product, g	69	129	200	194	203	173
Carbon, Wt%						86.16
Hydrogen, Wt%						13.83
Nitrogen, ppm	1	2	18	13	95	12
Sulfur, ppm	37	125	202	188	160	127
Pour Point, °F						55
Viscosity, cst (104°F)						1.93
Simulated Distillation						
IBP, °F						19
IBP-360°F, Wt%						28.7
360-650°F, Wt%						55.5
650°F+, Wt%						15.8
FBP, °F						1000+
JP-4, Wt%						58.3
Gas Rate, SCFB x 10^{-3}						12.9
Hydrogen Consumption, SCFB						1557
Wt%, C_1-C_4 on Feed						3.9
Volume Expansion, %						107

TABLE 14 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, SUPPORT TYPE

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-179, 1.5/10/10 on 30% US Sieve Alumina
Run ID: AU-75-42

Days on Oil	7	8	9	10	11	12
Avg Cat Temperature, °F	780.8	781.4	--	--	780.6	780.3
Gravity, API°	43.1	43.4	42.3	41.7	40.1	40.3
Liquid Product, g	189	202	201	181	225	185
Carbon, Wt%						
Hydrogen, Wt%						
Nitrogen, ppm	12	9	5	29	2	17
Sulfur, ppm	103	106	530	228	55	75
Pour Point, °F						
Viscosity, cst (104°F)						
Simulated Distillation						
IBP, °F						
IBP-360°F, Wt%						
360-650°F, Wt%						
650°F+, Wt%						
FBP, °F						
JP-4, Wt%						
Gas Rate, SCFB x 10^{-3}						
Hydrogen Consumption, SCFB						
Wt%, C_1-C_4 on Feed						
Volume Expansion, %						

TABLE 15

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, SUPPORT TYPE

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-182-1, 1.5/10/15 on 30% US Sieve Alumina
Run ID: AU-75-46

Days on Oil	1	2	3	4	5A	6
Avg Cat Temperature, °F	782.0	--	--	779.8	780.4	780.3
Gravity, API°	55.1	50.5	47.2	45.6	44.6	43.9
Liquid Product, g	85	186	197	204	141	212
Carbon, Wt%					85.93	
Hydrogen, Wt%					14.00	
Nitrogen, ppm	51	13	12	7	15	2
Sulfur, ppm	117	220	55	169	710	137
Pour Point, °F					30	
Viscosity, cst (104°F)					1.70	
Simulated Distillation						
IBP, °F					8	
IBP-360°F, Wt%					29.7	
360-650°F, Wt%					57.3	
650°F+, Wt%					13.0	
FBP, °F					840	
JP-4, Wt%					60.0	
Gas Rate, SCFB x 10^{-3}					12.0	
Hydrogen Consumption, SCFB					1660	
Wt%, C_1-C_4 on Feed					3.6	
Volume Expansion, %					108	

TABLE 15 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, SUPPORT TYPE

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-182-1, 1.5/10/15 on 30% US Sieve Alumina
Run ID: AU-75-46

Days on Oil	7	8	9	10	11	12A
Avg Cat Temperature, ^{o}F	780.8	780.8	--	--	780.4	780.5
Gravity, API^{o}	44.1	42.3	43.4	43.3	42.5	43.3
Liquid Product, g	110	141	203	195	210	180
Carbon, Wt%						86.12
Hydrogen, Wt%						13.87
Nitrogen, ppm	2	5	3	3	2	14
Sulfur, ppm	111	85	42	18	17	49
Pour Point, ^{o}F						45
Viscosity, cst (104^{o}F)						2.06
Simulated Distillation						
IBP, ^{o}F						42
IBP-360^{o}F, Wt%						24.4
360-650^{o}F, Wt%						58.0
650^{o}F+, Wt%						17.6
FBP, ^{o}F						879
JP-4, Wt%						52.1
Gas Rate, SCFB x 10^{-3}						15.0
Hydrogen Consumption, SCFB						1575
Wt%, C_1-C_4 on Feed						3.6
Volume Expansion, %						107

AD-A112 820 AMOCO OIL CO NAPERVILLE IL CATALYSIS RESEARCH DIV F/G 21/4
EVALUATION OF HYDROCRACKING CATALYSTS FOR CONVERSION OF WHOLE S--ETC(U)
OCT 81 A M TAIT, A L HENSLEY F33615-79-C-2098
UNCLASSIFIED M81-65 AFWAL-TR-81-2098 NL

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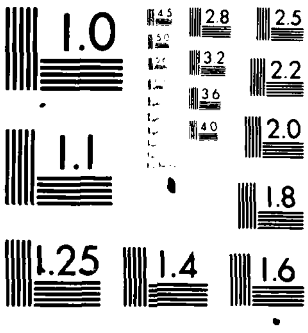


TABLE 16

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, SUPPORT TYPE

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-183, 1.5/10/15 on 20% Silica Alumina
Run ID: AU-75-47

Days on Oil	1	2A	3	4	5	6A	7	8
Avg Cat Temperature, °F	780.5	780.1	--	--	780.7	781.3	780.9	780.5
Gravity, API°	39.9	40.0	39.8	39.7	39.8	39.7	39.2	39.0
Liquid Product, g	93	162	206	210	225	159	231	191
Carbon, Wt%		86.19				86.35		
Hydrogen, Wt%		13.80				13.63		
Nitrogen, ppm	2	8	9	8	7	8	14	8
Sulfur, ppm	247	103	196	315	54	165	150	281
Pour Point, °F		70				65		
Viscosity, cst (104°F)		2.92				3.0		
Simulated Distillation								
IBP, °F		36				73		
IBP-360°F, Wt%		19.7				14.9		
360-650°F, Wt%		60.4				61.5		
650°F+, Wt%		19.9				23.5		
FBP, °F		950				902		
JP-4, Wt%		47.1				38.3		
Gas Rate, SCFB x 10^{-3}		12.1				11.8		
Hydrogen Consumption, SCFB		1500				1400		
Wt%, C_1-C_4 on Feed		2.9				3.1		
Volume Expansion, %		106				105		

TABLE 17

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 3
SUPPORT OPTIMIZATION STUDY, SILICA CONCENTRATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-194; 1.5/10/15 on 10% Silica Alumina
Run ID: AU-75-53

Days on Oil	1	2	3	4	5	6	7A	8	9	10A
Avg Cat Temperature, °F	779.6	780.5	--	--	--	781.2	779.2	779.9	779.8	779.8
Gravity, API°	40.4	38.5	38.6	38.5	38.4	37.8	38.0	38.5	38.0	37.2
Liquid Product, g	86	164	193	212	168	194	177	175	152	211
Carbon, Wt%							86.27			86.26
Hydrogen, Wt%							13.68			13.49
Nitrogen, ppm	100	260	140	100	100	820	320	90	250	900
Sulfur, ppm	530	372	324	232	353	460	153	180	500	980
Pour Point, °F							75			30
Viscosity, cst (104°F)							3.47			3.87
Simulated Distillation										
IBP, °F							100			106
IBP-360°F, Wt%							16.2			12.4
360-650°F, Wt%							47.8			57.0
650°F+, Wt%							36.0			30.6
FBP, °F							1000+			953
JP-4, Wt%							34.6			32.4
Gas Rate, SCFB x 10^{-3}							18.1			12.5
Hydrogen Consumption, SCFB							1400			1250
Wt%, C_1-C_4 on Feed							2.5			2.7
Volume Expansion, %							105			104

TABLE 18

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 3
SUPPORT OPTIMIZATION STUDY, SILICA CONCENTRATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-184; 1.5/10/15 on 30% Silica Alumina
Run ID: AU-75-45

Days on Oil	1	2	3	4	5	6A	7
Avg Cat Temperature, °F	780.0	780.0	--	--	780.2	780.1	781.1
Gravity, API°	40.5	39.6	39.4	39.4	39.4	39.8	39.4
Liquid Product, g	94	201	224	207	191	155	209
Carbon, Wt%						86.30	
Hydrogen, Wt%						13.68	
Nitrogen, ppm	67	42	26	33	18	58	8
Sulfur, ppm	460	199	168	172	128	56	59
Pour Point, °F						65	
Viscosity, cst (104°F)						3.03	
Simulated Distillation							
IBP, °F						125	
IBP-360°F, Wt%						12.9	
360-650°F, Wt%						59.3	
650°F+, Wt%						38.8	
FBP, °F						1000+	
JP-4, Wt%						36.0	
Gas Rate, SCFB x 10^{-3}						13.9	
Hydrogen Consumption, SCFB						1435	
Wt% C_1-C_4 on Feed						3.1	
Volume Expansion, %						105	

TABLE 19

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 3
SUPPORT OPTIMIZATION STUDY, SILICA CONCENTRATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-196; 1.5/10/15 on 50% Silica Alumina
Run ID: AU-75-52

Days on Oil	1	2	3	4	5	6	7A
Avg Cat Temperature, °F	781.4	782.1	780.8	--	--	779.8	779.9
Gravity, API°	40.3	39.6	38.5	38.7	39.0	38.7	39.0
Liquid Product, g	97	228	201	214	205	228	209
Carbon, Wt%							86.39
Hydrogen, Wt%							13.60
Nitrogen, ppm	166	323	109	25	16	18	20
Sulfur, ppm	650	540	150	219	257	67	70
Pour Point, °F							75
Viscosity, cst (104°F)							3.40
Simulated Distillation							
IBP, °F							104
IBP-360°F, Wt%							13.9
360-650°F, Wt%							58.3
650°F+, Wt%							27.8
FBP, °F							971
JP-4, Wt%							860
Gas Rate, SCFB x 10^{-3}							18.1
Hydrogen Consumption, SCFB							1360
Wt%, C_1-C_4 on Feed							2.8
Volume Expansion, %							105

TABLE 19 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 3
SUPPORT OPTIMIZATION STUDY, SILICA CONCENTRATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-196; 1.5/10/15 on 50% Silica Alumina
Run ID: AU-75-52

Days on Oil	8	9	10	11	12	13	14A
Avg Cat Temperature, °F	780.0	779.8	779.9	--	--	779.9	778.2
Gravity, API°	37.9	37.6	37.7	37.8	37.8	37.7	38.5
Liquid Product, g	218	184	203	204	205	224	195
Carbon, Wt%							86.32
Hydrogen, Wt%							13.63
Nitrogen, ppm	37	38	31	29	42	38	69
Sulfur, ppm	236	164	208	246	160	213	345
Pour Point, °F							75
Viscosity, cst (104°F)							3.36
Simulated Distillation							
IBP, °F							96
IBP-360°F, Wt%							13.0
360-650°F, Wt%							59.2
650°F+, Wt%							27.8
FBP, °F							924
JP-4, Wt%							36.0
Gas Rate, SCFB x 10^{-3}							14.8
Hydrogen Consumption, SCFB							1310
Wt%, C_1-C_4 on Feed							1.3
Volume Expansion, %							106

TABLE 20

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 3
SUPPORT OPTIMIZATION STUDY, SILICA CONCENTRATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3838-010; 1.5/10/15 on 70% Silica Alumina
Run ID: AU-76-42

Days on Oil	1	2	3	4	5	6	7	8	9	10	11	12A
Avg Cat Temperature, °F	779.3	--	--	779.0	779.7	779.5	779.8	778.5	--	--	780.0	779.9
Gravity, API°	38.1	36.4	36.6	36.8	36.4	36.3	36.1	36.1	35.7	35.8	36.1	36.1
Liquid Product, g	91	204	206	209	198	204	209	215	210	203	119	203
Carbon, Wt%												
Hydrogen, Wt%												
Nitrogen, ppm	512	371	504	421	385	435	719	637	637	697	619	773
Sulfur, ppm	970	490	319	320	206	170	191	224	126	115	64	193
Pour Point, °F												70
Viscosity, cst (104°F)												4.01
Simulated Distillation												
IBP, °F												146
IBP-360°F, Wt%												11.4
360-650°F, Wt%												56.8
650°F+, Wt%												31.8
FBP, °F												984
JP-4, Wt%												31.7
Gas Rate, SCFB x 10^{-3}												
Hydrogen Consumption, SCFB												1320
Wt%, C_1-C_4 on Feed												4.1
Volume Expansion, %												102

TABLE 21

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 3
SUPPORT OPTIMIZATION STUDY, SIEVE TYPE

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-189, 1.5/10/15 on 20% H-ZSM-5 Alumina
Run ID: AU-75-48

Days on Oil	1	2	3A	4	5	6	7	8A	9	10
Avg Cat Temperature, °F	780.9	781.0	781.0	781.0	--	--	780.6	780.6	780.7	780.8
Gravity, API°	40.5	39.7	40.2	39.6	39.9	40.7	40.7	40.8	39.7	39.7
Liquid Product, g	89	204	171	203	218	198	220	192	190	185
Carbon, Wt%			86.20					86.13		
Hydrogen, Wt%			13.79					13.75		
Nitrogen, ppm	23	44	45	42	32	31	29	34	34	32
Sulfur, ppm	165	139	61	102	120	374	360	91	120	190
Pour Point, °F			-15					-10		
Viscosity, cst (104°F)			2.64					2.72		
Simulated Distillation										
IBP, °F			91					1		
IBP-360°F, Wt%			21.8					20.8		
360-650°F, Wt%			60.7					59.6		
650°F+, Wt%			17.5					18.6		
FBP, °F			949					968		
JP-4, Wt%			48.5					46.3		
Gas Rate, SCFB x 10^{-3}			17.2					11.5		
Hydrogen Consumption, SCFB			1540					1505		
Wt%, C_1-C_4 on Feed			3.9					3.7		
Volume Expansion, %			106					106		

TABLE 22

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, Task 3
SUPPORT OPTIMIZATION STUDY, SIEVE TYPE

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-190; 1.5/10/15 on 20% Zeolon Alumina
Run ID: AU-75-49

Days on Oil	1	2	3	4	5A	6	7
Avg Cat Temperature, ^{o}F	780.1	--	--	780.3	780.1	779.3	779.8
Gravity, API^{o}	38.8	38.3	38.2	38.0	39.0	38.4	38.2
Liquid Product, g	144	202	210	204	139	214	186
Carbon, Wt%					86.22		
Hydrogen, Wt%					13.71		
Nitrogen, ppm	85	80	84	86	57	60	72
Sulfur, ppm	306	230	122	84	70	140	141
Pour Point, ^{o}F					65		
Viscosity, cst ($104^{o}F$)					3.27		
Simulated Distillation							
IBP, ^{o}F					52		
IBP-$360^{o}F$, Wt%					14.3		
360-$650^{o}F$, Wt%					57.7		
$650^{o}F$+, Wt%					28.0		
FBP, ^{o}F					933		
JP-4, Wt%					35.7		
Gas Rate, SCFB x 10^{-3}					8.0		
Hydrogen Consumption, SCFB					1450		
Wt%, C_1-C_4 on Feed					3.1		
Volume Expansion, %					105		

TABLE 23

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 3
SUPPORT OPTIMIZATION STUDY, SIEVE TYPE

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-191; 1.5/10/15 on 20% RE-Y Alumina
Run ID: AU-27-136

Days on Oil	1	2	3	4	5	6A	7	8
Avg Cat Temperature, °F	781.6	778.1	--	--	778.1	778.3	778.8	778.8
Gravity, API°	52.4	50.8	45.4	41.7	39.8	39.1	38.6	39.1
Liquid Product, g	91	195	212	196	215	156	206	208
Carbon, Wt%						86.21		
Hydrogen, Wt%						13.75		
Nitrogen, ppm	17	2	2	3	9	31	23	27
Sulfur, ppm	347	328	57	160	280	151	250	160
Pour Point, °F						75		
Viscosity, cst (104°F)						3.48		
Simulated Distillation								
IBP, °F						104		
IBP-360°F, Wt%						13.6		
360-650°F, Wt%						57.4		
650°F+, Wt%						29.0		
FBP, °F						960		
JP-4, Wt%						34.7		
Gas Rate, SCFB x 10^{-3}						11.1		
Hydrogen Consumption, SCFB						1470		
Wt%, C_1-C_4 on Feed						2.8		
Volume Expansion, %						105		

TABLE 24

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 3
SUPPORT OPTIMIZATION STUDY, SIEVE TYPE

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3747-177-1; 1.5/10/15 on 20% H-AMS Alumina
Run ID: AU-75-50

Days on Oil	1	2	3	4A	5	6	7	8	9	10	11A
Avg Cat Temperature, ^{o}F	--	--	780.4	780.1	780.4	779.9	779.9	--	--	781.2	782.4
Gravity, API^{o}	42.5	42.0	41.8	42.7	41.0	41.2	42.2	39.4	38.3	39.4	41.0
Liquid Product, g	98	193	200	170	206	183	194	140	187	148	158
Carbon, Wt%				86.12							86.30
Hydrogen, Wt%				13.87							13.69
Nitrogen, ppm	16	5	5	5	4	4	3	359	425	81	27
Sulfur, ppm	205	121	23	47	4	10	--	208	301	264	90
Pour Point, ^{o}F				-60							-30
Viscosity, cst (104^{o}F)				2.22							2.34
Simulated Distillation											
IBP, ^{o}F				24							-15
IBP-360^{o}F, Wt%				22.0							19.4
360-650^{o}F, Wt%				59.7							60.1
650^{o}F+, Wt%				18.3							20.5
FBP, ^{o}F				906							914
JP-4, Wt%				48.4							44.9
Gas Rate, SCFB x 10^{-3}				12.9							15.1
Hydrogen Consumption, SCFB				1610							1510
Wt%, C_1-C_4 on Feed				4.7							4.7
Volume Expansion, %				106							104

TABLE 25

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 3
SUPPORT OPTIMIZATION STUDY, SIEVE CONCENTRATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3838-007; 1.5/10/15 on 20% US Sieve Alumina
Run ID: AU-75-56

Days on Oil	1	2	3A	4	5	6	7A	8
Avg Cat Temperature, °F	781.1	780.7	781.2	--	--	780.5	781.0	780.9
Gravity, API°	47.3	43.4	40.2	37.1	37.3	36.8	38.3	37.6
Liquid Product, g	94	215	190	206	217	231	197	203
Carbon, Wt%			86.27				86.38	
Hydrogen, Wt%			13.72				13.58	
Nitrogen, ppm	108	23	28	36	45	37	55	64
Sulfur, ppm	570	279	80	152	105	357	342	183
Pour Point, °F			65				80	
Viscosity, cst (104°F)			2.76				3.20	
Simulated Distillation								
IBP, °F			65				86	
IBP-360°F, Wt%			17.6				15.4	
360-650°F, Wt%			58.4				47.0	
650°F+, Wt%			24.0				37.6	
FBP, °F			906				1000+	
JP-4, Wt%			41.5				33	
Gas Rate, SCFB x 10^{-3}			11.5				20.3	
Hydrogen Consumption, SCFB			1490				1340	
Wt%, C_1-C_4 on Feed			3.7				2.8	
Volume Expansion, %			105				103	

TABLE 25 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 3
SUPPORT OPTIMIZATION STUDY, SIEVE CONCENTRATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3838-007; 1.5/10/15 on 20% US Sieve Alumina
Run ID: AU-75-56

Days on Oil	9	10A	11	12	13	14	15A
Avg Cat Temperature, $^{\circ}F$	779.9	779.6	--	--	--	779.6	779.8
Gravity, API$^{\circ}$	37.5	38.3	37.6	37.7	37.2	37.6	38.2
Liquid Product, g	207	189	181	209	200	218	190
Carbon, Wt%		86.41					86.51
Hydrogen, Wt%		13.54					13.46
Nitrogen, ppm	57	76	73	72	72	66	88
Sulfur, ppm	144	395	205	182	420	141	187
Pour Point, $^{\circ}F$		75					75
Viscosity, cst (104°F)		3.96					3.60
Simulated Distillation							
IBP, $^{\circ}F$		147					154
IBP-360°F, Wt%		11.6					12.0
360-650°F, Wt%		56.9					57.0
650°F+, Wt%		31.5					31.0
FBP, $^{\circ}F$		1000+					977
JP-4, Wt%		31.7					31.7
Gas Rate, SCFB x 10^{-3}		18.2					18.1
Hydrogen Consumption, SCFB		1310					1260
Wt%, C_1-C_4 on Feed		2.7					2.6
Volume Expansion, %		103					105

TABLE 26

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 3
SUPPORT OPTIMIZATION STUDY, SIEVE CONCENTRATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3862-003; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-57

Days on Oil	1	2	3	4	5	6A	7
Avg Cat Temperature, °F	780.9	780.5	--	--	779.7	780.0	780.8
Gravity, API°	51.7	52.1	53.9	52.9	52.0	49.6	50.7
Liquid Product, g	66	197	198	192	192	190	203
Carbon, Wt%						85.79	
Hydrogen, Wt%						14.18	
Nitrogen, ppm	216	16	15	18	2	3	3
Sulfur, ppm	460	303	570	270	54	262	16
Pour Point, °F						-15	
Viscosity, cst (104°F)						1.25	
Simulated Distillation							
IBP, °F						50	
IBP-360°F, Wt%						42.0	
360-650°F, Wt%						52.6	
650°F+, Wt%						5.4	
FBP, °F						752	
JP-4, Wt%						76	
Gas Rate, SCFB x 10^{-3}						19.0	
Hydrogen Consumption, SCFB						1870	
Wt%, C_1-C_4 on Feed						6.0	
Volume Expansion, %						109	

TABLE 27

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 4
CATALYST PHYSICAL PROPERTIES STUDY

Conditions: 1800 psig
Catalyst: 3838-023
Run ID: AU-75-61

Days on Oil	1	2	3	4A	5	6	7	8A	9	10
Avg Cat Temperature, °F	780.9	--	--	780.1	780.4	781.4	781.5	780.9	780.8	779.5
LHSV, Vo/Vc/hr	0.5	→	→	→	0.75	→	→	→	→	→
Gravity, API°	52.9	50.1	49.6	51.9	40.7	38.8	37.6	38.5	39.4	39.4
Liquid Product, g	124	159	178	215	153	296	383	216	188	256
Carbon, Wt%				85.67				86.43		
Hydrogen, Wt%				14.31				13.56		
Nitrogen, ppm	31	--	2	1	13	--	117	44	--	19
Sulfur, ppm	238	--	11	210	30	130	175	527	290	89
Pour Point, °F				-50				75		
Viscosity, cst (104°F)				1.02				3.49		
Simulated Distillation										
IBP, °F				-4				90		
IBP-360°F, Wt%				48.1				13.6		
360-650°F, Wt%				43.4				53.9		
650°F+, Wt%				8.5				32.5		
FBP, °F				909				984		
JP-4, Wt%				79.5				33.8		
Gas Rate, SCFB x 10^{-3}				16.8				11.2		
Hydrogen Consumption, SCFB				1930				1310		
Wt%, C_1-C_4 on Feed				5.7				2.3		
Volume Expansion, %				111				105		

TABLE 28

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 4
CATALYST PHYSICAL PROPERTIES STUDY

Conditions: 1800 psig
Catalyst: 3838-028
Run ID: AU-75-62

Days on Oil	1	2	3	4	5A	6	7	8	9	10A
Avg Cat Temperature, °F	780.5	779.2	781.2	--	781.7	781.8	778.9	779.6	780.0	780.1
LHSV, Vo/Vc/hr	0.5	→				0.75	→			
Gravity, API°	53.9		--	46.8	46.4	36.8	35.9	36.3	36.0	36.6
Liquid Product, g	134	139	--	118	186	232	290	330	373	169
Carbon, Wt%					85.96					86.23
Hydrogen, Wt%					14.00					13.58
Nitrogen, ppm	17	8	--	11	4	--	1450	--	1390	1510
Sulfur, ppm	267	70	--	40	430	--	4030		83	350
Pour Point, °F					35					75
Viscosity, cst (104°F)					1.66					4.33
Simulated Distillation										
IBP, °F					17					121
IBP-360°F, Wt%					32.5					11.7
360-650°F, Wt%					54.0					51.3
650°F+, Wt%					13.5					37.0
FBP, °F					877					990
JP-4, Wt%					62.7					30.1
Gas Rate, SCFB x 10^{-3}					14.1					15.2
Hydrogen Consumption, SCFB					1670					1300
Wt%, C_1-C_4 on Feed					3.9					2.0
Volume Expansion, %					109					105

TABLE 29

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 4
CATALYST PHYSICAL PROPERTIES STUDY

Conditions: 1800 psig
Catalyst: 3838-030
Run ID: AU-75-65

Days on Oil	1	2	3	4A	5	6	7	8	9	10	11A
Avg Cat Temperature, °F	--	--	781.3	779.1	780.2	781.6	781.5	--	--	779.1	779.1
LHSV, Vo/Vc/hr	0.5	→			→	0.75	→				→
Gravity, API°	50.1	45.1	37.4	37.0	36.3	36.2	36.6	36.3	36.3	36.3	36.8
Liquid Product, g	77	184	265	172	186	155	319	373	278	336	288
Carbon, Wt%				86.47							86.47
Hydrogen, Wt%				13.44							13.40
Nitrogen, ppm	130	--	171	600	--	1200	1240	--	1240	--	1240
Sulfur, ppm	150	--	330	336	--	109	150	--	190	--	140
Pour Point, °F				75							75
Viscosity, cst (104°F)				4.10							4.12
Simulated Distillation											
IBP, °F				150							130
IBP-360°F, Wt%				9.1							9.1
360-650°F, Wt%				56.5							56.4
650°F+, Wt%				34.4							34.5
FBP, °F				958							952
JP-4, Wt%				29.6							29.4
Gas Rate, SCFB x 10^{-3}				13.4							12.4
Hydrogen Consumption, SCFB				1190							1190
Wt%, C_1-C_4 on Feed				1.6							2.1
Volume Expansion, %				105							104

TABLE 30

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 4
CATALYST PHYSICAL PROPERTIES STUDY

Conditions: 1800 psig
Catalyst: 3838-031
Run ID: AU-75-64

Days on Oil	1	2	3	4	5A	6	7	8	9	10A
Avg Cat Temperature, °F	780.6	780.6	--	--	781.5	781.5	780.4	780.7	780.4	780.7
LHSV, Vo/Vc/hr	0.5 →					0.75 →				
Gravity, API°	45.1	43.9	41.2	39.4	39.1	37.3	36.6	37.0	36.3	37.5
Liquid Product, g	133	159	234	181	167	228	318	334	332	305
Carbon, Wt%					86.27					86.48
Hydrogen, Wt%					13.64					13.42
Nitrogen, ppm	214	--	82	94	76	--	942	--	840	985
Sulfur, ppm	86	--	117	98	144	--	128	--	110	79
Pour Point, °F					70					75
Viscosity, cst (104°F)					3.04					3.96
Simulated Distillation										
IBP, °F					103					79
IBP-360°F, Wt%					14.9					12.0
360-650°F, Wt%					57.6					50.6
650°F+, Wt%					27.5					37.4
FBP, °F					922					1000+
JP-4, Wt%					36.8					30.1
Gas Rate, SCFB x 10^{-3}					11.0					7.1
Hydrogen Consumption, SCFB					1390					1200
Wt%, C_1-C_4 on Feed					2.7					2.0
Volume Expansion, %					105					105

TABLE 31

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 4
CATALYST PHYSICAL PROPERTIES STUDY

Conditions: 1800 psig
Catalyst: 3838-034
Run ID: AU-75-66

Days on Oil	1	2	3	4	5A	6	7	8
Avg Cat Temperature, °F	780.0	780.1	--	--	779.4	780.7	780.8	--
LHSV, Vo/Vc/hr	0.5	→	→	→	→	0.75	→	→
Gravity, API°	50.3	46.8	47.0	43.4	43.4	36.9	37.0	36.6
Liquid Product, g	78	177	205	194	199	136	333	314
Carbon, Wt%					86.17			
Hydrogen, Wt%					13.81			
Nitrogen, ppm	287	--	3	18	5	660	412	604
Sulfur, ppm	286	--	235	80	232	440	64	455
Pour Point, °F					55			
Viscosity, cst (104°F)					2.05			
Simulated Distillation								
IBP, °F					39			
IBP-360°F, Wt%					21.5			
360-650°F, Wt%					59.7			
650°F+, Wt%					18.8			
FBP, °F					875			
JP-4, Wt%					50.6			
Gas Rate, SCFB x 10^{-3}					14.0			
Hydrogen Consumption, SCFB					1520			
Wt%, C_1-C_4 on Feed					3.3			
Volume Expansion, %					107			

TABLE 32

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 4
CATALYST PHYSICAL PROPERTIES STUDY

Conditions: 1800 psig
Catalyst: 3838-035
Run ID: AU-75-68

Days on Oil	1	2	3	4	5A	6	7	8	9A	10
Avg Cat Temperature, °F	780.1	780.1	780.0	780.1	780.4	--	781.0	780.5	780.6	780.5
LHSV, Vo/Vc/hr	0.5	→	→	→	→	0.75	→	→	→	→
Gravity, API°	51.3	48.3	40.8	40.5	41.0	36.2	36.2	35.9	36.4	36.0
Liquid Product, g	78	229	223	163	154	129	346	300	263	320
Carbon, Wt%					86.34				86.49	
Hydrogen, Wt%					13.63				13.30	
Nitrogen, ppm	140	--	37	42	46	1760	1520	--	1950	--
Sulfur, ppm	58	--	47	107	326	398	289	--	191	--
Pour Point, °F					65				75	
Viscosity, cst (104°F)					2.56				4.16	
Simulated Distillation										
IBP, °F					52				132	
IBP-360°F, Wt%					20.4				10.5	
360-650°F, Wt%					55.2				54.0	
650°F+, Wt%					34.4				35.5	
FBP, °F					900				945	
JP-4, Wt%					43.9				29.3	
Gas Rate, SCFB x 10^{-3}					10.7				13.6	
Hydrogen Consumption, SCFB					1380				1120	
Wt%, C_1-C_4 on Feed					2.7				2.0	
Volume Expansion, %					106				104	

TABLE 33

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 4
CATALYST PHYSICAL PROPERTIES STUDY

Conditions: 1800 psig
Catalyst: 3838-037
Run ID: AU-75-69

Days on Oil	1	2	3	4	5A	6	7	8	9	10A
Avg Cat Temperature, °F	780.3	--	--	779.9	779.9	781.1	781.5	781.2	--	781.0
LHSV, Vo/Vc/hr	0.5	→	→	→	→	0.75	→	→	→	→
Gravity, API°	50.7	49.3	45.5	40.7	39.4	36.6	36.6	36.6	36.5	36.6
Liquid Product, g	73	178	181	207	235	280	314	334	325	281
Carbon, Wt%					86.34					86.46
Hydrogen, Wt%					13.62					13.36
Nitrogen, ppm	210	--	4	3	77	--	1010	--	1380	1560
Sulfur, ppm	255	--	129	200	220	--	100	--	130	150
Pour Point, °F					70					--
Viscosity, cst (104°F)					3.02					3.99
Simulated Distillation										
IBP, °F					107					186
IBP-360°F, Wt%					16.4					9.4
360-650°F, Wt%					57.6					57.0
650°F+, Wt%					26.0					31.6
FBP, °F					918					934
JP-4, Wt%					39.9					28.8
Gas Rate, SCFB x 10^{-3}					19.1					14.0
Hydrogen Consumption, SCFB					1360					1150
Wt%, C_1-C_4 on Feed					2.4					2.0
Volume Expansion, %					106					104

TABLE 34

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 4
CATALYST PHYSICAL PROPERTIES STUDY

Conditions: 1800 psig
Catalyst: 3838-039
Run ID: AU-75-70

Days on Oil	1	2	3	4A	5	6	7	8	9	10A	11
Avg Cat Temperature, °F	780.1	779.4	780.3	780.2	--	--	--	781.4	780.6	781.5	781.1
LHSV, Vo/Vc/hr	0.5				→	0.75					→
Gravity, API°	51.7	53.5	46.2	45.8	42.8	38.2	--	37.2	36.8	37.7	36.9
Liquid Product, g	62	186	219	210	178	223	--	157	328	308	298
Carbon, Wt%				85.95						86.46	
Hydrogen, Wt%				14.03						13.49	
Nitrogen, ppm	2320	--	2	1	2	230	--	326	280	289	
Sulfur, ppm	340	--	79	165	171	225	--	257	205	176	127
Pour Point, °F				46						75	
Viscosity, cst (104°F)				1.77						--	
Simulated Distillation											
IBP, °F				-2						38	
IBP-360°F, Wt%				30.1						16.0	
360-650°F, Wt%				49.4						44.4	
650°F+, Wt%				20.5						39.6	
FBP, °F				968						1000+	
JP-4, Wt%				57.1						33.3	
Gas Rate, SCFB x 10^{-3}				6.1						6.0	
Hydrogen Consumption, SCFB				1660						1260	
Wt%, C_1-C_4 on Feed				3.2						2.1	
Volume Expansion, %				109						105	

TABLE 35

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	1	2	3A	4	5	6	7	8
Avg Cat Temperature, °F	770.4	770.7	770.1	770.5	--	--	770.4	770.0
Gravity, API°	--	52.2	52.4	48.9	46.6	47.2	45.5	45.2
Liquid Product, g	--	185	176	177	163	177	197	152
Carbon, Wt%			85.61					
Hydrogen, Wt%			14.39					
Nitrogen, ppm	--	3	2	2	--	1	1	--
Sulfur, ppm	--	100	18	24	--	156	59	--
Pour Point, °F			-30					
Viscosity, cst (104°F)			1.11					
Simulated Distillation								
IBP, °F			-37					
IBP-360°F, Wt%			51.9					
360-650°F, Wt%			44.8					
650°F+, Wt%			3.3					
FBP, °F			737					
JP-4, Wt%		83	84	81	73	75	69	68
Gas Rate, SCFB x 10^{-3}	--	11.5	11.3	12.0	12.0	12.1	12.3	12.3
Hydrogen Consumption, SCFB			1980					
Wt%, C_1-C_4 on Feed			5.5					
Volume Expansion, %			111					

JP-4 yields from simulated distillation data for mass balance periods. Daily JP-4 yields estimated from whole product API gravity, Figure 22. Daily yields of JP-4 for the first sixteen days on oil were corrected for product light-end losses as detailed in Appendix F.

TABLE 35 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	9A	10	11	12	13	14	15	16
Avg Cat Temperature, ^{o}F	770.3	772.7	772.3	--	--	772.3	775.5	775.5
Gravity, API^{o}	48.0	45.0	45.0	49.5	46.1	45.4	46.6	46.2
Liquid Product, g	190	126	195	79	209	174	144	196
Carbon, Wt%	85.76							
Hydrogen, Wt%	14.23							
Nitrogen, ppm	1	1	112	--	3	--	1	--
Sulfur, ppm	133	106	160	--	91	--	134	--
Pour Point, ^{o}F	5							
Viscosity, cst (104^{o}F)	3.11							
Simulated Distillation								
IBP, ^{o}F	-16							
IBP-360^{o}F, Wt%	37.4							
360-650^{o}F, Wt%	50.3							
650^{o}F+, Wt%	12.3							
FBP, ^{o}F	890							
JP-4, Wt%	67.7	67	68	82	71	68	80	79
Gas Rate, SCFB x 10^{-3}	7.8	12.0	4.6	23.6	10.7	10.8	10.4	10.7
Hydrogen Consumption, SCFB	1770							
Wt%, C_1-C_4 on Feed	3.0							
Volume Expansion, %	111							

TABLE 35 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	17A	18	19A	20	21	22	23	24
Avg Cat Temperature, °F	775.6	775.8	774.5	775.5	--	--	775.4	774.9
Gravity, API°	51.2	51.6	47.0	47.8	47.8	47.3	47.8	44.8
Liquid Product, g	178	144	159	174	211	211	196	206
Carbon, Wt%	85.79		85.92					
Hydrogen, Wt%	14.14		14.08					
Nitrogen, ppm	1	--	2	--	2	--	2	--
Sulfur, ppm	728	--	36	--	86	--	341	--
Pour Point, °F	-10		20					
Viscosity, cst (104°F)	1.35		2.72					
Simulated Distillation								
IBP, °F	-36		--					
IBP-360°F, Wt%	47.0		--					
360-650°F, Wt%	47.4		--					
650°F+, Wt%	5.6		--					
FBP, °F	900		--					
JP-4, Wt%	79.3	80	64	67	67	65	67	57
Gas Rate, SCFB x 10^{-3}	9.1	9.0	15.6	14.1	12.3	13.9	13.4	5.4
Hydrogen Consumption, SCFB	1740		1740					
Wt%, C_1-C_4 on Feed	3.6		4.9					
Volume Expansion, %	112		108					

TABLE 35 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	25	26	27A	28	29	30	31	32A
Avg Cat Temperature, °F	775.3	777.2	777.2	--	--	777.2	777.1	777.1
Gravity, API°	46.4	48.5	48.8	49.5	49.2	49.4	51.6	49.2
Liquid Product, g	218	141	204	188	194	196	196	202
Carbon, Wt%			85.76					85.89
Hydrogen, Wt%			14.23					14.11
Nitrogen, ppm	6	--	1	--	1	--	4	2
Sulfur, ppm	136	--	64	--	500	--	140	92
Pour Point, °F			-15					-15
Viscosity, cst (104°F)			1.26					1.28
Simulated Distillation								
IBP, °F			6					-4
IBP-360°F, Wt%			40.0					41.2
360-650°F, Wt%			51.1					50.5
650°F+, Wt%			8.9					8.3
FBP, °F			834					838
JP-4, Wt%	62.0	69.0	71.6	73	72	73	80	79.3
Gas Rate, SCFB x 10^{-3}	12.1	13.8	15.0	14.7	14.5	14.7	26.8	15.9
Hydrogen Consumption, SCFB			1850					1800
Wt%, C_1-C_4 on Feed			5.1					5.3
Volume Expansion, %			109					109

TABLE 35 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	33	34	35	36	37	38	39A	40
Avg Cat Temperature, °F	777.5	777.0	--	--	776.9	777.4	777.5	--
Gravity, API°	49.2	49.5	48.0	--	42.7	50.1	48.9	48.2
Liquid Product, g	143	104	--	--	96	136	160	159
Carbon, Wt%							85.86	
Hydrogen, Wt%							14.12	
Nitrogen, ppm	--	4	22	--	--	3	6	--
Sulfur, ppm	--	47	170	--	--	69	234	--
Pour Point, °F							20	
Viscosity, cst (104°F)							1.41	
Simulated Distillation								
IBP, °F							27	
IBP-360°F, Wt%							37.6	
360-650°F, Wt%							51.0	
650°F+, Wt%							11.4	
FBP, °F							866	
JP-4, Wt%	72	74	67	--	49	75	66.8	68
Gas Rate, SCFB x 10^{-3}	14.9	14.5	14.6	13.0	12.3	32.3	16.0	16.3
Hydrogen Consumption, SCFB							1800	
Wt%, C_1-C_4 on Feed							5.4	
Volume Expansion, %							109	

TABLE 35 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	41	42	43	44	45	46A	47	48
Avg Cat Temperature, °F	--	777.5	--	--	777.4	777.0	781.4	781.3
Gravity, API°	51.3	52.9	40.4	41.3	42.7	42.4	43.6	44.2
Liquid Product, g	195	112	100	185	216	192	151	213
Carbon, Wt%						86.20		
Hydrogen, Wt%						13.77		
Nitrogen, ppm	9	--	--	15	--	11	--	6
Sulfur, ppm	505	--	--	23	--	22	--	194
Pour Point, °F						60		
Viscosity, cst (104°F)						2.34		
Simulated Distillation								
IBP, °F						28		
IBP-360°F, Wt%						23.7		
360-650°F, Wt%						54.9		
650°F+, Wt%						21.4		
FBP, °F						914		
JP-4, Wt%	80	84	42	44	49	49.3	53	55
Gas Rate, SCFB x 10^{-3}	35.1	35.4	--	15.3	15.4	15.2	15.2	16.0
Hydrogen Consumption, SCFB						1515		
Wt%, C_1-C_4 on Feed						4.0		
Volume Expansion, %						106		

TABLE 35 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	49	50	51	52	53A	54	55	56
Avg Cat Temperature, $^{\circ}$F	786.0	--	--	786.0	786.0	785.5	785.0	785.8
Gravity, API$^{\circ}$	46.4	47.9	46.2	49.9	50.3	51.9	53.4	51.4
Liquid Product, g	142	215	180	195	163	162	180	221
Carbon, Wt%					85.75			
Hydrogen, Wt%					14.24			
Nitrogen, ppm	3	--	2	--	3	--	2	--
Sulfur, ppm	287	--	89	--	60	--	63	--
Pour Point, $^{\circ}$F					-15			
Viscosity, cst (104°F)					1.09			
Simulated Distillation								
IBP, $^{\circ}$F					-7			
IBP-360°F, Wt%					45.0			
360-650°F, Wt%					49.4			
650°F+, Wt%					5.6			
FBP, $^{\circ}$F					768			
JP-4, Wt%	62	67	62	74	76.9	81	86	79
Gas Rate, SCFB x 10^{-3}	11.1	18.4	19.2	20.1	19.7	28.2	35.3	20.6
Hydrogen Consumption, SCFB					1920			
Wt%, C_1-C_4 on Feed					6.7			
Volume Expansion, %					108			

TABLE 35 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	57	58	59	60A	61	62	63	64
Avg Cat Temperature, °F	--	--	785.9	785.5	785.6	785.6	785.8	--
Gravity, API°	50.6	49.9	51.8	48.6	49.1	49.6	50.3	48.0
Liquid Product, g	168	173	174	161	243	167	190	187
Carbon, Wt%				85.86				
Hydrogen, Wt%				14.13				
Nitrogen, ppm	9	--	1	2	--	1	--	1
Sulfur, ppm	40	--	19	36	--	18	--	101
Pour Point, °F				5				
Viscosity, cst (104°F)				1.30				
Simulated Distillation								
IBP, °F				44				
IBP-360°F, Wt%				39.6				
360-650°F, Wt%				49.8				
650°F+, Wt%				10.6				
FBP, °F				849				
JP-4, Wt%	77	74	81	69.5	71	73	76	68
Gas Rate, SCFB x 10^{-3}	27.1	27.5	29.2	15.1	15.8	14.9	15.4	13.6
Hydrogen Consumption, SCFB				1890				
Wt%, C_1-C_4 on Feed				7.5				
Volume Expansion, %				106				

TABLE 35 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	65	66	67A	68	69	70	71	72
Avg Cat Temperature, °F	--	785.4	785.4	785.7	786.0	--	--	785.8
Gravity, API°	42.7	46.0	47.4	47.7	49.7	48.8	46.3	49.2
Liquid Product, g	86.2	213	179	180	164	215	165	248
Carbon, Wt%			85.97					
Hydrogen, Wt%			14.00					
Nitrogen, ppm	--	33	15	8	--	1	--	1
Sulfur, ppm	--	440	229	90	--	31	--	43
Pour Point, °F			10					
Viscosity, cst (104°F)			1.45					
Simulated Distillation								
IBP, °F			-86					
IBP-360°F, Wt%			37.4					
360-650°F, Wt%			51.9					
650°F+, Wt%			10.7					
FBP, °F			835					
JP-4, Wt%	49	61	68	67	73	71	63	72
Gas Rate, SCFB x 10^{-3}	17.2	23.0	22.6	22.9	14.9	14.6	14.9	14.1
Hydrogen Consumption, SCFB			1740					
Wt%, C_1-C_4 on Feed			5.7					
Volume Expansion, %			108					

TABLE 35 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	73A	74	75	76	77	78	79	80A
Avg Cat Temperature, ^{o}F	786.0	785.7	785.9	786.0	--	--	785.8	786.0
Gravity, API^{o}	48.4	48.5	49.6	50.7	49.7	49.3	49.1	48.9
Liquid Product, g	178	207	148	188	197	197	210	196
Carbon, Wt%	85.86							85.78
Hydrogen, Wt%	14.13							14.21
Nitrogen, ppm	1	--	--	1	--	1	--	1
Sulfur, ppm	76	--	--	--	--	--	--	70
Pour Point, ^{o}F	10							-5
Viscosity, cst (104^{o}F)	1.36							1.23
Simulated Distillation								
IBP, ^{o}F	-107							16
IBP-360^{o}F, Wt%	41.5							40.7
360-650^{o}F, Wt%	49.4							51.0
650^{o}F+, Wt%	9.1							8.3
FBP, ^{o}F	815							837
JP-4, Wt%	73	70	74	78	74	73	72	73
Gas Rate, SCFB x 10^{-3}	15.1	16.1	21.3	18.4	14.2	17.2	18.8	17.2
Hydrogen Consumption, SCFB	1810							1850
Wt%, C_1-C_4 on Feed	5.3							5.5
Volume Expansion, %	108							109

TABLE 35 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	81	82	83	84	85	86	87A	88
Avg Cat Temperature, ^{o}F	785.9	785.8	785.9	--	--	785.5	785.8	785.7
Gravity, API^{o}	48.6	48.4	48.2	49.3	46.2	47.9	48.1	48.0
Liquid Product, g	231	163	195	152	155	190	150	182
Carbon, Wt%							85.81	
Hydrogen, Wt%							14.18	
Nitrogen, ppm	--	1	--	41	--	3	30	--
Sulfur, ppm	--	--	--	--	--	--	121	--
Pour Point, ^{o}F							-10	
Viscosity, cst (104^{o}F)							1.31	
Simulated Distillation								
IBP, ^{o}F							-95	
IBP-360^{o}F, Wt%							40.0	
360-650^{o}F, Wt%							50.2	
650^{o}F+, Wt%							9.8	
FBP, ^{o}F							881	
JP-4, Wt%	71	70	69	73	62	68	70	68
Gas Rate, SCFB x 10^{-3}	17.8	17.8	18.2	17.8	17.3	17.3	16.7	16.7
Hydrogen Consumption, SCFB							1850	
Wt%, C_1-C_4 on Feed							5.9	
Volume Expansion, %							108	

TABLE 35 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	89	90	91	92	93A	94	95	96A
Avg Cat Temperature, ^{o}F	785.0	--	--	785.4	785.5	789.4	789.8	789.7
Gravity, API^{o}	47.8	47.7	47.6	47.4	47.4	48.1	48.7	50.3
Liquid Product, g	204	203	210	240	176	152	194	180
Carbon, Wt%					85.97			85.72
Hydrogen, Wt%					14.03			14.27
Nitrogen, ppm	1	--	1	--	1	--	1	1
Sulfur, ppm	--	--	--	--	20	--	--	85
Pour Point, ^{o}F					5			-10
Viscosity, cst (104^{o}F)					1.48			1.12
Simulated Distillation								
IBP, ^{o}F					-16			-25
IBP-360^{o}F, Wt%					35.5			43.5
360-650^{o}F, Wt%					53.9			49.7
650^{o}F+, Wt%					10.6			6.8
FBP, ^{o}F					831			787
JP-4, Wt%	68	67	67	66	67	68	71	76
Gas Rate, SCFB x 10^{-3}	16.7	16.7	17.3	16.7	16.7	16.6	16.7	15.9
Hydrogen Consumption, SCFB					1720			1940
Wt%, C_1-C_4 on Feed					5.1			6.9
Volume Expansion, %					108			108

TABLE 35 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 5
ACTIVITY MAINTENANCE TEST

Conditions: 2000 psig, 0.4 LHSV
Catalyst: 3838-043; 1.5/10/15 on 50% US Sieve Alumina
Run ID: AU-75-71

Days on Oil	97	98	99	100	101A	102	103
Avg Cat Temperature, ^{o}F	--	--	779.8	779.9	779.9	780.0	779.8
Gravity, API^{o}	50.1	50.2	--	45.3	43.8	40.7	40.5
Liquid Product, g	201	185	--	236	182	167	165
Carbon, Wt%					86.42		
Hydrogen, Wt%					13.57		
Nitrogen, ppm	--	1	--	--	10	--	19
Sulfur, ppm	--	--	--	--	100	--	
Pour Point, ^{o}F					55		
Viscosity, cst (104^{o}F)					1.88		
Simulated Distillation							
IBP, ^{o}F					-31		
IBP-360^{o}F, Wt%					28.5		
360-650^{o}F, Wt%					56.0		
650^{o}F+, Wt%					15.5		
FBP, ^{o}F					876		
JP-4, Wt%	76	76	--	59	57	43	42
Gas Rate, SCFB x 10^{-3}	16.5	16.7	17.0	17.2	17.4	20.3	20.5
Hydrogen Consumption, SCFB					1400		
Wt%, C_1-C_4 on Feed					4.3		
Volume Expansion, %					106		

TABLE 36

AIR FORCE CONTRACT F33615-79-C-2095
PROPERTIES OF JET FUEL FRACTIONS FROM HYDROCRACKED WHOLE SHALE OIL

	Composite	JP-4	JP-8
API°	48.7	49.4 (45-57)	43.4 (37-51)
Weight %	100	76	61
Carbon, Wt%	85.82	85.99	86.10
Hydrogen, Wt%	14.17	14.00 (13.6)	13.86 (13.6)
Nitrogen, ppm	1.1	0.7	1.1
Pour Point, °F	-5	<-85	-40
Viscosity (104°F), cst	1.33	--	--
Aromatics, Vol%	--	16.0 (25.0)	18.0 (25.0)
Olefins, Vol%	--	1.0 (5.0)	2.5 (5.0)
Distillation, D-2887			
IBP, °F	-47	22	250
10%	203	190	322 (367)
20%	268	238 (266)	353
30%	321	276	390
40%	372	312	413
50%	410	346 (365)	436
60%	446	377	461
70%	487	408	489
80%	547	440	520
90%	624	480 (482)	564
EP, °F	789	553 (608)	622 (626)

Values in parentheses are maximum (minimum for hydrogen content) specification limits.

VI. CONCLUSIONS

A single-catalyst system capable of direct hydrocracking of a whole shale oil containing large amounts of nitrogen has been developed. The novel catalyst, consisting of cobalt, chromium, and molybdenum salts on a base of 50% US sieve in alumina is multifaceted in that it serves to promote saturation, denitrogenation, and cracking reactions of shale oil containing large amounts of organic nitrogen compounds.

The catalyst was developed by a logical optimization of catalyst chemical and physical properties. The metals combination is the key to the catalyst stability. Since temperatures high enough to minimize the adsorption of ammonia and organic nitrogen compounds on the hydrocracking sites were necessary for effective cracking, the catalyst required high-temperature stability. Although the presence of chromium salts as the stabilizer was shown to reduce activity for nitrogen removal, its absence would lead to rapid catalyst deactivation as shown by the results for varying chromium concentration.

The support combination of sieve and alumina combines both the saturation and denitrogenation activity of alumina with the cracking activity of the sieve. Although this combination is less effective for nitrogen removal than alumina alone at high nitrogen concentration, it becomes more effective as nitrogen content decreases down the bed. The combination is more effective than alumina alone for hydrocracking with the cracking zone confined to that part of the bed at the bottom where the nitrogen content has been reduced to <10 ppm. This cracking zone would vary with changes in process conditions. An increase in temperature, for instance, would also lower the effective space velocity over the cracking zone, providing an additional boost in cracking activity.

The ability of the optimized catalyst to hydrocrack a whole shale oil into high yields of jet fuel boiling-range material was demonstrated in a 103-day (approximately 2500 hours) test. Although several unit upsets marred the results and perhaps affected catalyst activity, a high yield of JP-4 material was sustained. The whole product was water white in color and contained only a few ppm nitrogen. Even though unit operations were poor during the catalyst life test, a minimum life of 4.5-months was demonstrated and a catalyst life of six months is expected for the specified 75 weight percent yield of JP-4 boiling-range material. It should be emphasized that a guard bed to remove arsenic and other metal contaminants was not used for the life test. The presence of such a bed should extend the catalyst life considerably.

VII. RECOMMENDATIONS

The work reported is related to the development of novel catalysts capable of direct upgrading of a whole shale oil into military fuels. This objective was achieved. Sufficient process variable studies were conducted to aid in the optimization of the catalyst, to define important kinetic parameters, and to help define the feasibility of using such a catalyst to upgrade shale oil by a one-step process. Further study would be required to optimize the process used and to better demonstrate the continued high activity for denitrogenation and hydrocracking. No guard bed to remove arsenic was used, although one would be required commercially. Catalyst performance in the absence of arsenic should be evaluated.

An economic analysis and a comparison with a more conventional two-step hydrotreating/hydrocracking scheme should be done. The catalyst should also be tested with shale oils more refractory than the sample used in this study.

APPENDIX A

RESEARCH TECHNICAL PLAN

The technical plan, as originally submitted, but with slight modifications to conform to this report, is reproduced on the following pages. The plan was designed to determine the feasibility of using a catalyst developed by Amoco Oil for producing jet fuel from shale oil and to refine and optimize catalyst components to maximize performance. The catalyst on which the original contract proposal was based consisted of cobalt, molybdena, and chromia on a porous oxide support.

In most cases the plan requirements were exceeded.

General Description of Task and Purpose

Task 1. Process Variable Study on Existing Catalyst

Using an existing cobalt/chromia/moly on gamma alumina catalyst, 3609-162, a study of the effects of feed rate, pressure, and temperature on nitrogen removal and conversion of a shale oil to be furnished by Wright-Patterson shall be carried out. Using automated high-pressure catalyst screening units, the catalyst will be tested using the following conditions:

Test No.	Operating Temperature	Pressure	LHSV
1	790°F	1800 psig	0.5
2	790°F	1800 psig	1.0
3	790°F	1800 psig	0.25
4	790°F	1800 psig	0.5
5	790°F	2400 psig	0.5
6	790°F	1400 psig	0.5
7	790°F	1800 psig	0.5
8	770°F	1800 psig	0.5
9	810°F	1800 psig	0.5
10	790°F	1800 psig	0.5

At each set of test conditions the catalyst will be operated for a continuous period of at least 72 hours. During that time, at least two samples will be taken and analyzed for nitrogen and sulfur content. At least one test period will be used to obtain a material balance on the operation. For a mass balance, the total weight of shale oil delivered to the unit will be determined by measuring the volume of oil, its temperature and density at the temperature used. Total liquid products obtained from the unit during the period will be collected and weighed and analyzed for nitrogen, sulfur, carbon and hydrogen. In addition, pour point, viscosity and boiling point distribution of the product will be determined.

The total gas volume, hydrogen, NH_3, H_2S, and light hydrocarbons from the unit during the test period will be measured using a wet test meter. A portion of the off-gas will be collected and analyzed by gas chromatography to determine the concentration of the different hydrocarbons present. Elemental analysis and quantities of feed and products will allow calculation of a material balance based on carbon. In addition, yield of light C_4- hydrocarbons, H_2S, NH_3, and hydrogen consumed will be calculated.

The amount of material produced in the different boiling ranges, IBP-360°F, 360-650°F, and 650°F+ will be determined from the simulated distillation test. Analytical methods used and accuracy of the test will be discussed in a later section.

Also in Task 1, a two-catalyst system will be used. A Ni/Mo/P catalyst, 3609-161, will be held at 735°F in the first reactor. An equal volume of the cobalt/chromia/moly catalyst, 3609-162, will be used in a second reactor. Using this catalyst system the following tests will be performed to determine the effects of temperature, pressure, and feed rate.

	Temperature, °F			
Test No.	Cat Bed 1	Cat Bed 2	Pressure, psig	LHSV
1	735	790	1800	0.5
2	735	790	1400	0.5
3	735	790	1800	0.5
4	735	770	1800	0.5
5	735	810	1800	0.5
6	735	790	1800	0.5
7	735	790	1800	1.0
8	735	790	1800	0.25
9	735	790	1800	0.5

Time of operation, samples taken, analysis, material balance periods and calculations will be performed as described for the single-catalyst system.

When the preceding tests and sample analyses have been completed, data reduction will be used to determine the relative activities for nitrogen removal and 650°F+ conversion. Kinetic data will be developed to show effects of feed rate, pressure, and temperature. When this is done a decision will be made (based on the results) whether to use a single-catalyst or two-catalyst system for Tasks 2, 3, and 4. Based on the kinetic data, conditions to be used in the above-named tasks will be chosen.

Task 2. Catalyst Composition Study--Metals Optimization

In this task a minimum of eight catalysts, with the concentration of each hydrogenation metal varied systematically, will be made on a single batch of an alumina support. All catalysts will be analyzed to determine metal concentration, surface area, pore volume, and pore size distribution as described by the methods given in the analytical test section. Catalysts with approximately the following compositions will be made and tested.

Cat No.	% CoO	% Cr_2O_3	% MoO_3	% NiO
1	1.5	10.0	10.0	--
2	5.0	10.0	10.0	--
3	1.5	10.0	15.0	--
4	1.5	15.0	10.0	--
5	1.5	5.0	10.0	--
6	1.5	10.0	5.0	--
7	--	10.0	10.0	1.5
8	3.5	10.0	10.0	--

Each catalyst will be tested in the automated catalyst screening units as follows. A constant volume of each catalyst will be loaded into the reactor and presulfided using an 8% H_2S, 92% hydrogen mixture for a period not less than two hours. After pretreatment, conditions based on the results of Task 1 will be established and maintained until the catalyst has reached a lined-out conditions or a minimum of 90 hours.

During the line-out period, a minimum of three liquid samples will be taken from the unit and analyzed for nitrogen and sulfur content as described in the analytical section. After the catalyst has stabilized, a material balance test will be performed on each catalyst as described in the analytical section on Task 1.

Using data obtained from these tests, the relative activities for nitrogen removal and 650°F+ material conversion will be determined for each catalyst composition. Using these data the composition giving the overall best performance, highest denitrogenation and conversion activities will be chosen for determining the effects of support composition.

Task 2. Support Type

A minimum of three support compositions, in addition to gamma alumina, will be evaluated. These will include silica, silica-alumina and alumina containing a molecular sieve (crystalline alumino silicate). Catalyst with a composition determined from results of the preceding task will be made on at least the above-named supports, analyzed and evaluated as outlined in Task 1 and using conditions chosen for the Metals Optimization Study.

Task 3. Catalyst Physical Properties Study

Using the support composition and metals concentrations determined in Tasks 2, the effect of physical properties, surface area and pore volume per unit mass, pore size distribution, and catalyst activity for denitrogenation and boiling-range conversion will be determined. Since the surface area, pore volume, and pore size distribution are all controlled by the shape, size and size distribution of the support crystallites, it is impossible to study any one of these properties completely independently of the others; however, three catalysts having surface areas covering the range of about 150 m^2/g to about 300 m^2/g will be made while keeping the pore volume relatively constant. A second series of three catalysts having pore volume of about 0.4, 0.6, and 0.8 cc/g with the surface area held relatively constant (180-220

m^2/g) will be made. At least two catalysts having approximately the same pore volumes and surface areas but different pore size distributions will also be made. All of the above catalyst will be analyzed to determine chemical composition and physical properties and tested as outlined under Task 2. Data from the runs will be developed to give the relative activities of all the catalysts for nitrogen removal and boiling-point conversion.

Task 4. Catalyst Maintenance Test

Based on results from Tasks 1 through 3, a catalyst will be prepared having a near-optimum combination of chemical composition and physical properties. The catalyst will be analyzed to determined chemical composition and physical properties (surface area, pore volume, and pore size distribution). It will be loaded into a micro catalyst test unit, pretreated, and operated at conditions as determined in Task 1 for a minimum of two months. Liquid samples will be taken from the unit daily. These will be analyzed for API gravity, sulfur and nitrogen. Catalyst activity for nitrogen removal as a function of time will be provided throughout the run.

At intervals of not greater than ten days, a material balance test will be performed as in Task 1. The liquid sample from the material balance period will be analyzed for API gravity, pour point, viscosity, boiling-point distribution, sulfur, carbon, hydrogen and nitrogen. The off gas will be measured volumetrically and analyzed for hydrocarbons by gas chromatography.

Distillation of Research Samples

Products will be distilled so that each run will provide samples of the products boiling below 350°C and above 350°C. Samples will be distilled for each set of conditions tested for each run.

Distillations will be conducted in a manner similar to that specified in ASTM method D-1160. 150-200 ml product samples will be used for distillation at 45 mm Hg with an overhead temperature of 250°C and a reflux ratio of 5:1 near the cut point. A nitrogen bleed will be used. Distilled samples will be stored in suitable containers in a cold room prior to shipment via the best available method. Samples will be labeled to allow identification of origin, i.e., catalyst and process conditions.

Discussion of Potential Problems

No major problems are anticipated in carrying out this program; however, some minor ones are to be expected. These include:

Malfunction of automated catalyst test units. On occasion, controls on the units do malfunction to cause loss of hydrogen or feed flow, low operating pressure, or high or low operating temperatures. If the nature of the malfunction causes deactivation of the catalyst, the run will be redone after the malfunction is corrected. If no damage to the catalyst is observed, the run will be continued after the malfunction has been corrected.

In catalyst screening it is known that some compositions may have properties that cause the catalyst to coke and deactivate very rapidly. When testing such catalysts it may not be possible to achieve lined-out performance. However, since the life of such catalyst is expected to be very short, they are of little or no commercial interest and will be evaluated in a nonsteady state.

One catalyst support composition to be tested will contain molecular sieves; if this is the support composition selected for physical property effects it will cause some difficulty. Since the surface area, pore volume, and pore size distribution of these materials are fixed, only the properties of the matrix in which they are dispersed can be altered to some degree.

Analysis of both catalysts and products use complex instruments that can break down. Such equipment malfunction could slow work, but is not expected to cause any major delays.

Data To Be Taken, Accuracy and Procedure for Acquiring Data

Operating Unit Data

Data	Frequency of Test	Instrument	Accuracy
Reactor Temperature	Daily Reading	Thermocouples	± 2°F
Unit Pressure	Constant Monitoring	Strip Chart	± 5 psi
Hydrogen Flow Rate	Daily Reading	Wet Test Meter	± 2%
Wt of Liquid Product Recovered	Daily Reading	Balance	± .1 g

Catalyst Analysis

Task No.	Surface Area Measurements	Pore Volume Measurements	Pore Size Distributions	CoO	Cr_2O_3	MoO_3
1	1	1	1	1	1	1
2	8	8	8	8	8	8
3	8	8	8	8	8	8
4	1	1	1	1	1	1

Product Analysis

Task No.	S	N	C	H	Simulated Dist	API Gravity	Viscosities	Gas Analysis
1	60	60	19	19	19	60	19	19
2	33	33	11	11	11	33	11	11
3	24	24	8	8	8	24	8	8
4	50	50	6	6	6	50	6	6

Analytical methods to be used for the above analysis are detailed subsequently.

Usefulness and Adequacy of Data

The data obtained in this study will be useful in that it will show the effects of catalyst composition and physical properties on initial activity for nitrogen removal and boiling-point conversion of shale oil. The process variable study will be adequate to show effects of feed rate, pressure, and temperature on the rates of reactions. The life test will give a good measure of catalyst activity decline rate from which an estimate of the life of the catalyst chosen can be made.

The scope of this study is limited and will leave many questions unanswered. It will not be adequate to tell whether or not the best catalyst composition was chosen for the life test. It is possible that a catalyst with lower initial activity will have a lower activity decline rate so that its average activity throughout the catalyst life would be higher. Also, it is possible that the optimum metals loading found for an alumina support is not optimum for the support chosen. The present state of the art for catalyst development leaves much to be desired. Complex interactions between support and the hydrogenation metals added require a great deal of work to arrive at the proper balance to give high activity for the desired reaction and a minimum of the undesired side reactions that cause deactivation. The nature of this work will give no information on the long-range effects of arsenic which is found in shale oil.

Many other questions are outside the scope of this project. Our studies are directed at finding conditions and catalyst that give high boiling-point conversion, denitrogenation and long catalyst life. It is possible that operating at a lower pressure with a shorter catalyst life would be more economical. Also we operate at a relatively high temperature in order to get higher boiling-point conversion; it is possible that a lower operating temperature with a portion of the heavy material cracked in a separate unit would be more economical. These are only a few of the questions outside the scope of this study that should be answered if the catalyst system shows promise.

Specific Types of Instrumentation Used

The catalyst test unit has the following instruments:

1. Thermocouples
2. Temperature Control Units--Eurotherm
3. Pressure Transmitters--Foxboro
4. Differential Pressure Transmitters--Foxboro
5. Pressure Control Valves--Research Control
6. Recorders--Honeywell
7. Digital Temperature Instrument--Newport
8. Counters--Sedeco
9. Pressure Regulators--Circle Seal
10. Solid State Controllers--Helicoid

Research Technical Plan Update

As detailed in the body of the text, the original contract was modified after the completion of the Support Type Study to allow for a more thorough investigation of the effect of silica concentration and sieve type and concentration on catalyst activity.

For this modification, four additional silica alumina based catalysts and six additional sieve alumina based catalysts were tested in accordance with Task 2.

For the catalyst physical properties study, a molecular sieve containing support was selected. As indicated under the previous "Discussion of Potential Problems," it was difficult to vary catalyst physical properties within the limits of the specifications given under Task 3.

APPENDIX B

WORK SCHEDULE

TABLE B-1

AIR FORCE CONTRACT F33615-79-C-2095
ORIGINAL WORK SCHEDULE

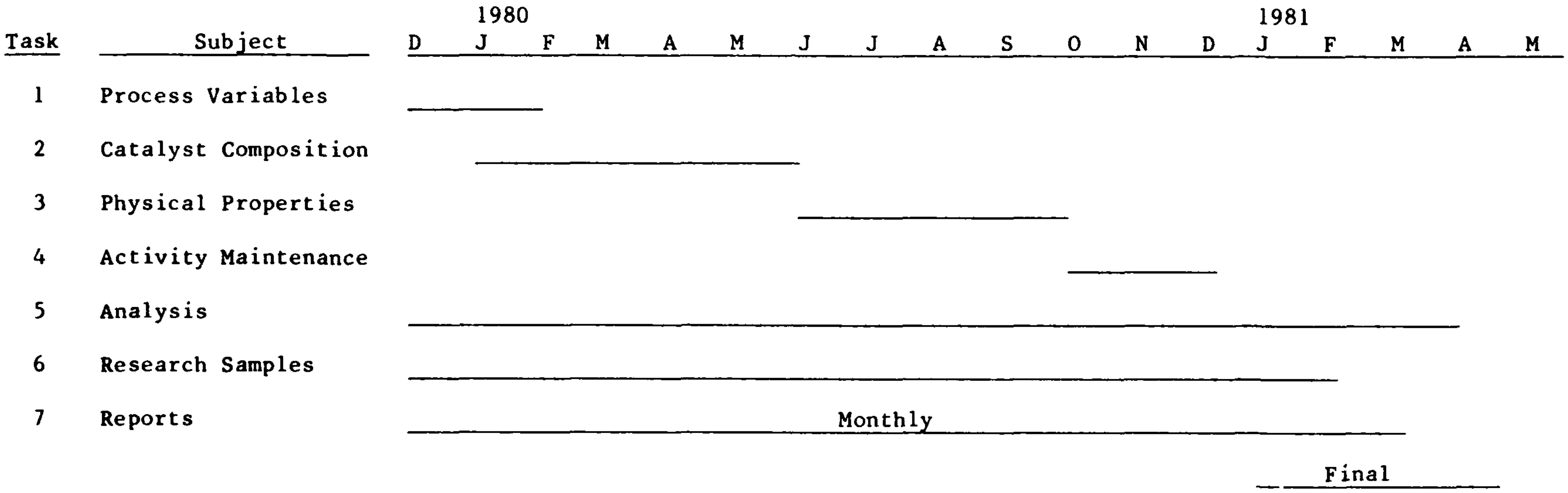
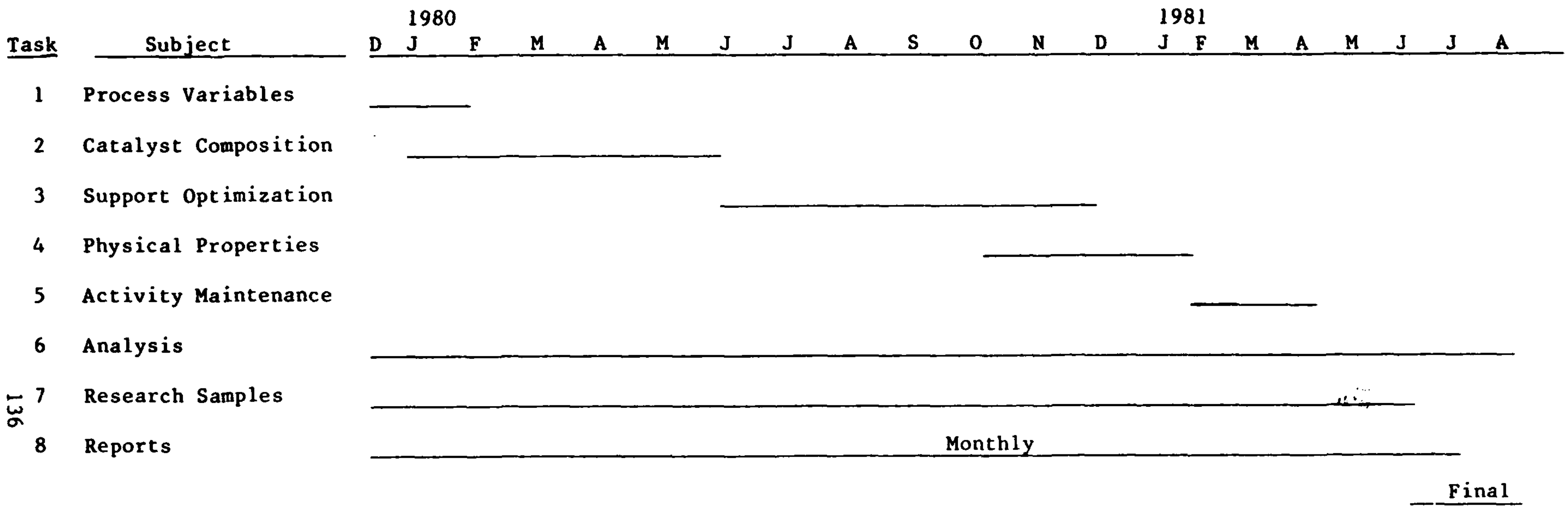


TABLE B-2

AIR FORCE CONTRACT F33615-79-C-2095
MODIFIED WORK SCHEDULE



APPENDIX C

PROCESS UNIT OPERATIONS AND PROCEDURES

Operations

All catalyst screening runs were conducted in one of two small-scale, automatic high-pressure units. Briefly, a regulated supply of hydrogen, after passage through a pressure control valve and a flow control valve, was combined with the feed from a metered pump at a point prior to the catalyst bed. The effluent gaseous products, after separation from the liquid products at process pressure, were passed through a pressure control valve and a wet test meter. The liquid product was passed through a liquid level control valve and collected in a sample bottle.

The reactor consisted of a 3/8-inch internal diameter high-pressure pipe containing an axially traversing thermocouple within a 1/8-inch thermowell. Heat was supplied to the reactor by four separately controlled heating circuits to ensure isothermal temperature control.

Procedures

Catalysts were ground to 14/20 mesh (Tyler) and calcined at 1000°F for at least one hour just prior to loading into the reactor. Approximately 20 cc of catalyst was loaded into the reactor within the 1/8-inch annular space between the reactor walls and the thermowell. Support for the catalyst was provided by 10 inches of small, inert balls at the bottom of the reactor. The space above the catalyst, approximately six to eight inches, also contained the small inerts and served as a mild preheat section for the hydrogen and feed.

All catalysts were sulfided with a mixture of 8% hydrogen sulfide in hydrogen at greater than atmospheric pressure. An initial temperature of 300°F was used with the temperatures raised to 400°F and then 700°F, each being held for one hour. At least one SCF of sulfiding gas was used at each temperature.

After the sulfiding period, the unit was pressurized with hydrogen to operating pressure. After increasing temperature to attain operating temperature, the feed pump was started. Generally, the products collected in the first eight to ten hours on stream were discarded to prevent contamination from previous runs.

APPENDIX D

ANALYTICAL METHODS

All analytical procedures used are listed below and where necessary are detailed in the following text.

Analysis	Reference
Carbon, Hydrogen--High Accuracy	(5)
Nitrogen, Automatic Kjeldahl	(6)
Nitrogen, Chemiluminescence	See text.
Oxygen, Direct	(7)
Sulfur, XRF	See text.
Pour Point	ASTM D-2500
Viscosity	ASTM D-445
API Gravity	ASTM D-287
Simulated Distillation	ASTM D-2887
Aromatics/Olefins	ASTM D-1319
Chromium on Catalyst	(8)
Cobalt/Molybdenum on Catalyst	Amoco Method C-363
Nickel on Catalyst	Amoco Method C-145
Catalyst Surface Area/Pore Size Distribution	See text.
Mercury Porosimetry	See text.
Hydrocarbon Gases	See text.

Nitrogen--Chemiluminescence

Products containing less than 500 ppm nitrogen were analyzed using a Dohrman Envirotech DN-100 nitrogen analyzer by oxidative pyrolysis of the sample and subsequent chemiluminescence measurements on the nitric oxide produced.

Sulfur--X-Ray Fluorescence

Products were analyzed using a Philips PW1450 XRF spectrometer in an argon atmosphere using a chromium target X-ray tube, a graphite analyzing crystal and a gas flow proportional counter as the X-ray detector.

Light Hydrocarbon Gases

Reaction product off-gases, methane through hexane, were analyzed by gas chromatography. Small amounts of heptanes and octanes were sometimes detected but were not analyzed. A HP-5840 gas chromatograph equipped with a flame ionization detector was used in conjunction with a column temperature programmed from 40° to 150°C with a nitrogen carrier gas flow rate of 25 cc/min.

A standard gas mixture consisting of methane (.634 mole %), ethane (.262), propane (.172), iso- and normal-butanes (.02, .053), iso- and normal-pentanes (.02, .039), and iso- and normal-hexanes (.021, .043 mole %) in hydrogen obtained from Matheson was used as an external standard. The instrument was calibrated in duplicate twice daily. The calibration method was such that daily updating of retention times and response factors was automatically done for the standard mixture, allowing for slight changes in instrument and column performance.

Samples of unit off-gas were collected at the beginning and end of a mass balance period. 0.5 ml of gas was injected manually and the gas analyzed. Analysis was done in duplicate (reproducibility ± 5% relative) and all four results were averaged.

Catalyst Surface Areas/Pore Size Distributions

Catalyst physical properties were determined by adsorption of nitrogen gas at various relative pressures at liquid nitrogen temperature. The classical BET equation and a modification of the Kelvin equation were used for data reduction. Operation was by a computer-controlled Digisorb 2500 manufactured by Micromeritics Corporation of Narcross, Georgia, with data acquired according to the Digisorb 2500 instruction manual. The sample size was typically 150 mg such that 20 to 100 m^2 of surface area was used for the test. Precision is ± 2% to 3% at the 200 m^2/g level with measurements limited to 10 to 600°A pore radii.

Mercury Porosimetry

The pore size distribution for catalysts containing pores of size >600°A radius was measured by mercury intrusion at pressures from substmospheric to 50,000 psi using an American Instrument Company 60,000 psi porosimeter. The pore volume in pores >600°A as obtained by mercury porosimetry was added to the pore volume in pores <600°A as obtained by nitrogen adsorption, to give the total catalyst pore volume.

APPENDIX E

CATALYST PREPARATIONS AND PROPERTIES

General

The primary objective of this work was to identify the optimum combination of catalyst chemical and physical properties, which in conjunction with realistic operating conditions, would result in the conversion of whole shale oil into jet fuels in high yields. The optimum catalyst resulted from logical and stepwise improvements in both chemical and physical properties.

Catalyst properties are detailed in Table E-1 (Process Variable Study, Task 1), Table E-2 (Catalyst Composition Study, Task 2), Table E-3 (Catalyst Support Optimization Study, Task 3), and Table E-4 (Catalyst Physical Properties Study, Task 4). These tables detail the support, metals composition, physical properties such as surface area, pore volumes, and average pore size and gross pore size distributions.

BET surface areas were taken from digisorb measurements over the range 20 to 1200°A pore diameters. Average pore diameters were calculated as APD = 4 x pore volume x 10^4 ÷ BET surface area. For Tables E-1 through E-3, pore volumes were obtained by digisorb measurements only within the range of 20 to 1200°A pore diameters. For the catalyst physical properties study, Table E-4, the pore volumes were measured over the range 20 to 100,000°A pore diameters, with the volume in pores greater than 1200°A diameter obtained from mercury porosimetry. For the sieve-containing catalysts, the sieve micropore volumes were not measured.

Preparation of Supports, Synopsis

Data for supports or support components are detailed in Table E-5. Some supports were available commercially; others were available as experimental supports from manufacturers while others were prepared "in house." These differences are detailed in the following discussion.

Process Variable Study. Catalyst 3609-162 was prepared by Cyanamid on an experimental alumina support. The support for 3609-161 was a high-purity alumina extrudate available commercially.

Catalyst Composition Study. Catalysts based on alumina (3609-165 through -168, -170, -171, -173 through -176), silica (3609-177), or 20% silica alumina (3609-178, -183) were prepared on commercially available supports. Supports for catalysts 3609-179, -182-1 were prepared by blending the US sieve with an alumina sol (Method A).

Catalyst Support Optimization Study. All supports for sieve-containing catalysts (3609-189 to 191, 3838-007, and 3862-003) were prepared by blending the sieve with alumina sol (Method A). The 30% silica alumina and 70% silica alumina supports for catalysts 3609-184 and 3838-010 were commercially available. The 10% and 50% silica alumina supports for catalysts 3609-194, -196 were prepared by blending a silica alumina sol with an alumina sol (Method B).

Catalyst Physical Properties Study. All catalyst for this study were prepared on 50% US sieve/50% alumina supports with the alumina physical properties varied so as to obtain finished catalysts with properties spanning as wide a range as possible. All supports were prepared in powder form (to pass 100 mesh), then extruded with water followed by drying and calcination. (See Preparation of Supports, Method A.)

Supports for catalysts 3838-023 and -034 were prepared by incorporation of an additive into the sieve-alumina mixture (Method C). Supports for catalysts 3838-028, -035, -037, and -039 were prepared by dry blending the sieve with an alumina powder (Method D). The support for 3838-031 was prepared from aluminum salts (Method E) and a modified alumina was used for 3838-030 (Method E).

Preparation of Supports, Methods

(A) 30% US Sieve In Alumina. One hundred fifty-four grams of US sieve previously ground to pass 100 mesh (Tyler equivalent, USA Standard

Testing Sieve, ASTME-11 specification, No. 100), and dried in an oven at 250°F in air, was made into a slurry with distilled water. The slurry was added to 3600 g alumina sol (10% alumina) in a large blender and the mixture blended for 10 to 15 minutes. Two hundred fifty ml ammonium hydroxide solution (1:1, distilled water and concentration ammonium hydroxide) was added rapidly and all at once with immediate blending to cause a thick gel to form. The gel was removed from the blender and placed in a large drying pan. The above procedure was repeated.

The combined gel batches were dried in an oven at 250°F in air, then ground to pass 100 mesh. Distilled water[a] was added to the powder with thorough blending (Mulling) and the mixture extruded as 5/64-inch extrudates.

The extrudates were dried in an oven at 250°F in air, then placed in a calcining oven at room temperature. The oven temperature controls were set for 1000°F and the material was calcined with make-up air at 1000°F at least overnight.

This method was used for all sieve-containing supports prepared for the Catalyst Composition and Support Optimization Studies with the sieve type and amounts varied.

(B) 50% Silica Alumina. Six hundred ninety-one grams of alumina sol (10% alumina) were added to 3000 g of silica alumina sol (5.24% solids, 70.7% silica, 29.3% alumina) in a large blender and the mixture blended for 10 to 15 minutes. Four hundred ml ammonium hydroxide (1:1, distilled water and concentrated ammonium hydroxide solution) was added, with immediate blending to cause gelation. Two additional batches were made. The remaining steps to produce an extrudate were identical to those described under Method A.

---

[a] Water is commonly used as an extrusion aid. The amount of water required to obtain the correct consistency depends upon the type of sieve and the relative amount of sieve. Experience was the main guidance.

The method for preparing the 10% silica alumina support was identical to that just described except that 3105 g of alumina sol was blended with 922 g of the silica alumina sol.

(C) The support for catalyst 3838-023 was prepared by blending the US sieve, alumina sol, and an additive in accordance with Method A. For catalyst 3838-030, the support was prepared by blending the US sieve with an alumina powder obtained by modification of the alumina sol. The support for catalyst 3838-034 was prepared by modification of the powder obtained from the US sieve and alumina sol.

(D) Catalysts 3838-028, -035, -037, -039 were prepared on supports obtained by dry blending the US sieve and the appropriate alumina powder (both to pass 100 M) indicated in Table E-5.

(E) The alumina for the support for catalyst 3609-031 was prepared from alumina salts, then dry blended (100 mesh) with the US sieve.

Preparation of Catalysts, Synopsis

Metal salts used for impregnation of catalyst supports were used as received from commercial manufacturers. The amounts of each salt required to produce catalyst having specified nominal metal oxide contents are given in Table E-6. The actual metal oxide contents, as determined by analytical methods (see appendix D), are given in Tables E-1 to E-4. Specification of metals composition in terms of oxides is a matter of convenience. Under processing conditions, the active species are predominantly metal sulfides.

Catalyst 3609-161, a Ni/Mo/P on alumina, was prepared by Method A. All other catalysts were prepared by a dual impregnation procedure (Methods B or C).

Preparation of Catalysts, Methods

(A) Two hundred eighty-eight grams of ammonium molybdate were added to one liter of distilled water with stirring to dissolve. One hundred seventy-nine grams of nickel nitrate hexahydrate were added followed by 74.4 g of 85% hypophosphoric acid. The clear solution was stirred for a few minutes and the volume made up to 1400 cc. Half of the solution was added to 1000 g alumina extrudates. After one hour with occasional mixing, the material was dried overnight in air at 250°F. After cooling, the remaining solution was added and the material again dried. The catalyst was finally calcined at 1000°F in air.

(B) This method was used to prepare catalysts 3609-165 to -168. Table E-6 should be consulted for the exact amount of each component used.

Ammonium dichromate was added to distilled water followed by ammonium molybdate. The mixture was stirred until all solids had dissolved. The solution volume was made up to the required volume[a] and added to the support. After standing for one hour with occasional mixing, the material was dried under a heat lamp, then at 250°F in air overnight. The material was then calcined for at least one hour at 1000°F in air to produce a $Cr_2O_3/MoO_3/Al_2O_3$ catalyst base. Cobalt nitrate hexahydrate or nickel nitrate hexahydrate was dissolved in distilled water[b] and added to the previously mentioned base. The drying and calcining steps were the same as just described.

(C) This method was used for all catalysts not covered by the two previous methods. The method was similar to Method B except that the first impregnating solution contained only ammonium dichromate to produce a Cr_2O_3/Al_2O_3 intermediate base, and the second impregnating solution contained both ammonium molybdate and cobalt nitrate hexahydrate.

---

[a] The solution volume was determined in one of two ways: direct measurement of the amount of water required to just completely wet (incipient wetness) a specified weight of support; or by calculation using 1.25 x pore volume (cc/g) x support weight (g).

[b] The final solution volume for the second impregnation was the same or slightly less than that for the first impregnation depending upon whether the first impregnation resulted in incipient wetness or excess solution.

TABLE E-1

AIR FORCE CONTRACT F33615-79-C-2095
CATALYST PHYSICAL PROPERTIES
PROCESS VARIABLE STUDY

Catalyst Number	3609-162	3609-161
Support	Alumina	Alumina
Run Number Tested, AU-	75-35	27-125
Composition, Wt%		
MoO_3	10.1	15.2
Cr_2O_3	8.6	
CoO	1.5	
NiO		3.8
P		1.5
Surface Area, m^2/g	179	178
Pore Volume, cc/g	.5790	.4274
APD (4V/A), °A	130	96
% Total Pore Volume in		
20-50 °A Diameter Pores	4.9	18.8
50-100 °A	75.0	75.1
100-150 °A	19.0	5.6
150-1200 °A	1.0	0.5

TABLE E-2

AIR FORCE CONTRACT F33615-79-C-2095
CATALYST PHYSICAL PROPERTIES
CATALYST COMPOSITION STUDY

Catalyst Number	3609-165	3609-166	3609-167	3609-168	3609-170
Support[a]	Alumina	Alumina	Alumina	Alumina	Alumina
Run Number Tested, AU-	27-127	75-37	75-36	75-38	27-128
Composition, Wt%					
MoO_3	9.6	9.6	9.5	9.3	10.9
Cr_2O_3	9.6	9.0	9.8	9.8	14.2
CoO (NiO)[b]	1.6	5.1	(2.0)	(4.5)	1.7
Surface Area, m^2/g	189	167	195	184	175
Pore Volume, cc/g	.5321	.5026	.5357	.5297	.4923
APD (4V/A), °A	112	121	116	115	113
% Total Pore Volume in					
20-50°A diameter pores	10.1	8.1	10.9	9.3	11.4
50-100°A	67.8	72.1	68.0	70.5	70.3
100-150°A	19.8	17.8	19.4	18.5	15.4
150-1200°A	2.3	1.9	1.6	1.7	2.9

---

[a] All catalysts were prepared on the same alumina support (Cyanamid).

[b] See Appendix J for screening studies with catalysts containing NiO.

TABLE E-2 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
CATALYST PHYSICAL PROPERTIES
CATALYST COMPOSITION STUDY

Catalyst Number	3609-171	3609-173	3609-174	3609-175	3609-177
Support[a]	Alumina	Alumina	Alumina	Alumina	Silica
Run Number Tested, AU-	27-129	75-39	75-40	27-130	27-131
Composition, Wt%					
MoO_3	10.6	11.0	16.0	5.3	10.4
Cr_2O_3	9.8	5.3	9.7	9.2	9.2
CoO	3.6	1.7	1.5	1.4	1.4
Surface Area, m^2/g	180	182	174	195	268
Pore Volume, cc/g	.5335	.6021	.5307	.5717	.9115
APD (4V/A), ^{o}A	119	132	122	117	136
% Total Pore Volume in					
20-50^{o}A diameter pores	8.4	7.2	7.5	8.1	3.8
50-100^{o}A	72.4	73.3	70.8	68.1	33.3
100-150^{o}A	16.4	17.3	20.9	21.8	58.9
150-1200^{o}A	2.8	2.3	0.9	1.9	4.0

---

[a] All alumina-based catalysts were prepared on the same support (Cyanamid).

TABLE E-2 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
CATALYST PHYSICAL PROPERTIES
CATALYST COMPOSITION STUDY

Catalyst Number	3609-176	3609-178	3609-179	3609-182-1	3609-183
Support	Alumina[a]	20% Silica[b]	30% US Sieve[b]	30% US Sieve[b]	20% Silica[b]
Run Number Tested, AU-	75-41	27-132	75-42	75-46	75-47
Composition, Wt%					
MoO_3	9.6	11.1	10.7	13.7	15.2
Cr_2O_3	9.1	10.5	9.9	8.8	9.0
CoO	1.5	1.6	1.6	1.5	1.5
Surface Area, m^2/g	196	235	311	263	227
Pore Volume, cc/g	.7811	.6701	.4016	.3839	.6622
APD (4V/A), ^{o}A	160	114	52	58	117
% Total Pore Volume in					
20-50^{o}A diameter pores	8.9	21.4	49.8	41.7	21.7
50-100^{o}A	34.8	43.3	44.8	51.8	43.2
100-150^{o}A	18.4	10.6	2.0	2.3	9.4
150-1200^{o}A	37.9	24.6	3.4	4.3	25.7

---

[a] Alumina/alumina phosphate.

[b] Balance of the support was alumina.

TABLE E-3

AIR FORCE CONTRACT F33615-79-C-2095
CATALYST PHYSICAL PROPERTIES
CATALYST COMPOSITION STUDY

Catalyst Number	3747-177-1	3609-189	3609-190
Support Sieve[a]	20% H-AMS	20% H-ZSM-5	20% H-Zeolon
Run Number Tested, AU-	75-50	75-48	75-49
Composition, Wt%			
MoO_3	14.8	13.2	14.0
Cr_2O_3	7.8	8.9	8.6
CoO	1.8	1.8	1.5
Surface Area, m^2/g	223.6	209.3	209.1
Pore Volume, cc/g	0.397	0.386	0.384
APD (4V/A), °A	71.1	73.8	73.4
% Total Pore Volume in			
20-50°A diameter pores	48.6	33.9	36.3
50-100°A	48.2	61.1	59.1
100-150°A	0.8	2.0	0.9
150-1200°A	2.4	3.0	3.7

---

1 Balance of support was alumina.

TABLE E-3 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
CATALYST PHYSICAL PROPERTIES
CATALYST COMPOSITION STUDY

Catalyst Number	3609-191	3838-007
Support Sieve[a]	20% RE-Y	20% US
Run Number Tested, AU-	27-136	75-56
Composition, Wt%		
MoO_3	13.1	14.6
Cr_2O_3	9.4	9.9
CoO	1.8	1.6
Surface Area, m^2/g	236.2	238.2
Pore Volume, cc/g	0.375	0.369
APD (4V/A), ^{o}A	63.4	61.9
% Total Pore Volume in		
20-50^{o}A diameter pores	31.5	43.1
50-100^{o}A	65.1	54.3
100-150^{o}A	0.9	0.5
150-1200^{o}A	2.5	2.1

---

1 Balance of support was alumina.

TABLE E-3 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
CATALYST PHYSICAL PROPERTIES
CATALYST COMPOSITION STUDY

Catalyst Number	3609-194	3609-184	3609-196	3862-003	3862-010
Support[a]	10% Silica	30% Silica	50% Silica	50% US Sieve	70% Silica
Run Number Tested, AU-	75-53	75-45	75-52	75-57	76-42
Composition, Wt%					
MoO_3	13.5	16.6	13.1	15.9	15.6
Cr_2O_3	8.9	9.4	9.5	9.8	9.5
CoO	1.2	1.5	1.6	1.5	1.7
Surface Area, m^2/g	193.6	227.4	170.2	285.7	199.1
Pore Volume, cc/g	0.395	0.784	0.475	0.365	0.368
APD (4V/A), °A	81.6	137.9	111.5	37.8	74.0
% Total Pore Volume in					
20-50°A diameter pores	32.8	15.2	14.0	39.9	51.5
50-100°A	59.9	37.8	56.8	33.8	38.5
100-150°A	4.5	7.8	17.4	4.8	1.9
150-1200°A	2.8	39.2	11.8	21.5	8.1

---

[a] Balance of support was alumina.

TABLE E-4

AIR FORCE CONTRACT F33615-79-C-2095
CATALYST PHYSICAL PROPERTIES
CATALYST COMPOSITION STUDY

Catalyst Number	3838-023	3838-028	3838-031	3838-030
Support[a]	50% US Sieve	50% US Sieve	50% US Sieve	50% US Sieve
Run Number Tested, AU-	75-61	75-62	75-64	75-65
Composition, Wt%				
MoO_3	15.3	14.1	14.7	15.0
Cr_2O_3	9.6	9.9	10.0	9.3
CoO	1.5	1.6	1.6	1.5
Surface Area, m^2/g	280.5	255.2	312.5	222.4
Pore Volume, cc/g	0.477	0.545	0.824	0.505
APD (4V/A), $^{\circ}$A	68.0	85.5	105.4	90.8
PV in Pores >1200°A Diam	0.153	0.269	0.362	0.244
% Total Pore Volume in				
20-50°A diameter pores	34.8	12.0	14.3	11.7
50-100°A	14.4	25.0	10.0	17.9
100-150°A	3.5	4.3	3.7	6.2
>150°A	47.3	58.7	72.0	64.2

---

[a] Balance of support was alumina.

TABLE E-4 (continued)

AIR FORCE CONTRACT F33615-79-C-2095
CATALYST PHYSICAL PROPERTIES
CATALYST COMPOSITION STUDY

Catalyst Number	3838-034	3838-035	3838-037	3838-039
Support[a]	50% US Sieve	50% US Sieve	50% US Sieve	50% US Sieve
Run Number Tested, AU-	75-66	75-68	75-69	75-70
Composition, Wt%				
MoO_3	15.0	13.5	14.4	14.2
Cr_2O_3	9.8	9.9	9.6	10.8
CoO	1.6	1.4	1.42	1.6
Surface Area, m^2/g	305.0	276.3	280.4	234
Pore Volume, cc/g	0.589	0.784	0.710	0.417
APD (4V/A), ^{o}A	77.2	113.4	101.3	71.5
PV in Pores >1200^{o}A Diam	0.261	0.336	0.354	.092
% Total Pore Volume in				
20-50^{o}A diameter pores	27.6	4.3	11.0	10.7
50-100^{o}A	14.4	7.8	16.2	39.3
100-150^{o}A	3.4	7.4	8.5	10.4
>150^{o}A	54.6	80.5	64.3	39.6

---

a Balance of support was alumina.

TABLE E-5

AIR FORCE CONTRACT F33615-79-C-2095
DATA FOR CATALYST SUPPORTS OR SUPPORT COMPONENTS

Support, Component	Type	Source	Used for Catalyst
Alumina	Extrudates	Conoco	3609-161
Alumina	Extrudates	Cyanamid	3609-162
Alumina	Extrudates	Cyanamid	See Text
Alumina	Extrudates	Katalco	3609-176
Silica	Gel	Davison	3609-177
20% Silica/Alumina	Extrudates	Davison	3609-178, 183
Alumina	Sol	Cyanamid	See Text
30% Silica/Alumina	Extrudates	Davison	3609-184
H-AMS Sieve	Powder	Archem	3747-177-1
H-ZSM-5 Sieve[a]	Powder	Mobil	3609-189
H-Zeolon Sieve	Powder	Norton	3609-190
RE-Y Sieve[b]	Powder	Davison	3609-191
US Sieve	Powder	Davison	See Text
70% Silica/Alumina	Sol	Cyanamid	3609-194, 196
70% Silica/Alumina	Extrudates	Davison	3838-010
Alumina	Powder	Amoco	3838-023
Alumina	Powder	Conoco	3838-028
Alumina	Powder	Amoco	3838-030
Alumina	Powder	Amoco	3838-031
Alumina	Extrudates	Katalco	3838-035
Alumina	Powder	Kaiser	3838-037
Alumina	Extrudates	Cyanamid	3838-039

(a) Actual sample used was prepared within Amoco Oil by proprietary methods.

(b) Actual sample used was prepared within Amoco Oil by multiple exchange of SK-40, a Y-type sieve (Davison), with rare-earth chloride solution.

TABLE E-6

AIR FORCE CONTRACT F33615-79-C-2095
COMPONENT AMOUNTS REQUIRED FOR IMPREGNATION[a]

	Finished Catalyst Metal Oxide Content											
	CoO			Cr_2O_3			MoO_3			NiO		Support, g
Nominal Composition, Wt%[b]	1.5	3.5	5.0	5.0	10.0	15.0	5.0	10.0	15.0	1.5	3.5	
Impregnation Salt, g	$Co(NO_3)_2 \cdot 6H_2O$			$(NH_4)_2Cr_2O_7$			$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$			$Ni(NO_2)_2 \cdot 6H_2O$		
	11.7				33.2			24.5				157
		27.2			33.2			24.5				153
			38.8		33.2			24.5				150
	11.7			16.6				24.5				167
	11.7					49.8		24.5				147
	11.7				33.2		12.3					167
	11.7				33.2				36.8			147
					33.2			24.5		11.7		157
					33.2			24.5			27.2	153

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[a] Based upon 200 g of finished oxide catalyst.

[b] Weight percent on finished oxide catalyst.

APPENDIX F

ACTIVITY MAINTENANCE TEST PROCESS HIGHLIGHTS

In contrast to all other previous runs on the unit used, the activity maintenance test was subjected to several unit upsets, some of which seriously affected catalyst activity, particularly with respect to the cracking function. These upsets and subsequent processing adjustments are detailed in this Appendix. One consequence of these upsets was that the activity test was extended beyond 60 days to generate sufficient data at lined-out conditions.

On day 9, after collection of the sample, reactor temperature was raised from 770°F to 772°F to compensate for an "apparent" loss in saturation and cracking activity as judged by the decline in product API gravities from 52.2° on day 2 to 45.2° on day 8. This "apparent" loss will be discussed subsequently.

During the 24-hour collection period for sample 11, the once-through hydrogen flow was only 6.3 SCF (approximately 4000 SCFB hydrogen) due to a fouled off-gas pressure control valve. This low throughput resulted in a product with a low API gravity of 42.5° and a high product nitrogen of 112 ppm. After cleaning the off-gas pressure control valve and increasing the hydrogen throughput, product API gravities declined from 49.5° on day 12 to 45.4° on day 14. At that time, it appeared that the previous low gas flow had caused some degree of deactivation as reflected in the API gravities, and to compensate, reactor temperature was raised from 772°F to 775°F prior to collection of sample 15.

Surprisingly, the API gravities for the next two samples indicated no response, whereas on day 17, a mass balance period, the API gravity jumped 5° at the same processing conditions. A review of unit operations pinpointed two contributing factors.

(a) It was noticed that the API gravities for the previous mass balance periods, i.e., days 3 and 9, were significantly higher than non-mass balance periods. During mass balances, the sample collection system was operated as a closed system. That is, the liquid sample bottle was sealed with a vent loop connected to the off-gas stream, down stream from the pressure control valve. The sample was therefore blanketed with the hydrogen off-gas and was subjected to a slight positive pressure due to an in-line, wet-test meter used to measure gas volumes.

(b) Conversely, non-mass balance liquid samples were exposed to the atmosphere and this in conjunction with the heated sample-receiving container (approximately 150°F) resulted in losses in liquid light ends, hence a lowered gravity.

All future samples were consequently collected in a closed system at ambient temperature. The response to this change is reflected in the high API gravity for sample 18 (51.6°) as compared to the mass balance sample 17 (API of 51.2°, closed system) and to sample 16 (API of 46.2, open system).

It should be noted that in retrospect, the API gravities of all non-mass balance samples prior to sample 17 are low by perhaps up to 5 API units. Also, the previous indication that a low gas flow for sample 11 caused some catalyst deactivation may be somewhat suspect.

During collection of sample 19, a 50 psig pressure drop developed across the reactor and a few hours later during unattended weekend operation, a pressure relief valve set at 2450 psi failed. The unit immediately depressurized. Automatic safeguards cut power to the feed pump and reactor heaters and stopped hydrogen input. The catalyst was, however, subjected to process temperatures in the absence of hydrogen until natural cooling reduced the temperature to ambient over an extended time period.

All five pressure relief valves on the unit were subsequently repacked and reset. To determine the cause of the failure, the reactor was removed from the heating block and inspected. The layer of balls on top of the catalyst bed was clean and free flowing. The small reactor outlet, however, was found blocked by a packing ball. After removal of this ball, the reactor was brought back on stream at 775°F with flowing hydrogen. No further high-pressure differentials were observed for the remainder of the run.

After six hours with hydrogen flow, the feed pump was restarted and sample collection began 16 hours later. Processing conditions remained at 775°F, 0.4 LHSV, and 2000 psi for samples 19 through 25. Sample gravities were consistently 46° to 48°, indicating a drop in catalyst activity after failure of the safety relief valve. It is likely that some coking of the catalyst occurred during the period of high temperature with no hydrogen flow.

To compensate, temperature was raised 2°F to 777°F prior to collection of sample 26. API gravities for the next nine samples increased to 49°-51°.

During collection of sample 35 under unattended weekend operation, the off-gas control valve fouled and became nonfunctioning in the full open position. Since the hydrogen supply control valve could not compensate for the high discharge rate, the unit pressure was reduced to 1000 psig over a four-hour period. Because of the set points of the alarm functions the feed pump continued to operate with reactor temperatures at 777°F.

Sample 37, collected after this upset, had a very low API gravity of 42.7°, indicating a loss in activity probably due to adsorption of contaminants due to the period of low-pressure operation. Feed to the unit was discontinued and the catalyst regenerated in flowing hydrogen at 777°F for 24 hours. The success of this procedure was reflected in the high product gravities for samples 38 through 42.

After collection of sample 42, the main building hydrogen supply generator failed to maintain sufficient inlet hydrogen pressure and hydrogen flow fell to 1 SCF for a 16-hour period of unattended night operation. After repairs and during catalyst regeneration with flowing hydrogen another safety relief valve failed in the off-gas hydrogen line again during unattended operation. Unit shutdown was automatic but reactor temperatures remained high with no hydrogen flow for a period of about one hour until hydrogen flow was reestablished. Hydrogen flow was maintained overnight until the unit was shut down.

After repairs and after 24 hours with flowing hydrogen at reactor temperature, product API for sample 43 at 40.4° indicated severe catalyst deactivation as a result of the low hydrogen flow rate and following depressurization. API gravities for samples 44 through 46 indicated a slow catalyst reactivation but in view of the time remaining to complete the activity test, temperature was raised to 781°F prior to sample 47.

A slow recovery was evident, but because of the time factor, temperature was raised to 786°F for samples beginning with 49. Recovery at this temperature was rapid and catalyst activity remained constant through sample 64.

During collection of sample 65, an upset occurred to cause the product API gravity to drop to 42.7°. The reason for the upset during unattended operation is not known but the dark color of the sample suggests a lack of hydrogen flow or a low reactor temperature. No corrective action was taken and the catalyst recovered and maintained high activity for the remainder of the run.

APPENDIX G

SIMULATED DISTILLATION DATA

Mass balance samples for all processing runs were analyzed to determine conversion to naphtha, distillate, and gas oils. Results from Simulated Distillations, ASTM Method D2887-73, are presented in their entirety in the following tables. JP-4 yields given in the previously detailed run data tables were taken from these results with the following limits:

20% distilled; not more than 290^{o}F

90% distilled; not more than 470^{o}F

TABLE G-1

AIR FORCE CONTRACT F33615-79-C-2095
SIMULATED DISTILLATION DATA
PROCESS VARIABLE STUDY

							Weight Percent							
	IBP	1.0	5.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	95.0	99.0	FBP
Sample								Temperature, °F							
FHC-337	290	325	404	446	513	566	623	683	744	798	878				1000+
27-125-4	182	224	321	386	454	506	559	601	649	707	774	845	912	1011	1000+
27-125-10	124	172	278	349	429	478	526	567	619	672	741	824	899	1002	1000+
27-125-13	127	181	279	350	435	486	534	579	626	684	754	837	907		1000+
27-125-15	66	126	240	310	394	478	523	571	612	667	733	817	875	977	1000+
27-125-18	76	143	246	316	398	482	528	574	617	672	741	822	886	1006	1000+
27-125-22	81	147	261	336	414	500	552	595	643	699	769	842	913		1000+
27-125-26	116	146	268	335	419	470	513	562	602	652	714	798	856	999	1000+
27-125-32	126	162	330	395	458	505	555	594	635	687	746	811	854	926	939
27-125-35	144	190	323	393	462	512	563	603	650	705	767	833	885	950	962
27-125-41	161	198	309	376	443	490	535	575	616	664	718	788	832	902	916
27-125-48	99	144	266	338	425	477	524	569	613	664	726	795	839	900	909
75-35-5	68	121	238	309	399	451	497	544	584	630	692	772	823	908	925
75-35-8	82	130	259	332	422	476	519	571	611	66[illegible]	728	808	860	953	984
75-35-14	114	138	251	312	398	448	491	535	577	621	676	755	809	890	912
75-35-17	0	66	234	303	395	444	489	536	576	620	679	756	808	883	905
75-35-20	75	122	250	315	401	449	494	540	581	633	687	766	813	895	914
75-35-22	170	194	274	330	412	455	500	545	584	628	687	764	815	894	915
75-35-27	142	166	309	367	429	473	510	553	587	625	676	732	768	801	805
75-35-30	183	203	298	362	437	483	527	572	611	661	719	793	836	911	922
75-35-36	74	124	245	317	400	449	490	534	574	615	668	740	790	853	866
75-35-43	131	169	256	309	389	434	476	525	564	610	672	753	813	1013	1000+

TABLE G-2

AIR FORCE CONTRACT F33615-79-C-2095
SIMULATED DISTILLATION DATA
CATALYST COMPOSITION STUDY

							Weight Percent							
	IBP	1.0	5.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	95.0	99.0	FBP
Sample								Temperature, °F							
27-127-5	123	154	259	326	407	451	496	543	583	629	688	769	819	908	929
27-128-5	130	158	266	329	418	467	510	559	599	646	708	785	834	919	941
27-129-4	-6	45	199	276	413	461	505	555	594	640	701	780	829	913	930
27-130-6	-1	112	245	315	406	453	498	542	581	625	687	769	819	903	919
27-131-5	192	213	301	365	440	487	531	576	615	664	723	799	847	927	945
27-132-5	62	100	238	305	401	451	499	547	589	639	708	793	862		1000+
75-36-3	122	165	272	335	422	469	512	559	598	643	706	786	835	919	944
75-36-10	113	153	297	368	437	482	524	569	606	655	712	786	829	896	911
75-37-5	117	148	258	322	403	449	495	541	581	628	688	768	819	908	928
75-38-5	145	189	271	331	416	461	505	554	594	640	701	780	828	913	932
75-39-5	74	127	238	298	385	439	481	524	568	614	674	761	814	906	928
75-40-7	5	117	244	313	399	449	491	534	574	619	676	758	811	897	915
75-41-7	71	123	242	313	406	456	503	555	597	648	718	807	891		1000+
75-42-6	19	61	185	235	307	369	421	458	502	556	613	721	798		1000+
75-46-5	8	59	181	230	299	361	415	452	497	547	597	680	746	822	840
75-46-12	42	76	195	251	332	395	442	483	528	577	633	722	786	860	879
75-47-2	36	90	222	279	363	410	458	501	545	592	649	745	807	911	950
75-47-6	73	131	250	320	401	450	490	534	575	618	672	751	804	883	902

TABLE G-3

AIR FORCE CONTRACT F33615-79-C-2095
SIMULATED DISTILLATION DATA
CATALYST SUPPORT OPTIMIZATION STUDY

							Weight Percent							
	IBP	1.0	5.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	95.0	99.0	FBP
Sample								Temperature, °F							
27-136-6	104	145	259	324	415	463	508	557	597	645	709	788	843	933	960
75-45-6	125	161	258	320	408	456	502	548	589	637	702	789	854		1000+
75-48-3	91	107	190	255	346	413	452	493	536	579	633	717	780	880	907
75-48-8	1	51	182	258	354	416	463	503	550	591	647	727	781	883	903
75-49-5	52	119	249	322	409	457	504	550	591	639	700	781	830	918	933
75-50-4	24	61	163	241	333	407	453	496	542	584	638	722	783	885	906
75-50-11	-15	20	181	252	355	423	468	510	559	601	653	732	790	890	914
75-52-7	104	150	258	321	410	456	502	550	589	635	695	774	820	902	919
75-52-14	96	140	259	321	410	456	502	551	591	638	698	777	823	906	924
75-53-7	100	114	215	288	397	462	517	574	625	694	780	909	1008		1000+
75-53-10	106	150	267	337	423	474	517	565	604	655	720	798	850	933	953
75-56-3	65	106	222	281	384	438	481	524	572	617	678	768	820	891	906
75-56-7	86	124	232	298	407	472	526	579	636	703	785	908			1000+
75-56-10	147	181	278	345	426	477	519	569	607	659	721	798	853	958	1000+
75-57-6	50	62	154	203	260	303	351	395	435	478	532	601	656	735	752
76-42-12A	146	178	277	342	427	476	523	565	609	659	722	794	845	939	984

TABLE G-4

AIR FORCE CONTRACT F33615-79-C-2095
SIMULATED DISTILLATION DATA
CATALYST PHYSICAL PROPERTIES STUDY

	Weight Percent														
	IBP	1.0	5.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	95.0	99.0	FBP
Sample	Temperature, °F														
75-61-4	-4	26	129	171	238	280	324	369	417	459	523	624	753	889	909
75-61-8	90	135	251	321	417	468	515	567	608	664	731	810	868	958	984
75-62-5	17	67	164	222	287	346	401	444	486	540	598	688	757	850	877
75-62-10	121	159	271	342	430	486	536	582	631	690	755	827	883	966	990
75-64-5	103	155	253	314	402	454	499	547	588	635	697	779	828	906	922
75-64-10	79	134	265	338	429	485	536	581	633	694	765	846	922		1000+
75-65-4	150	184	294	372	439	487	532	578	621	674	737	811	861	939	958
75-65-11	130	172	291	371	439	487	533	578	623	675	738	812	360	936	952
75-66-5	39	76	194	253	348	409	450	489	536	581	642	730	791	862	875
75-68-5	52	111	222	278	357	423	472	516	569	618	684	768	813	883	900
75-68-9	132	171	282	354	437	486	537	579	628	683	748	807	851	928	945
75-69-5	107	152	244	298	388	442	486	535	576	629	694	783	833	903	918
75-69-10	186	208	302	370	441	486	534	573	620	668	732	802	842	921	934
75-70-4	-2	37	162	220	288	359	416	463	514	574	656	775	850	952	968
75-70-10	38	92	213	289	402	470	529	586	648	725	810	934			1000+

TABLE G-5

AIR FORCE CONTRACT F33615-79-C-2095
SIMULATED DISTILLATION DATA
CATALYST ACTIVITY MAINTENANCE STUDY

							Weight Percent							
	IBP	1.0	5.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	95.0	99.0	FBP
Sample								Temperature, °F							
75-71-3	-37	-9	117	161	227	270	311	352	396	439	492	570	624	713	737
75-71-9	-16	6	143	202	267	320	376	422	465	516	582	680	761	862	890
75-71-17	-36	-9	124	183	240	283	326	374	420	462	521	603	671	811	900
75-71-27	6	56	150	204	263	313	360	408	450	497	560	640	711	810	834
75-71-32	-4	53	138	194	256	305	354	403	444	489	554	631	705	812	838
75-71-39	27	47	136	199	267	319	374	423	469	521	585	675	748	837	866
75-71-46	28	66	192	249	330	403	450	495	547	597	662	758	817	895	914
75-71-53	-7	36	126	184	241	287	333	386	429	475	532	602	662	747	768
75-71-60	44	59	139	193	259	312	362	413	456	508	574	660	732	823	849
75-71-67	-86	-27	133	190	267	320	378	421	465	514	574	662	732	818	835
75-71-73	-107	-61	129	188	249	302	351	400	441	494	559	641	710	798	815
75-71-80	16	35	155	198	261	309	357	405	444	493	551	632	698	792	811
75-71-87	-95	-55	132	190	252	308	360	414	453	502	559	647	721	818	839
75-71-93	-16	-4	152	205	275	329	388	428	471	517	573	657	729	815	831
75-71-96	-25	-14	133	186	243	289	340	395	434	480	539	615	676	770	787
75-71-101	-31	42	168	229	300	369	420	463	508	566	619	709	787	858	876

APPENDIX H

BULK DISTILLATION DATA

"The contractor shall provide to the Air Force, small (50 milliliter) research samples of the products from each hydroprocessing run. The products will be distilled so that each run provides a sample of the products boiling below 350°C (662°F) and a sample of the products boiling above 350°C."

Results, as percent yield of each charge are detailed in the following tables for all catalyst screening runs, Task 2 through Task 5. In the tables, the designation 10A/9, for example indicates a composite of samples 10 and 9 was used with the first listed constituting more than 50% of the composite volume. The designation 14A,13, for example, indicates equal volumes of the two samples were used. The letter A indicates a mass balance sample. No adjustments for losses, if any, were made.

A 200 cc sample or sample composite was distilled at 45 mm Hg under nitrogen with an overhead cut point of 253°C (487.4°F). Distillation reflux ratio was 1:1 above 210°C and 5:1 above 240°C. In general, the bottoms temperature reached approximately 300°C.

TABLE H-1

AIR FORCE CONTRACT F33615-79-C-2095
BULK DISTILLATION DATA
PROCESS VARIABLE STUDY

Sample	Weight Percent Distilled IBP-662°F	 662°F+
27-125-10A/9	68.6	28.5
27-125 13A/12	66.6	30.0
27-125-15A/14	68.1	31.6
27-125-18A/19	66.5	31.7
27-125-22A/23	64.8	34.4
27-125-26A/27	72.6	26.6
27-125-32A/31	69.6	29.0
27-125-35A	63.7	35.4
27-125-41A[a]	--	--
27-125-48A[a]	--	--
75-35-5A/4	79.3	20.8
75-35-8A	72.6	26.0
75-35-14A,13	81.3	18.2
75-35-17A/16	77.8	23.5
75-35-20A/19	76.8	22.5
75-35-22A,23	78.4	20.3
75-35-27A/26	78.3	20.2
75-35-30A/31	70.2	28.7
75-35-36A/35	82.7	15.6
75-35-43A/42	77.7	21.6

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[a] Data or sample lost.

TABLE H-2

AIR FORCE CONTRACT F33615-79-C-2095
BULK DISTILLATION DATA
CATALYST COMPOSITION STUDY

Sample	Weight Percent Distilled	
	IBP-622°F	662°F+
27-127-5A/6	75.4	23.0
27-128-5A/6	74.1	24.9
27-129-4A/3	73.8	25.2
27-130-6A	73.7	24.9
27-131-5A/6	74.8	23.4
27-132-5A/6	76.2	22.6
75-36-3A	--	--
75-36-10A/9	75.5	22.9
75-37-6/5A	75.1	24.1
75-38-5A/6	75.4	23.9
75-39-5A/6	75.1	23.0
75-40-6/7A	76.2	23.3
75-41-6/7A	76.3	22.2
75-42-6A/7	86.0	12.0
75-46-4/5A	86.6	12.5
75-46-11/12A	83.8	15.7
75-47-5/6A	76.2	22.8

TABLE H-3

AIR FORCE CONTRACT F33615-79-C-2095
BULK DISTILLATION DATA
CATALYST SUPPORT OPTIMIZATION STUDY

Sample	Weight Percent Distilled	
	IBP-662°F	662°F+
27-136-5/6A	74.8	24.5
75-45-7/6A	76.5	23.0
75-48-4/3A	79.0	20.3
75-48-8A,6	79.5	20.3
75-49-6/5A	75.3	24.0
75-50-3,4A	83.2	16.0
75-50-10,11A	79.0	20.0
75-52-6,7A	73.7	25.5
75-52-13/14A	73.0	26.3
75-53-4,5	68.9	22.1
75-56-4/3A	75.0	23.8
75-56-14,15A	72.2	27.8
75-57-6A,7	92.8	4.0

TABLE H-4

AIR FORCE CONTRACT F33615-79-C-2095
BULK DISTILLATION DATA
CATALYST PHYSICAL PROPERTIES STUDY

Sample	Weight Percent Distilled IBP-662°F	 662°F+
75-61-4A/3	93.3	5.4
75-61-8A,9	71.3	28.5
75-62-5A/4	89.8	9.8
75-62-10A	67.0	32.4
75-64-4/3	72.3	27.1
75-64-10A	66.1	32.6
75-65-3/4A	72.5	27.2
75-65-11A	66.2	33.0
75-66-4,5A	84.3	15.7
75-68-4,5A	74.9	25.0
75-68-9A	65.9	33.8
75-69-4,5A	76.4	23.4
75-69-10A	66.7	32.7
75-70-4A,5	82.2	17.1
75-70-10A	67.9	31.9

TABLE H-5

AIR FORCE CONTRACT F33615-79-C-2095
BULK DISTILLATION DATA
CATALYST ACTIVITY MAINTENANCE STUDY

Sample*	Weight Percent Distilled JP-4		 520°F+
75-71-1-73	75.5		21.3
	77.1		21.9
	75.5		23.2
	IBP-300°F	JP-8	620°F+
	26.1	60.8	12.7
	27.8	60.4	11.7
	26.0	62.6	11.1

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* Composite did not include samples with greater than 10 ppm nitrogen or having API gravity less than 45°.

APPENDIX I

CATALYST DIGISORB PORE-SIZE DISTRIBUTIONS

As part of the catalyst characterizations, all catalysts tested were subjected to pore-size, surface-area analysis by adsorption of nitrogen using the Digisorb technique for pores in the range 20-1200^{o}A pore diameters. Data is plotted for the following systems as incremental pore volume per unit radii ($\Delta PV/\Delta PR$, cc/gm/Å) versus pore diameter, ^{o}A.

Figure I-1	1.5% CoO, 9.7% Cr_2O_3, 16.0% MoO_3 on alumina, the most active alumina-based catalyst (3609-174). The pore-size distribution shown was typical for all alumina-based catalysts tested.
Figure I-2	1.5% CoO, 9.0% Cr_2O_3, 15.2% MoO_3 on 20% silica alumina (3609-183), the most active silica-alumina-based catalyst.
Figures I-3 to I-10	1.5% CoO, 10% Cr_2O_3, 15% MoO_3 on 50% US sieve alumina catalysts tested in Task 4, Catalyst Physical Properties.
Figure I-11	The optimized catalyst, 3838-043, used for the Activity Maintenance test.

Appendix E gives broad pore-size distributions for all catalysts tested. Mercury penetration data for pores >1200^{o}A pore diameter is included in Appendix E only for those catalysts tested in Task 4 on Catalyst Physical Properties, but is not reflected in Figures I-3 through I-10.

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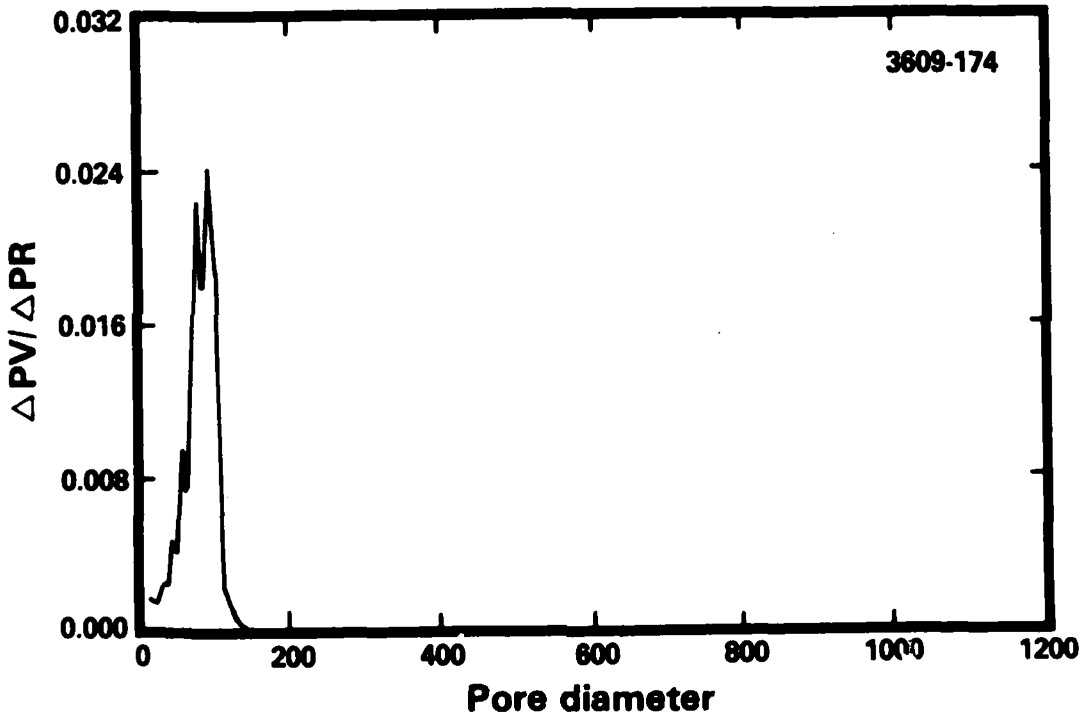


Figure I-1

Air Force contract F33615-79-C-2095

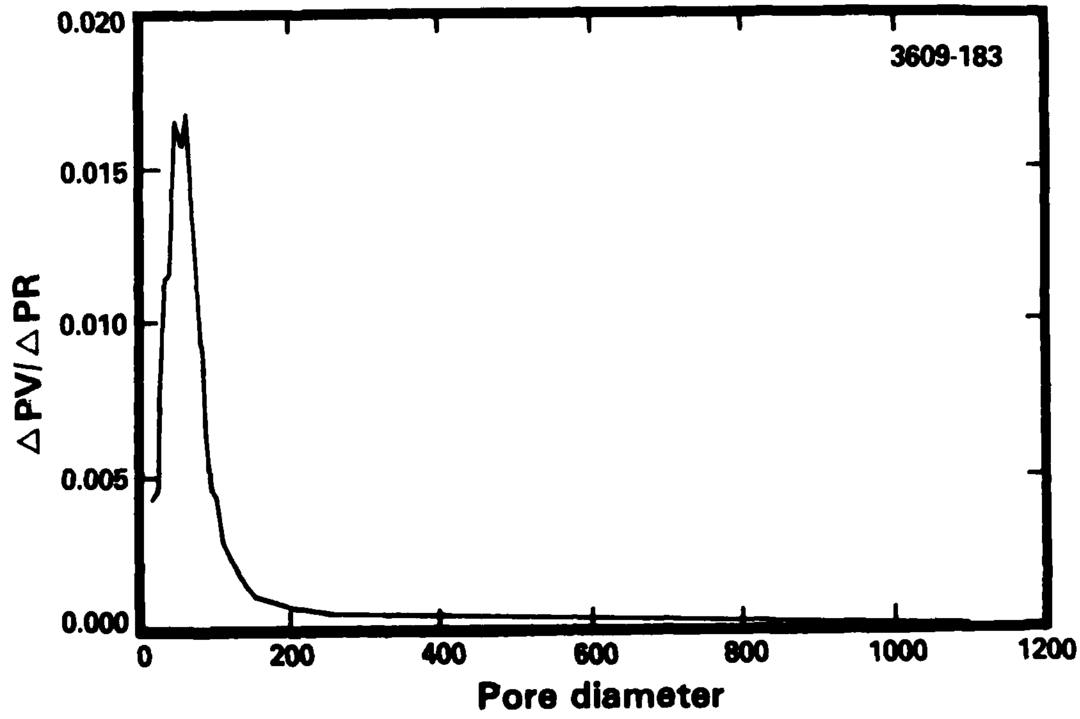


Figure I-2

Air Force contract F33615-79-C-2095

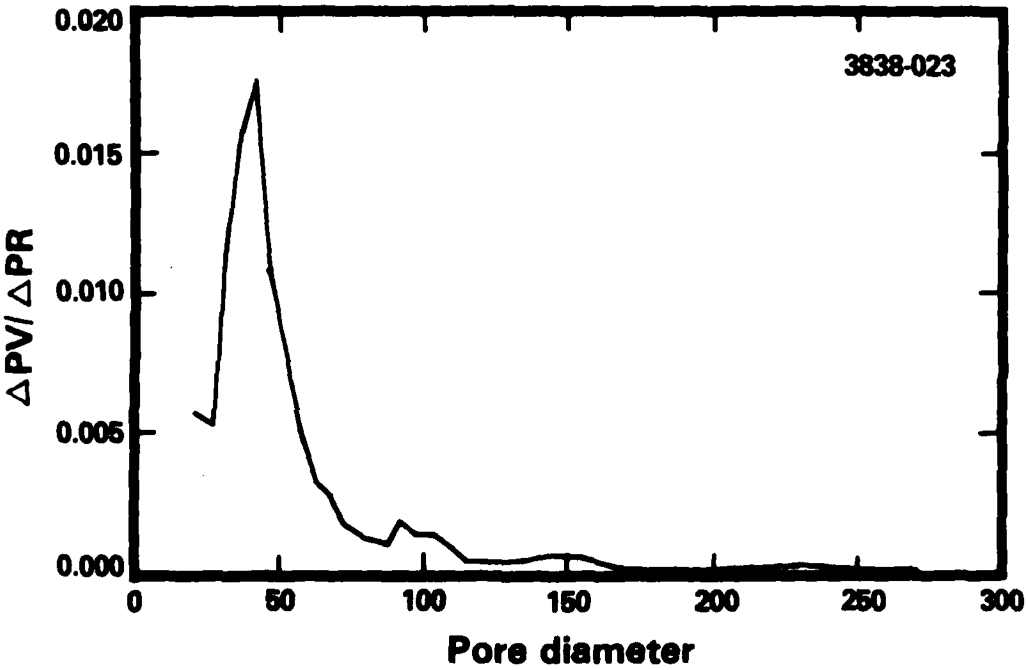


Figure I-3

Air Force contract F33615-79-C-2095

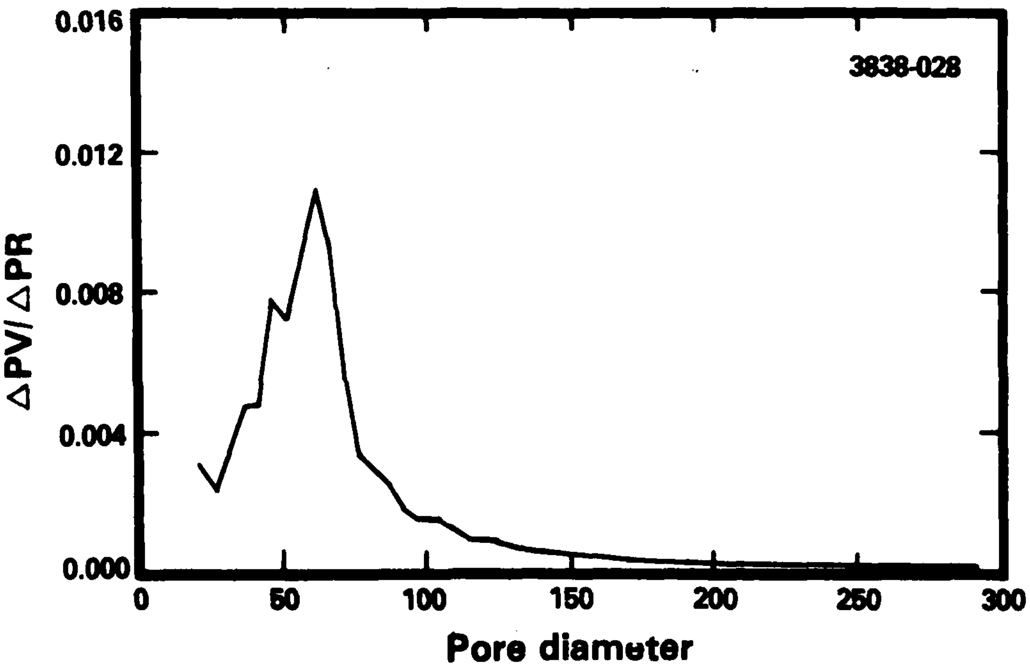


Figure I-4

Air Force contract F33615-79-C-2095

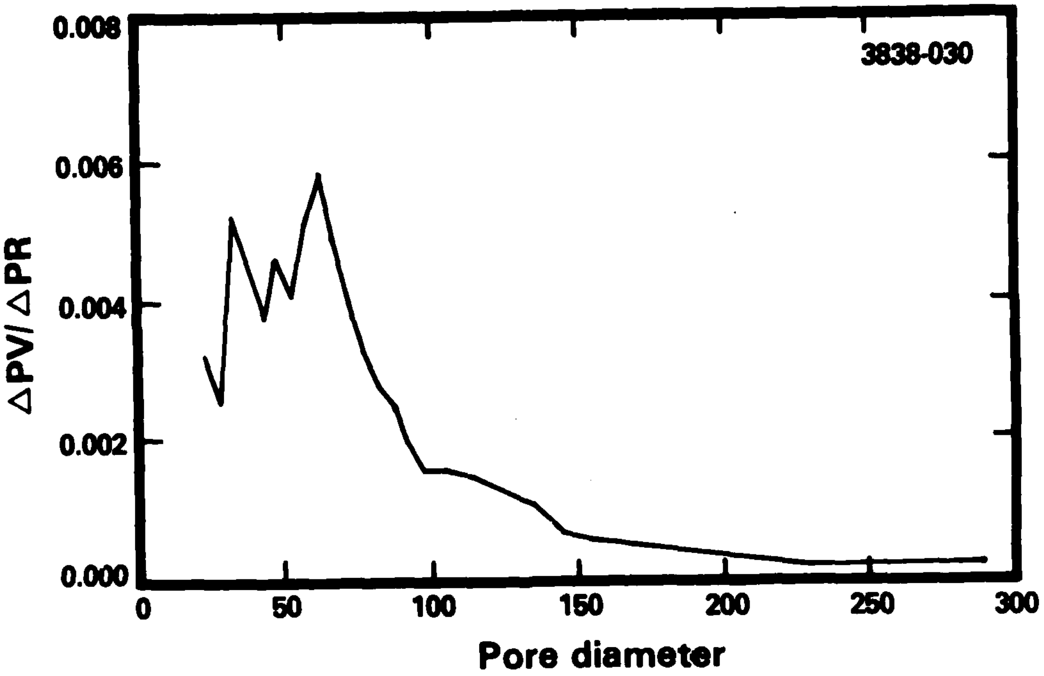


Figure I-5

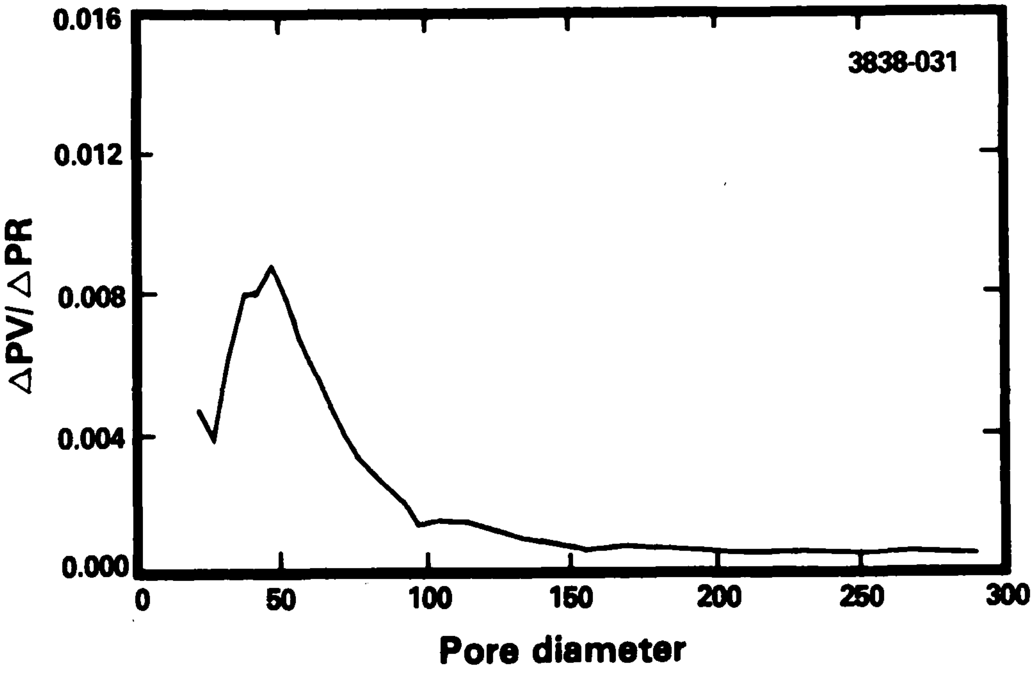

Air Force contract F33615-79-C-2095

Figure I-6

Air Force contract F33615-79-C-2095

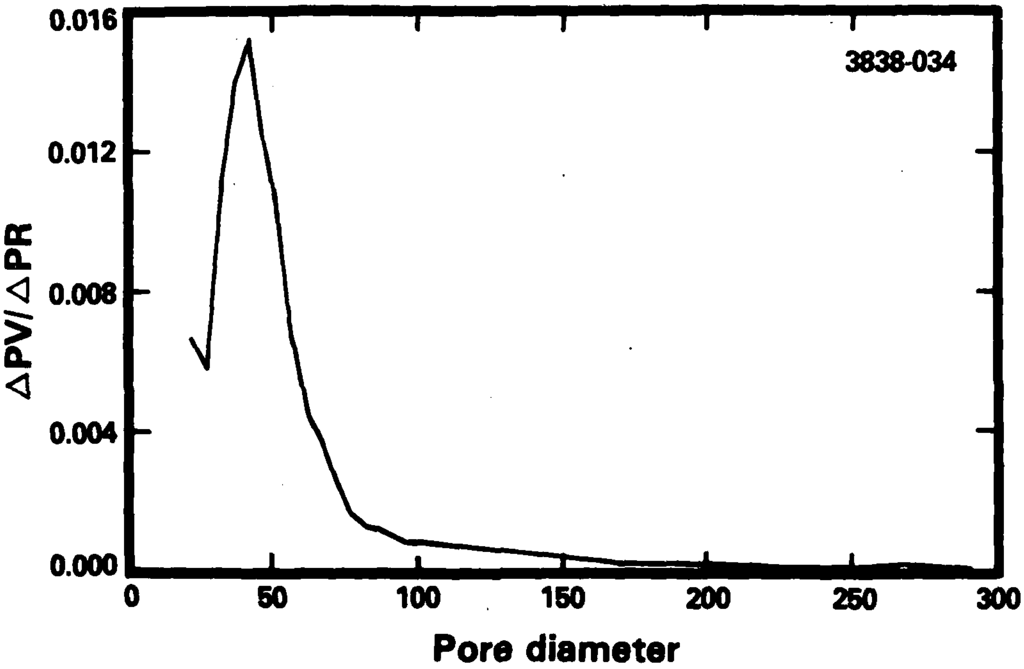


Figure I-7

Air Force contract F33615-79-C-2095

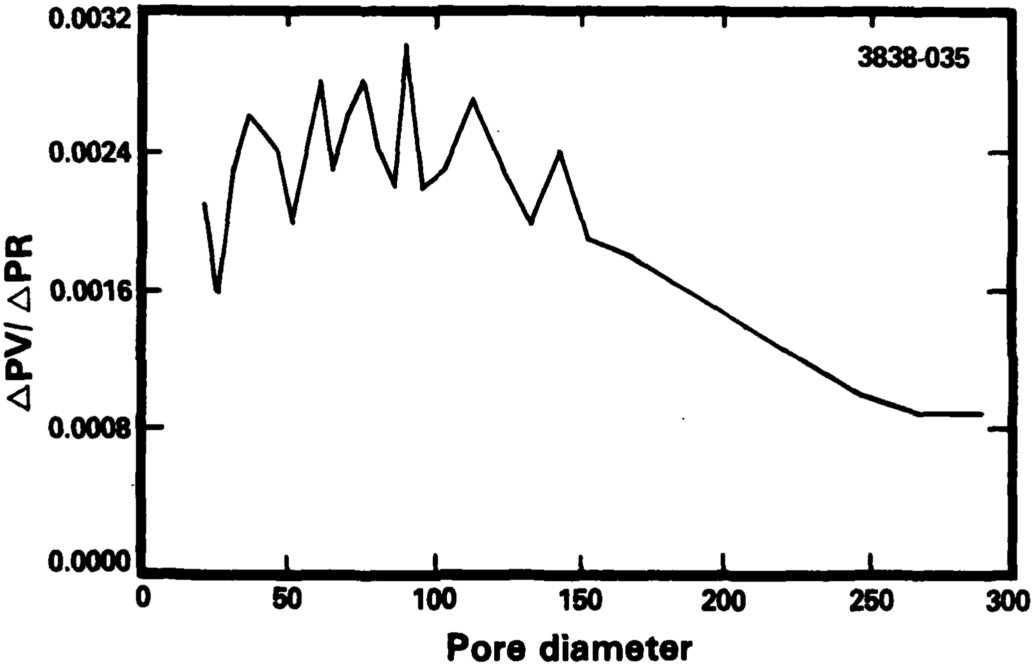
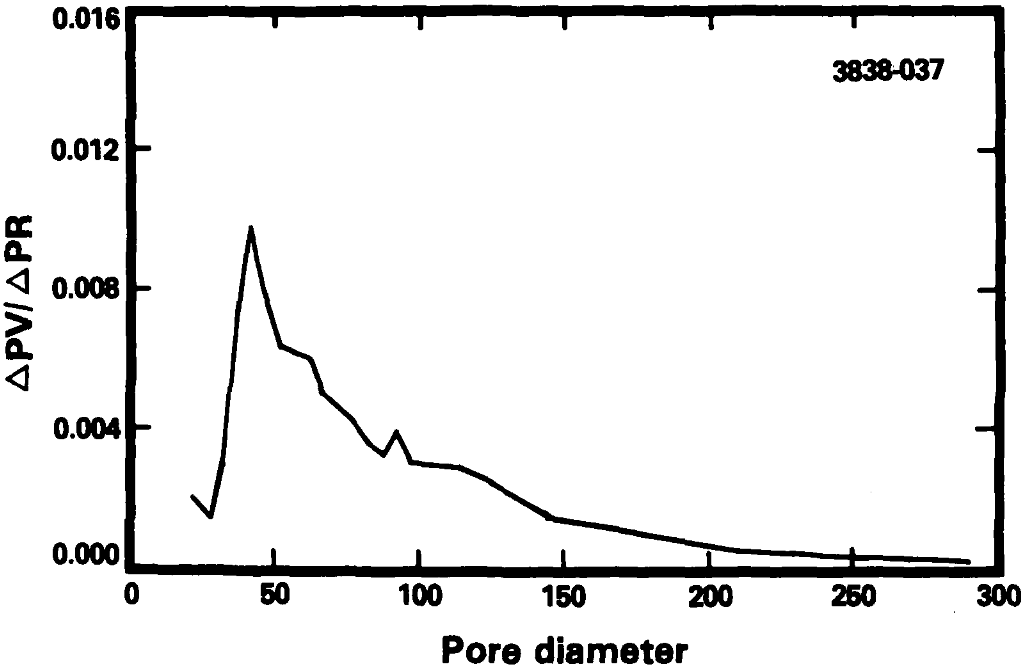


Figure I-8



Air Force contract F33615-79-C-2095

Figure I-9

Air Force contract F33615-79-C-2095

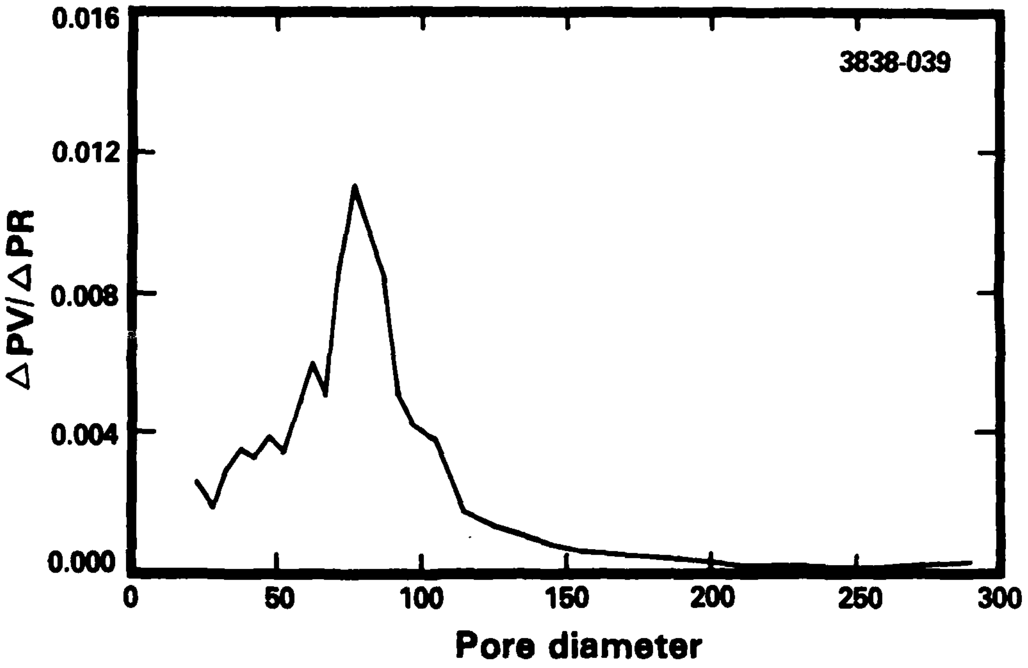


Figure I-10

Air Force contract F33615-79-C-2095

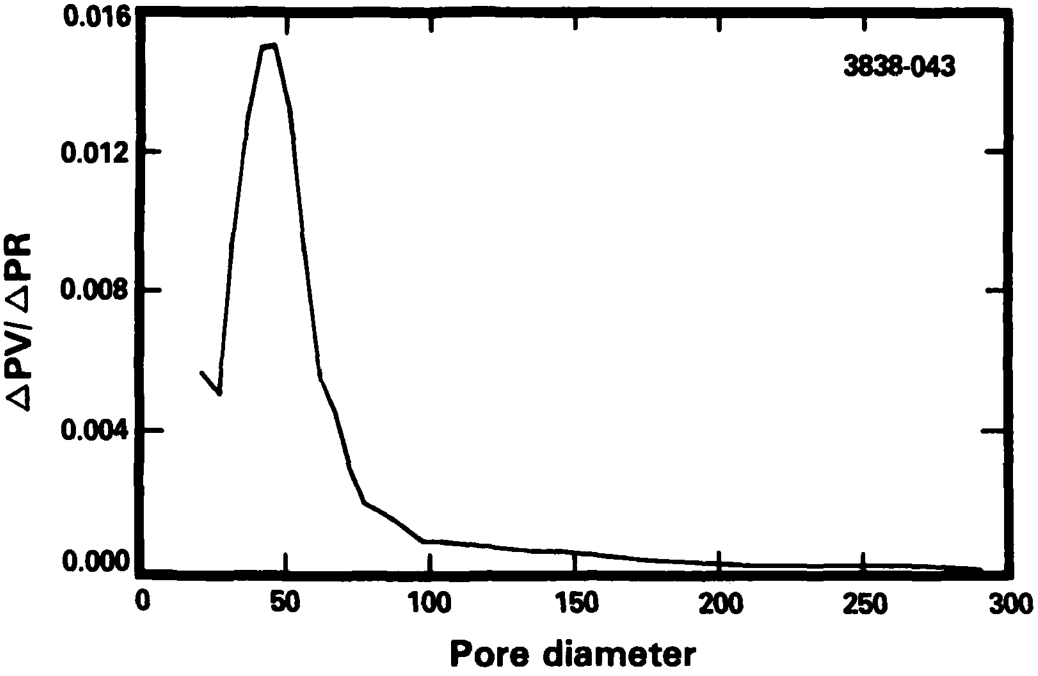


Figure I-11

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EVALUATION OF HYDROCRACKING CATALYSTS FOR CONVERSION OF WHOLE S--ETC(U)
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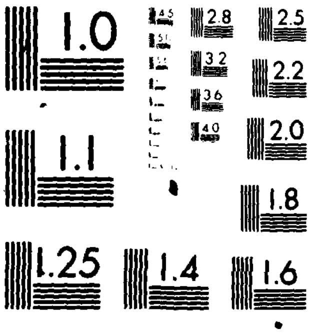

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

APPENDIX J

CATALYSTS CONTAINING NICKEL

As part of Task 2, Catalyst Composition Study--Metals Optimization, two Ni/Cr/Mo catalysts were prepared and tested in order to compare the activity of nickel to that of cobalt. The two catalysts containing 2% NiO and 4.5% NiO (compared to 1.6% and 5.1% CoO) along with approximately 10% Cr_2O_3 and 10% MoO_3 were prepared on the same alumina used for all Co/Cr/Mo on alumina catalysts tested in Task 2. Catalyst screening results at 780°F, 1800 psig and 0.5 LHSV are given in Tables J-1 and J-2. The two nickel catalysts have activities for nitrogen removal comparable to their cobalt counterparts (Tables 5 and 8), but produced slightly less JP-4 boiling-range material.

No nickel-containing sieve/alumina catalysts were tested.

TABLE J-1

AIR FORCE CONTRACT F33615-79-C-2095
PROCESS WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, METALS OPTIMIZATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-167, 2% NiO, 9.8% Cr_2O_3, 9.5% MoO_3 on Alumina
Run ID: AU-75-36

Days on Oil	1	2	3A	4	5	6	7	8	9	10A
Avg Cat Temperature, °F	781.0	780.8	780.7	781.1	781.1	780.3	--	--	780.0	780.6
Gravity, API°	38.3	38.3	38.8	38.5	38.6	38.4	38.3	38.6	38.5	38.8
Liquid Product, g	208	199	150	207	209	212	223	197	203	158
Carbon, Wt%			86.37							86.36
Hydrogen, Wt%			13.60							13.60
Nitrogen, ppm	138	148	129	147	140	150	195	135	210	198
Sulfur, ppm	140	140	170	120	200	130	110	200	90	120
Pour Point, °F			70							75
Viscosity, cst (104°F)			3.56							3.50
Simulated Distillation										
IBP, °F			122							113
IBP-360°F, Wt%			12.5							9.3
360-650°F, Wt%			59.0							60.0
650°F+, Wt%			28.5							30.7
FBP, °F			944							911
JP-4, Wt%			33.4							30.0
Gas Rate, SCFB x 10^{-3}			11.1							12.3
Hydrogen Consumption, SCFB			1370							1365
Wt%, C_1-C_4 on Feed			2.7							2.7
Volume Expansion, %			105							105

TABLE J-2

AIR FORCE CONTRACT F33615-79-C-2095
PROCESSING WHOLE SHALE OIL, TASK 2
CATALYST COMPOSITION STUDY, METALS OPTIMIZATION

Conditions: 1800 psig, 0.5 LHSV
Catalyst: 3609-168, 4.5% NiO, 9.8% Cr_2O_3, 9.3% MoO_3 on Alumina
Run ID: AU-75-38

Days on Oil	1	2	3	4	5A	6
Avg Cat Temperature, °F	777.7	--	781.0	780.4	780.3	780.3
Gravity, API°	38.5	39.3	39.3	38.8	38.9	38.7
Liquid Product, g	208	194	214	204	163	195
Carbon, Wt%					86.33	
Hydrogen, Wt%					13.64	
Nitrogen, ppm	88	96	88	104	113	121
Sulfur, ppm	930	680	113	163	151	74
Pour Point, °F					80	
Viscosity, cst (104°F)					3.39	
Simulated Distillation						
IBP, °F					145	
IBP-360°F, Wt%					13.0	
360-650°F, Wt%					60.5	
650°F+, Wt%					26.5	
FBP, °F					932	
JP-4, Wt%					35.0	
Gas Rate, SCFB x 10^{-3}					12.0	
Hydrogen Consumption, SCFB					1370	
Wt%, C_1-C_4 on Feed					2.6	
Volume Expansion, %					105	

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