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JET FUEL LOOKS TO SHALE OIL: 1980 TECHNOLOGY REVIEW.(U)
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# JET FUEL LOOKS TO SHALE OIL: 1980 TECHNOLOGY REVIEW

Dr Herbert R. Lander
Fuels Branch
Fuels and Lubrications Division

May 1981

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Proceedings of Symposium
19 - 20 November 1980
Cincinnati, Ohio

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The progress of several Air Force shale oil related programs is reported. Three shale oil processing studies evaluating the yield, cost, and quality of JP-4 and JP-8 turbine fuel produced from whole crude shale oil are discussed. Details of a fourth program that produced 11,300 gallons of specification JP-4 from Geokinetics shale oil are reported. Some of this jet fuel was tested in Air Force Fuel Mainburner/Turbine Effects Programs and was shown to behave very similar to petroleum derived JP-4. An additional study concentrated on developing hydrotreating catalysts that would more efficiently convert shale oil into aviation turbine fuel.

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## FOREWORD

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I

# THE AIR FORCE AVIATION TURBINE FUEL TECHNOLOGY PROGRAM - BACKGROUND

By

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THE AIR FORCE AVIATION TURBINE FUEL TECHNOLOGY PROGRAM - BACKGROUND

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JP-4, the primary fuel of the Air Force for more than a quarter of a century, now accounts for nearly half of the Department of Defense (DOD) petroleum requirement. As recently as 1973, the Air Force procured JP-4 for less than 11¢ per gallon. The availability of desirable domestic crudes for producing this fuel had decreased over the years, but the shortfall had been made up by inexpensive imported crudes and fuels. The supply interruptions of the 1973 Oil Embargo and the subsequent price increases caused the Air Force to question all of the old assumptions about the low cost and ready availability of jet fuel. The Air Force jet fuel costs have doubled just in the last year even though conservation measures have reduced fuel consumption to the minimum level of consistent with operational readiness. In 1980 jet fuel will cost the Air Force approximately 4 billion dollars.

Conservation measures alone are not sufficient. In 1974 the Air Force Aero Propulsion Laboratory (AFAPL) initiated programs to evaluate the feasibility of increasing jet fuel availability and minimizing future cost increases. Specification broadening studies indicate that modifications of the specification limits on boiling range, freeze point, and aromatic content offer the greatest potential availability impact (2). Oil from shale is the most promising alternate source of jet fuel; shale oil is closer to commercialization than coal liquefaction and is more amenable to conversion into jet fuel than are coal liquids (3,4,6). A review of the studies leading to these conclusions is given in "Shale Oil - The Answer to the Jet Fuel Availability Problem," which describes the Air Force Aviation Turbine Fuel Technology Program (1).

A secure domestic source of jet fuel is important to the Department of Defense. JP-4 alone constituted 47% of the total DOD fuel procurements for 1978. JP-5, a high flash point jet fuel designed to reduce fire hazards on aircraft carriers, constituted another 12%. Other jet fuels include commercial jet fuel and JP-8, a kerosene based jet fuel similar to commercial Jet A-1. Consumption of JP-8 is increasing, as NATO aircraft operations in Europe are being converted to JP-8. Note that distillate fuels constitute the vast majority of the DOD procurement slate and that gasoline usage is only 5% of the total. Military jet fuel constitutes 60% of DOD usage, but less than 2% of the nation's petroleum requirement.

Because of the need to obtain a secure domestic source for military fuel and because it is evident that the DOD must be in the position to utilize fuel produced from domestic non-petroleum sources, the Air Force has embarked on an Aviation Turbine Fuel Technology Program. As part of this effort "A Program Leading to Specifications for Aviation Turbine Fuel Produced from Whole Crude Shale Oil" was initiated. This program is investigating jet fuel qualities, costs, and processes for producing high yields of aviation turbine fuel from crude shale oil. The program is being carried out in four phases over 30 months:

Phase I - Preliminary Process Analysis
Phase II - Bench Scale Process Evaluation
Phase III - Pilot Plant Evaluation/Sample Production
Phase IV - Overall Economic Evaluation

Contracts were awarded by the Air Force to three companies in January 1979. Ashland Research and Development - Ashland Petroleum Co., Suntech Inc. - Sun Company, and UOP Process Division - UOP, Inc., have completed the preliminary process designs and bench scale evaluations of each process.

Each contractor is required to provide approximately 1000 gallons of shale derived jet fuel samples for testing and evaluation to ascertain the effects of fuel characteristics upon aircraft components. Each contractor is also required to evaluate the economics of his processing scheme. The processing schemes used must meet the following goals: 1) be novel yet show demonstrated potential for scale-up, 2) maximize the yield of jet fuel while limiting the yield of residual fuel to no more than 10% of the products, 3) have an overall thermal efficiency of at least 70%, and 4) have potentially lower costs for converting whole crude shale oil into a slate of military specification products than "State-of-the-art" processing as exemplified by the Chevron Research Company work (5).

In 1980 the Air Force had the need for additional large quantities of shale derived aviation turbine fuel for test purposes. This fuel was provided through a program with Suntech Group and Hydrocarbon Research Inc. Over 10,000 gallons of specification quality JP-4 was produced from Geokinetics crude shale oil for the Air Force Aviation Turbine Fuel Technology Program. This fuel was consumed in combustor rig tests conducted by General Electric and Pratt & Whitney. The test results were compared with those obtained using other variable quality test fuels. These programs have been completed.

There is one other Air Force shale oil related program presently in progress. This program, with Amoco Research and Development Department, Amoco Oil Company, is investigating catalyst properties and developing hydrotreating catalysts that have a higher nitrogen tolerance than existing catalyst. Catalyst compositions and substrates were varied in order to determine the best possible combinations. This program is in the final stages and many of the results are available.

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II

# USAF SHALE OIL TO FUELS PROGRAM - PHASE II

By

A. O. Braun, V. A. Gembicki

L. Hilfman, and T. G. Board

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## INTRODUCTION

The objective of this program is to demonstrate innovative technology to reduce the cost of converting shale oil to high yields of aviation turbine fuels. To carry out this program, UOP selected a processing scheme involving hydrocracking as the primary conversion unit. Hydrocracking was the clear choice because of its inherent flexibility and its high aviation turbine fuel yield potential. The program has been in progress since early 1979. In September, 1979, UOP issued the Phase I Interim Report which included estimated product yields and qualities, and processing costs for converting 50,000 BPD of whole shale oil to a range of quality fuel products, principally jet fuel.

In Phase II of the program, the primary objective is the demonstration of process performance estimated in Phase I. Although some work on Phase II is still in progress at UOP, the process performance demonstrations have been completed: product qualities and yields have been determined and processing costs have been established.

### UOP Approach

As shown in Figure 1, the UOP approach to the problem of shale oil conversion to high quality fuels involves three distinct processing steps. Shale oil has unique characteristics relative to conventional petroleum. High metals content, specifically arsenic and iron, and high unsaturates content make conventional front-end refining processes unusable without pretreatment. Thus, the first step in the UOP scheme involves the use of low pressure hydrotreating to provide for metals removal and a degree of diolefin and olefin saturation necessary to render the resulting effluent suitable for subsequent processing. Another characteristic of shale oil is its high nitrogen content relative to conventional petroleum. Eliminating this contaminant requires the use of high pressure hydrotreating on the effluent from the low pressure hydrotreating unit. Once the metals and nitrogen contents have been reduced to a low level and the unsaturates hydrogenated, shale oil is ready for the primary conversion step -- hydrocracking to jet and other fuels. The hydrocracking process that UOP has selected is a parallel flow hydrocracker developed for conventional petroleum use. As will be shown later, one of the objectives of Phase II was to determine whether the advantages of this flow scheme evident in petroleum processing are achievable in shale oil processing.

The overall block flow diagram of the UOP approach is shown in Figure 2. In a shale oil refinery whole shale oil feed is first charged to a feed preparation section for deashing and dewatering. Following this step low pressure hydrotreatment is used to reduce metals content and to stabilize the shale oil. This pretreated material is then charged to a high pressure circuit. In this section high pressure hydrotreatment is used to reduce the nitrogen content to acceptable levels. Hydrocracking is then used to perform the primary conversion. Effluent from the hydrocracker is charged to a fractionator where the desired product cuts are made. A fractionator bottoms stream is recycled to the hydrocracker for the degree of conversion required. In the block diagram shown, diesel fuel and

gasoline are produced in addition to the jet fuel product. The naphtha cut is hydrotreated and reformed in a UOP Platforming® unit. The reformate is mixed with light hydrocracked naphtha and butanes to produce the finished gasoline. Facilities for sulfur recovery and hydrogen production are also required.

In Figure 3 a more detailed block flow diagram is presented, this one specifically designed for production of JP-8 jet fuel. Hydrogen production is supplied from two sections, a steam reforming plant operating on light naphtha and a partial oxidation unit operating on low pressure hydrotreated shale oil. In addition to the hydrocarbon fuels produced, sulfur and ammonia are also products of this operation.

In Figure 4 a block flow diagram for the production of JP-4 jet fuel is shown. The only significant difference between this scheme and that for JP-8 production is the elimination of the naphtha hydrotreating and Platforming units. When maximum JP-4 is desired, the heavy naphtha, otherwise available for gasoline production, is fully utilized in the production of JP-4. When less than maximum conversion to JP-4 is desired, hydrotreating and reforming can be added to produce a gasoline product.

## Shale Oil Inspections

Two Green River formation shale oils were evaluated during Phases I and II. The primary feedstock was Occidental shale oil derived from a modified in situ retort. Paraho shale oil derived from a direct heated above ground retort was also tested. Inspections of these two feedstocks are shown on Figure 5. Both have nominal boiling ranges of 400 - 1000°F, although the Occidental is somewhat lighter. The sulfur contents of both are similar and not out of the range of conventional petroleum. However, nitrogen and oxygen contents and bromine numbers are higher than that found in conventional petroleum. Once again, the Occidental material exhibited somewhat less of these contaminants than did the Paraho. Shale oil is alone among potential synfuel sources in its typically high arsenic content. The particular shale oil samples tested at UOP showed 27.5 and 19 ppm arsenic for Occidental and Paraho, respectively. With the exception of iron, no other metal is present in significant concentrations. Although the iron content is high for both materials, it is within the range seen in conventional petroleum.

## Shale Oil Fouling Studies

Since other investigators have found evidence of plugging and fouling propensities in their work with shale oil, raw and deashed shale oils were investigated for their fouling characteristics as part of Phase II. UOP used a Monirex® Fouling Monitor to study fouling characteristics of shale oil relative to a petroleum reference material. As shown on Figure 6, four shale oil feedstocks were tested over a temperature range of 175 - 400°C.

In Figure 7 a schematic of the Monirex fouling monitor is shown. From a charge vessel sparged with air to maintain a specified oxygen content,

the sample is pumped through heat exchangers and heaters to a test cell where fouling of a wire is measured as a function of temperature. In Figure 8, the effect of temperature on the fouling rate of Arabian light petroleum crude and kerosene derived therefrom is indicated. In Figure 9, this effect is shown for the shale oils tested and in Figure 10 the shale oil fouling rates are compared to that of the reference materials. Although the Paraho shale oil exhibited unusual behavior in the low temperature region, its fouling rate in general was lower than that of the reference material. The Occidental raw shale oil fouled at a higher rate than the deashed Occidental and both fouled at a higher rate than either of the Paraho shale oils. Compared to Arabian Light crude oil then, there is an indication of higher fouling anticipated from the Occidental shale oil and lower fouling anticipated from the Paraho shale oil.

## Phase II Pilot Plant Operations

The pilot plant operations performed during Phase II involved three specific processing steps; low pressure hydrotreating, high pressure hydrotreating and hydrocracking. The scope of the work consisted of catalyst and process variable studies.

### Low Pressure Hydrotreating

The objectives of the low pressure hydrotreating pilot plant operation were to assess: 1) the degree of arsenic and iron removal, 2) the thermal stability of shale oil, 3) the degree of saturation obtained across the hydrotreating reactor, and 4) catalyst stability on a short term basis. These items were studied with the use of several different hydrotreating catalysts. Operating conditions to achieve a maximum of 1 ppm arsenic in the low pressure hydrotreated product were determined. These conditions are shown on Figure 11 compared to base conditions commercially employed for the hydrotreatment of coke oven light oil. A range of pressures from base pressure to 450 psi above base was tested. Liquid hourly space velocities (LHSV) from 1/6 to 1/2 of that required for the base case were evaluated. Hydrogen circulation rates from 2/3 to 1-1/3 times the base rate were evaluated. Reactor temperature was varied from 300°F below base temperature to 100°F above base temperature. Shown in Figure 12 is a schematic flow diagram of the low pressure hydrotreating pilot plant. Deashed shale oil was processed down flow over a fixed catalyst bed. In the pilot plant, hydrogen re-circulation was not conducted. Hydrogen was processed once-through together with the charge stock. Figure 13 shows the results of the best operation obtained during the low pressure screening operation. At base pressure, 1/3 base LHSV, and 1-1/3 times equivalent hydrogen circulation rate, arsenic removal to approximately 1 ppm was achieved on Occidental shale oil at a temperature 50°F above base temperature. These conditions are considered within the acceptable range of a commercial operation.

Figure 14 shows a comparison of the Occidental and Paraho low pressure hydrotreating performance as a function of reactor temperature, indicated as catalyst average bed temperature. At all other conditions equal, that is, base pressure, 1/3 base space velocity and 1-1/3 times base equivalent

hydrogen circulation rate, the 1 ppm arsenic target was achieved at a lower temperature with Paraho charge than with Occidental. However, the bromine number of the hydrotreated product, an indication of degree of unsaturation, was significantly higher throughout the temperature range for the Paraho shale oil operation.

From the Phase II pilot plant operations of low pressure hydrotreating, the conclusions shown below and in Figure 15 were deduced.

1. 1 ppm maximum iron and arsenic content was achieved for both Occidental and Paraho shale oils.

2. No evidence of thermal instability (neither preheater nor reactor fouling) during the variable studies was seen on either shale oil.

3. Two UOP commercial catalysts showed essentially equivalent performance and are proposed for processing the shale oils.

4. Process conditions were determined that were used in a larger scale pilot plant to produce sample for subsequent high pressure hydrotreating testing.

High Pressure Hydrotreating

The objectives of the high pressure hydrotreating pilot plant operations were to: 1) determine process conditions required to achieve a maximum of 1000 ppm nitrogen in the product, and 2) select the best catalyst for the operation. Process conditions were evaluated compared to conditions required for high pressure hydrotreating of a petroleum gas oil. As shown on Figure No. 16, pressure of 1700 psi above base pressure was used. A range of liquid hourly space velocities of 1/6 to 1/2 that required for gas oil hydrotreatment was evaluated. A hydrogen circulation rate 5 times that required for petroleum processing was used, and temperatures from 20°F below to 50°F above base were investigated. A schematic flow diagram of the high pressure hydrotreating pilot plant is shown in Figure 17. This plant allows hydrogen recycle and includes water washing of the recycle separator gas.

On Figure 18 are shown the results of high pressure hydrotreating of the low pressure hydrotreated Occidental shale oil. Note that across the low pressure hydrotreater the nitrogen content was reduced from 1.51 wt-% to 1.1 wt-%. An acceptable high pressure hydrotreating operation required approximately 90% de-nitrogenation to less than 1000 wt ppm. The results of 4 runs, performed at the same conditions except for temperature and utilizing 3 different catalysts, are shown. Although two catalysts were found to be effective in reducing the nitrogen content to an acceptable level, one catalyst, UOP DCA, had a significant activity advantage.

On Figure 19, product API gravities are plotted as a function of temperature for these same catalysts. Once again UOP DCA catalyst is shown to be the most effective in producing a quality change. Consistent with the high degree of nitrogen removal and gravity increase the UOP DCA

operation also had the highest hydrogen consumption. This can be seen in Figure 20. In order to achieve the 1000 ppm nitrogen target (at approximately 15°F below base reactor temperature), approximately 825 standard cubic feet per barrel (SCFB) of hydrogen is required. This compares to approximately 650 SCFB required in the low pressure hydrotreating operation to produce a product with a $\leq 1$ ppm arsenic content.

Results of the high pressure hydrotreatment of low pressure hydrotreated Paraho shale oil are shown on Figure 21 for two catalysts. Once again the UOP DCA catalyst is the best performer. On Figure 22, product API gravities for the Paraho shale oil operations are shown. Very little difference between the two catalyst operations is apparent. On Figure 23 the results of testing with UOP DCA catalyst on both Paraho and Occidental shale oils are compared. Whereas in low pressure hydrotreating the Paraho shale oil required somewhat lower temperatures to achieve the target, high pressure hydrotreating of Paraho shale oil required substantially higher temperatures (in the range of 40°F) to achieve the product quality objective. Certainly, a primary reason for this is the higher nitrogen content of the Paraho charge to the high pressure hydrotreater (19,430 ppm for Paraho vs. 11,000 ppm for Occidental).

Based on the results of high pressure hydrotreating operations it was concluded that: 1) both Paraho and Occidental shale oils can be hydrotreated to target nitrogen levels, and 2) among the catalysts tested UOP DCA catalyst had the highest activity for this operation.

Hydrocracking

The objectives of the Phase II hydrocracking pilot plant operation were to establish the advantages of a novel process flow arrangement and to demonstrate required hydrocracking process conditions for the production of aviation jet fuel. In addition, small samples of selected fuels representative of the products from the proposed flow arrangement were to be produced for testing. The shale oil hydrocracking process conditions relative to base conditions for hydrocracking of petroleum vacuum gas oil are shown on Figure 25. An operating pressure of 150 psi below base was used. Other conditions included an LHSV three times that required for petroleum, a combined feed ratio the same as that required for petroleum, and hydrogen circulation 1.2 times the base petroleum operation requirement. These conditions produce an accelerated catalyst stability test which readily provides relative catalyst information. Commercial conditions are then determined indirectly, but based on the accelerated test data.

Reactor temperatures were adjusted to achieve 100% conversion to JP-8 in the operations reported herein. A schematic flow diagram of the single-stage hydrocracking pilot plant is shown on Figure 26. Fresh feed is combined with recycle liquid, recycle gas and make-up hydrogen and charged to the reactor. Gas is recycled from the high pressure separator and separator liquid effluent is charged to a series of fractionators which produce liquid product and a recycle liquid stream. In all of the flow schemes studied, no bottoms product was withdrawn as a net product (i.e. operations were conducted at 100% conversion).

Before describing the results obtained from the various hydrocracking flow schemes, the shale oil inspections will be reviewed. On Figure 27, properties of the Occidental shale oil at several points in the process flow scheme are shown. They represent the composites of larger scale production runs carried out in order to prepare sufficient amounts of feed for the subsequent processing steps. The high pressure hydrotreated shale oil with a nominal 1000 ppm nitrogen (the initial target level) is shown in the third column. The measured nitrogen content of a large sample of this material was 900 ppm. The sulfur content is less than 300 ppm, the bromine number is 1.1 and the oxygen content has been reduced to 651 ppm. A more severe high pressure hydrotreating operation with Occidental shale oil produced a substantially lower nitrogen level product. An analysis of this material is shown in the last column of Figure 27. Measured nitrogen content is 100 ppm, oxygen content is 144 ppm and the bromine number is less than 0.5. The availability of these different quality hydrocracker feeds would allow an evaluation of the preferred high pressure hydrotreater/hydrocracker severity combination. This evaluation, essentially one of economics, will be performed during the final stage of Phase II.

A similar inspection of Paraho shale oil feedstocks is shown on Figure 28. A low nitrogen, high pressure hydrotreated product was not obtained from Paraho shale oil primarily because of insufficient feedstock. The high pressure hydrotreated product produced from Paraho shale oil contained 700 ppm nitrogen.

Results of processing the Occidental high nitrogen content, high pressure hydrotreated product are shown in Figures 29 through 32. Three flow schemes were investigated. The reference flow scheme is conventional single-stage hydrocracking. As shown in Figure 29, start-of-run (SOR) temperature required for 100% conversion to JP-8 is 10°F below that required for petroleum based operations. Over a 300 hour operating period, the temperature requirement for 100% conversion increased 62°F. Figure 30 shows data indicating that a modified flow hydrocracking operation dramatically reduces the catalyst deactivation rate. With a SOR temperature essentially the same as that required for the conventional single-stage operation, the temperature requirement for 100% conversion with the modified flow increased only some 14°F over a 300 hour operating period. Figure 31 shows the results of operating with a third hydrocracking flow scheme, termed parallel-flow hydrocracking. Once again, initial activity is essentially the same as in conventional single-stage operation. The catalyst deactivation rate is essentially the same as seen in modified flow hydrocracking; however, other benefits result from the use of the parallel-flow hydrocracking flow, primarily from improved heat integration resulting in low cost operation. Data from all three flow schemes are compared on Figure 32.

The low nitrogen, high-pressure hydrotreated Occidental product was processed in a parallel-flow hydrocracking operation. Results are shown on Figure 33. Initial temperature requirement is almost 70°F below that required for hydrocracking the 900 ppm nitrogen feed, and the de-activation rate is only 4°F over a 300 hour operating period. These

effects of feed nitrogen on catalyst activity and stability are shown on Figure 34. At this writing hydrocracking of Paraho shale oil is still in progress.

Based on the hydrocracking pilot plant operations to date it is concluded that: 1)the advantages of modified flow and parallel flow hydrocracking have been demonstrated, 2) parallel flow hydrocracking is the selected flow scheme, 3) operating conditions to achieve maximum jet fuel production have been established, 4) yields, hydrogen consumption and product qualities have been determined, and 5) the sensitivity of hydrocracking catalyst stability to feed nitrogen content has been determined.

## Phase II Economic Evaluation

Incorporating the data generated during the pilot plant operations, material balances for a shale oil refinery processing Occidental shale oil were prepared and liquid fuel production costs were calculated. The results which follow are derived from a first pass analysis; they are preliminary.

### Overall Material Balances

Overall material balances were prepared for two cases: maximum JP-8 production and maximum JP-4 production. These maxima were established by selecting appropriate cut-points for product fractionator operation. In the JP-8 case, an end point less than MIL-spec maximum was required in order to meet the freeze point specification. In the JP-4 case, maximum (max) MIL-spec end point was possible without compromising any other specifications. The resulting overall material balances are presented in Figure Nos. 36 and 37 for max JP-8 and max JP-4 cases, respectively. These balances are based on 100 wt-% shale oil feed. Hydrogen is generated internally as are all process fuel and heat requirements. Only process water and electric power are required to be supplied externally.

Hydrogen requirements for both cases are similar, 4.18-% (2520 SCFB) for max JP-8 and 4.10 wt-% (2470 SCFB) for max JP-4. Jet fuel yields of 71.16 wt-% (81.05 vol-%) are shown in the JP-8 case; the JP-4 case shows jet fuel yields of 78.95 wt-% (92.67 vol-%). No other liquid fuel product is yielded from the refinery maximizing JP-4 production, whereas 6.59 wt-% (7.98 vol-%) gasoline is produced from the refinery designed to max JP-8 production. The total liquid fuel yields from the two refinery cases then, are 77.75 wt-% (89.03 vol-%) and 78.95 wt-% (92.67 vol-%) for max JP-8 and max JP-4, respectively.

### Capital and Operating Costs

The economic evaluation was performed using the basis shown on Figure No. 38 with one minor exception -- the capital cost basis used was third quarter, 1980. On Figure No. 39, estimated erected costs (EEC) for individual process units are shown. These costs for the two cases are similar with two exceptions: 1) a naphtha hydrotreater/Platforming unit combination is included only in the max JP-8 case, and 2) the hydrogen plant is

substantially more expensive for the JP-8 case. The latter difference is largely the result of assuming that fuel oil would be used to fuel this hydrogen plant -- this assumption is being reviewed. Substituting fuel gas for fuel oil should result in a significant capital savings. As shown on Figure No. 39, the EEC total for the max JP-8 refinery is $566 million and for the max JP-4 refinery is $504 million. In addition, an off-site allowance of $150 million has been included for each refinery.

The total costs of production are tabulated in Figure No. 40, assuming that all liquid fuels have equal value. Including feedstock cost, operating costs and capital charges, the total cost of liquid fuel production from the max JP-8 refinery is $41.01 per barrel of feed and from the max JP-4 refinery is $40.33 per barrel of feed. This difference is almost entirely due to the higher capital cost of the JP-8 refinery.

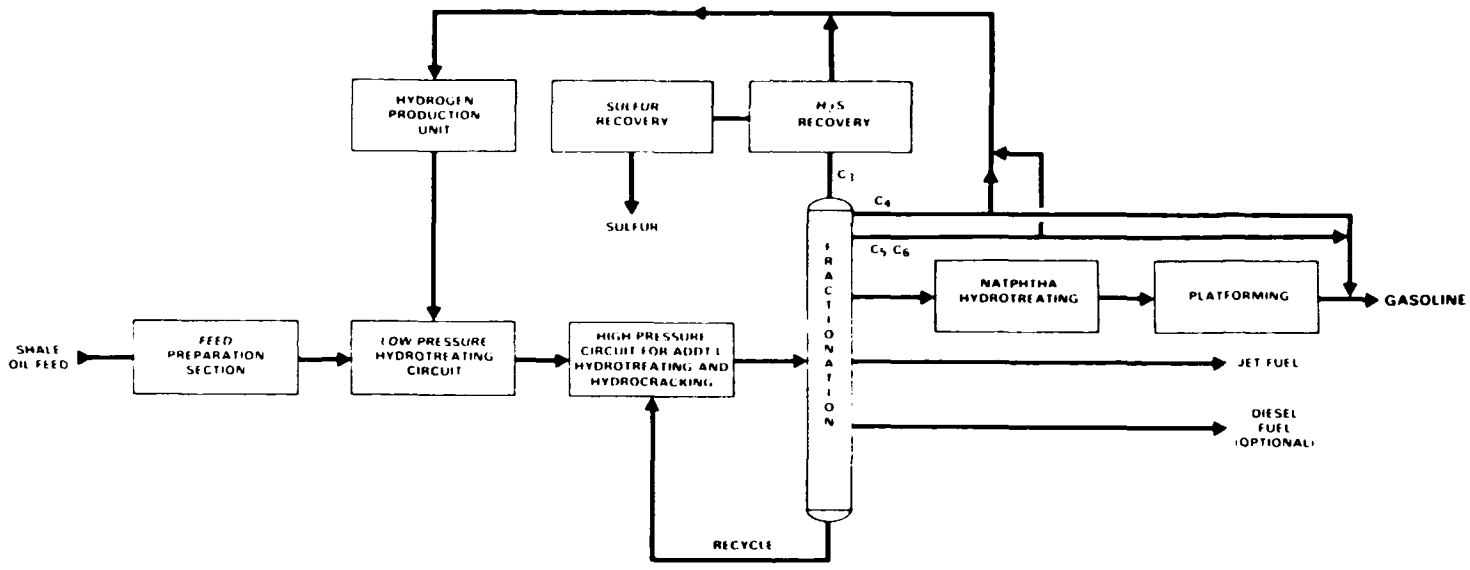
The production costs can be stated on a "per barrel of total liquid fuel" basis simply by dividing by the volume fraction yield of liquid fuel. This calculation results in total liquid fuel costs of $46.06 and $43.52 per barrel for the max JP-8 and max JP-4 cases, respectively.

USAF SHALE OIL TO FUELS PROGRAM

UOP APPROACH

| PROBLEM | PROCESS |
| --- | --- |
| METALS REMOVAL (AS, FE) | LOW PRESSURE HYDROTREATING |
| STABILIZATION-DIOLEFIN SATURATION | |
| NITROGEN REMOVAL | HIGH PRESSURE HYDROTREATING |
| CONVERSION TO JET AND OTHER FUELS | PARALLEL FLOW HYDROCRACKING |

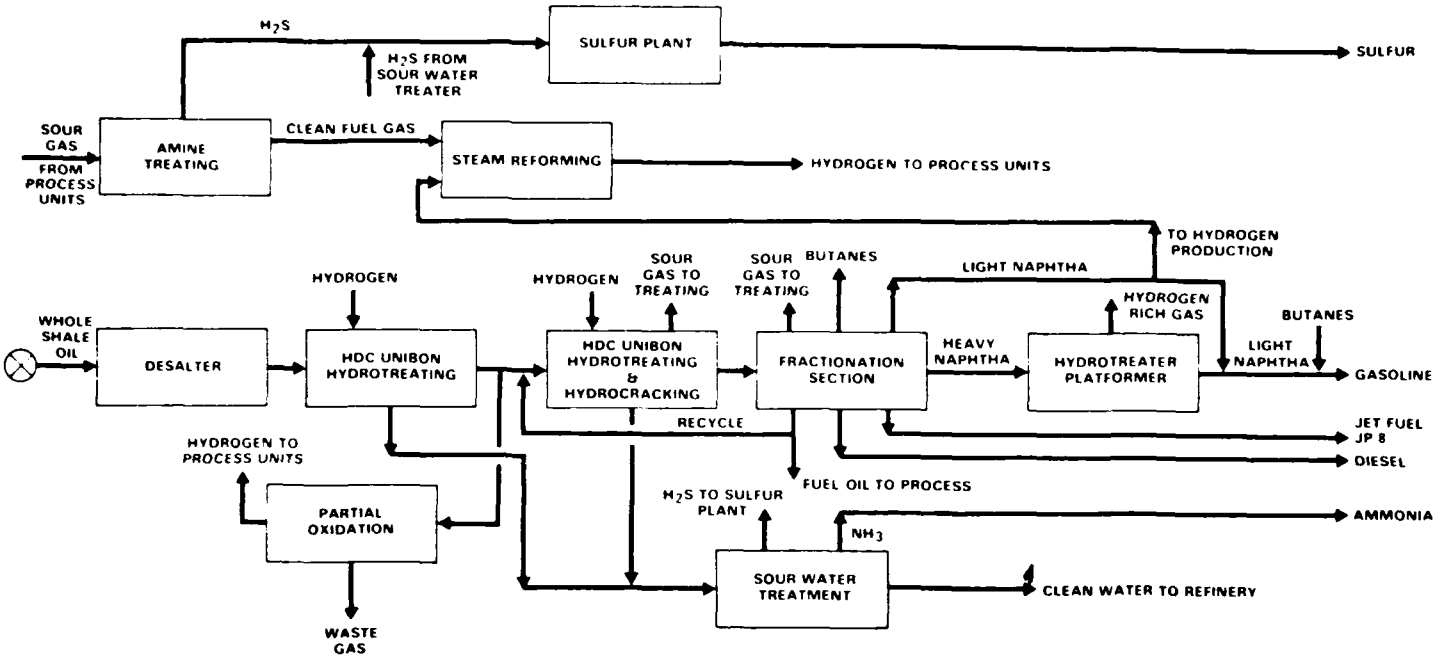
FIGURE #1




**UOP SHALE OIL TO FUELS**

**OVERALL BLOCK FLOW DIAGRAM**

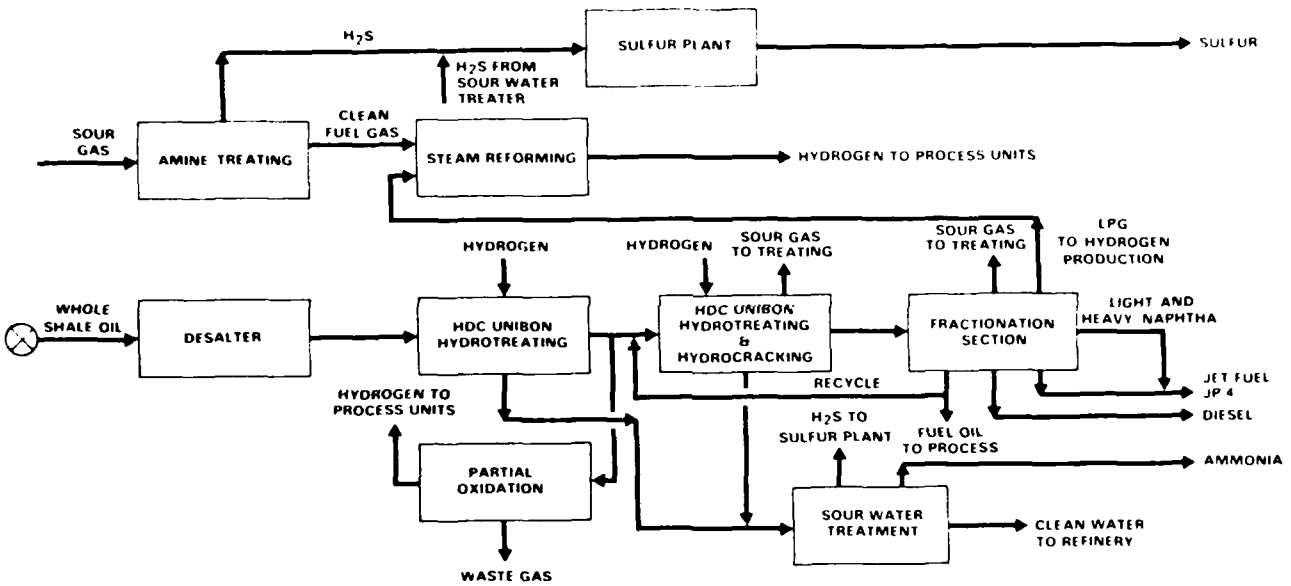
**FIGURE 2**




**UOP SHALE OIL TO FUELS**

**JP-8 PRODUCTION BLOCK FLOW DIAGRAM**

**FIGURE 3**




**UOP SHALE OIL TO FUELS**

**JP-4 PRODUCTION BLOCK FLOW DIAGRAM**

**FIGURE 4**

FIGURE 5

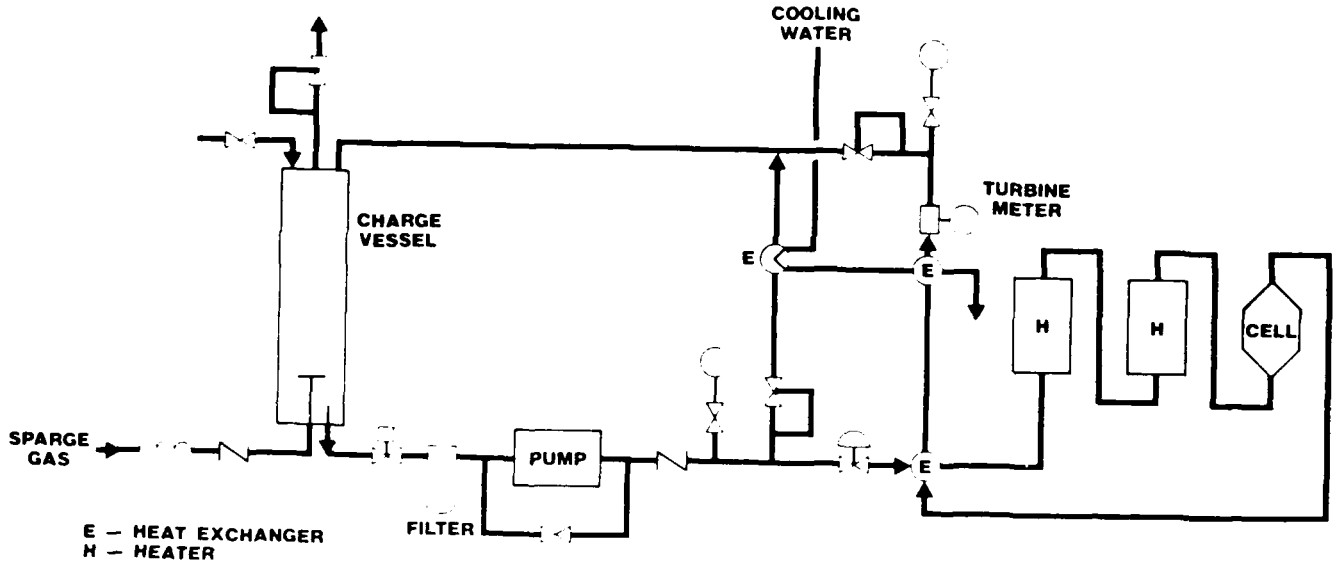
# SHALE OIL INSPECTIONS

| NAME | OCCIDENTAL | PARAHO |
|---|---|---|
| GRAVITY, °API | 22.9 | 19.8 |
| DISTILLATION, IBP, °F | 376 | 408 |
| 50% | 712 | 789 |
| EP | 953 | 1005 |
| % OVER | 87 | 90 |
| NITROGEN, WT-% | 1.51 | 2.19 |
| SULFUR, WT-% | 0.64 | 0.70 |
| OXYGEN, WT-% | 0.65 | 1.58 |
| HYDROGEN, WT-% | 12.17 | 11.70 |
| BROMINE NO. | 23.60 | 34.70 |
| ASH, WT-% | 0.014 | 0.007 |
| CONRADSON CARBON, WT-% | 1.36 | 2.71 |
| HEPTANE INSOLUBLES, WT-% | 0.34 | 0.47 |
| ARSENIC, ppm | 27.5 | 19 |
| IRON, ppm | 42.0 | 38 |

## SHALE OIL FOULING STUDIES

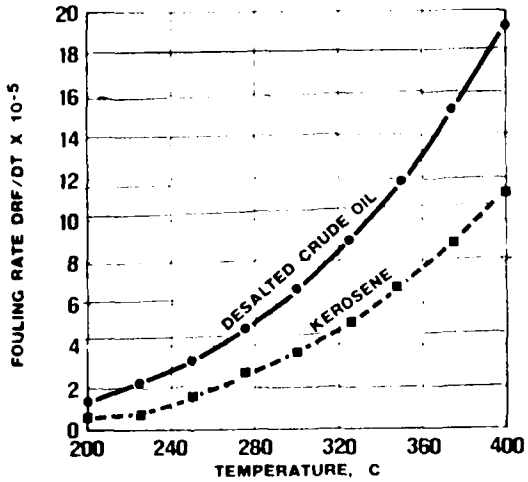
| | |
|---|---|
| INSTRUMENT: | MONIREX FOULING MONITOR |
| REFERENCE FEEDSTOCK: | ARABIAN LIGHT (BERRI) CRUDE |
| TEMPERATURE RANGE: | 175 - 400°C |
| FEEDSTOCKS TESTED: | 1) OCCIDENTAL RAW SHALE OIL<br>2) OCCIDENTAL DEASHED SHALE OIL<br>3) PARAHO DEASHED SHALE OIL<br>4) PARAHO DEASHED SHALE OIL W/ANTIFOULANT |

FIGURE #6



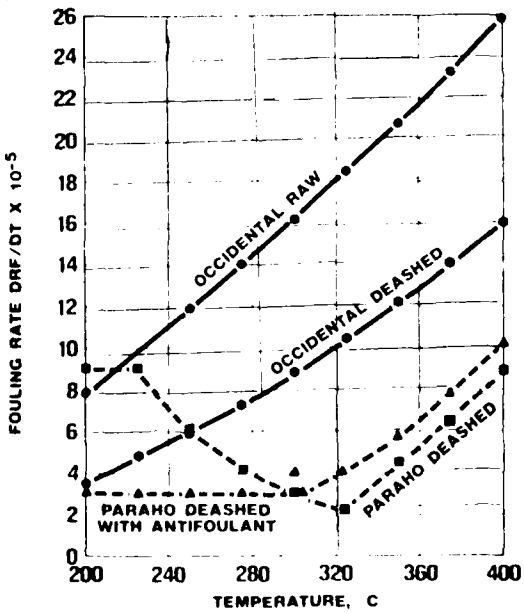

**UOP MONIREX® FOULING MONITOR**

FIGURE 7



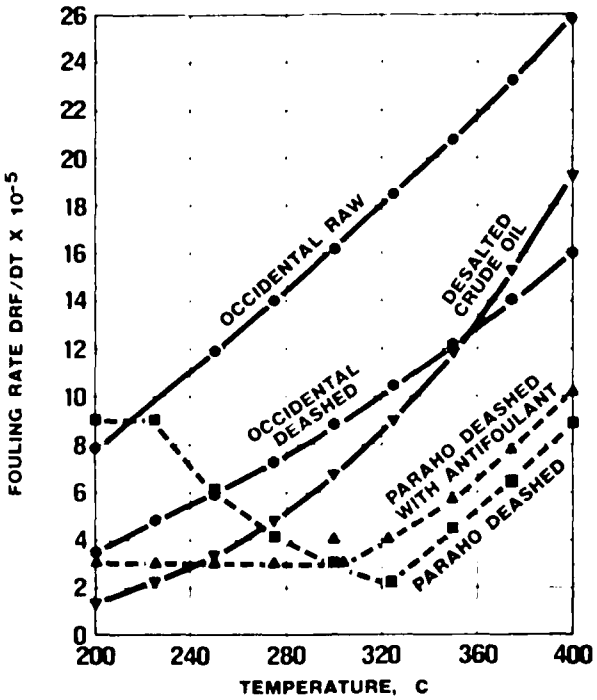

**EFFECT OF TEMPERATURE ON FOULING RATE OF ARABIAN LIGHT DESALTED CRUDE OIL AND KEROSENE**

FIGURE 8




**EFFECT OF TEMPERATURE ON FOULING RATE OF OCCIDENTAL RAW AND DEASHED AND PARAHO DEASHED SHALE OILS**

FIGURE 9




**EFFECT OF TEMPERATURE ON FOULING RATE OF OCCIDENTAL RAW AND DEASHED AND PARAHO DEASHED SHALE OILS**

FIGURE 10

# LOW PRESSURE HYDROTREATING

## PROCESS CONDITIONS

SEPARATOR PRESSURE, psi $(P\text{-}P_B)$: 0-450

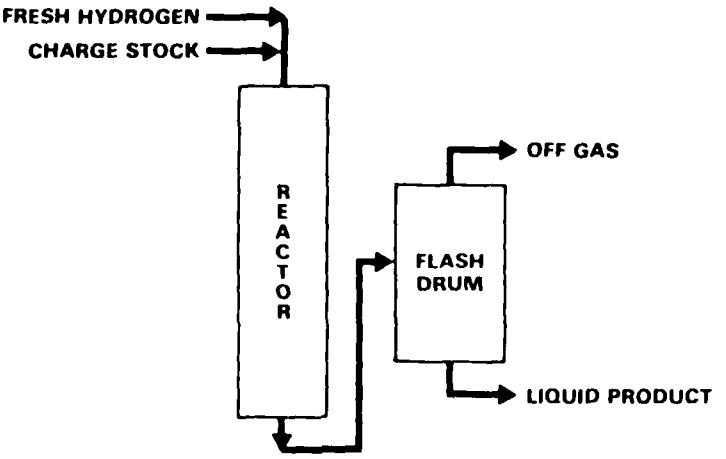
LIQUID HOURLY SPACE VELOCITY, $(L/L_B)$: 0.17-0.50

HYDROGEN CIRCULATION, $(H/H_B)$: 0.67-1.33

REACTOR TEMPERATURE, °F $(T\text{-}T_B)$: −300- + 100

JOP 525 78

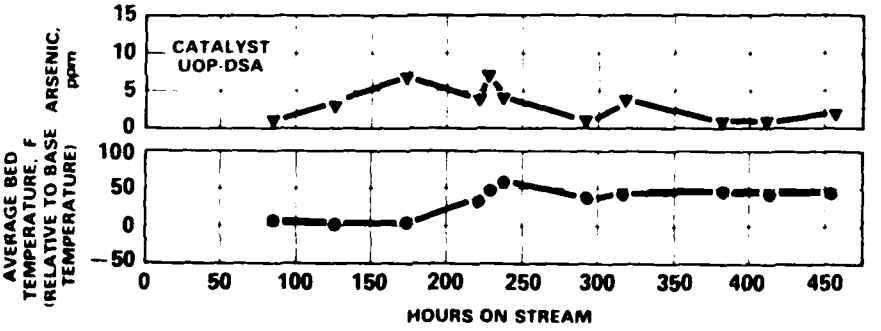
FIGURE 11




**PILOT PLANT SCHEMATIC FLOW DIAGRAM**

**LOW PRESSURE HYDROTREATING**

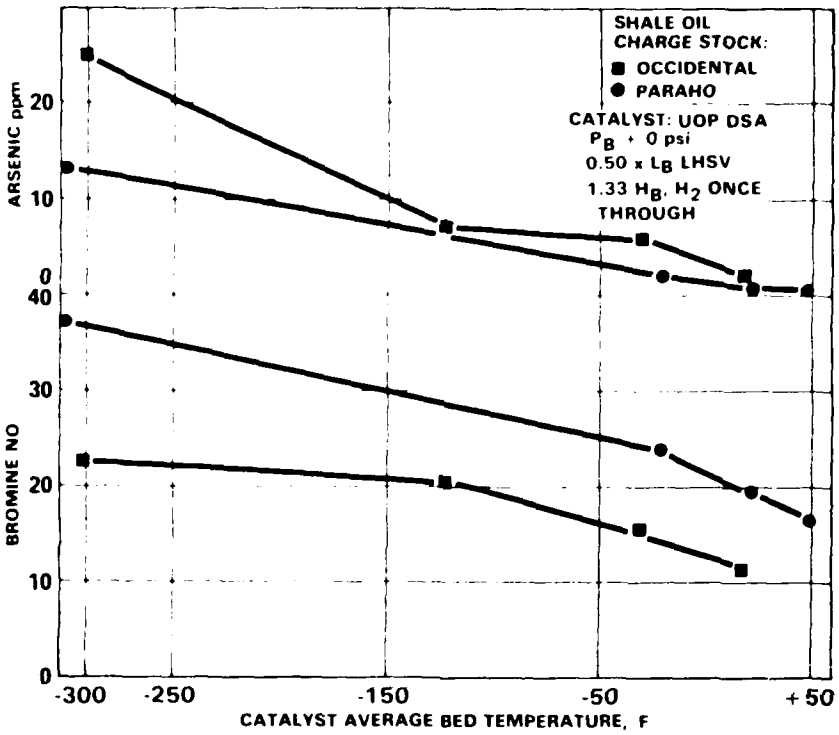
FIGURE 12




**LOW PRESSURE HYDROTREATMENT OF DEASHED OCCIDENTAL SHALE OIL**

$P_B + 0$, psig, $0.33 \times L_B$, LHSV
$1.33\ H_B$, $H_2$ ONCE THRU

FIGURE 13




**LOW PRESSURE HYDROTREATING**

FIGURE 14

# CONCLUSIONS

1) PROCESS CONDITIONS FOR THE REMOVAL OF IRON AND ARSENIC TO 1 ppm OR LESS WERE OBTAINED FOR BOTH OCCIDENTAL AND PARAHO SHALE OIL.

2) BOTH THE OCCIDENTAL AND PARAHO SHALE OILS SHOWED NO EVIDENCE OF THERMAL INSTABILITY DURING THE VARIABLE STUDIES.

3) UOP-DSA AND UOP-DRA CATALYSTS ARE PROPOSED FOR PROCESSING THE OCCIDENTAL AND PARAHO SHALE OILS.

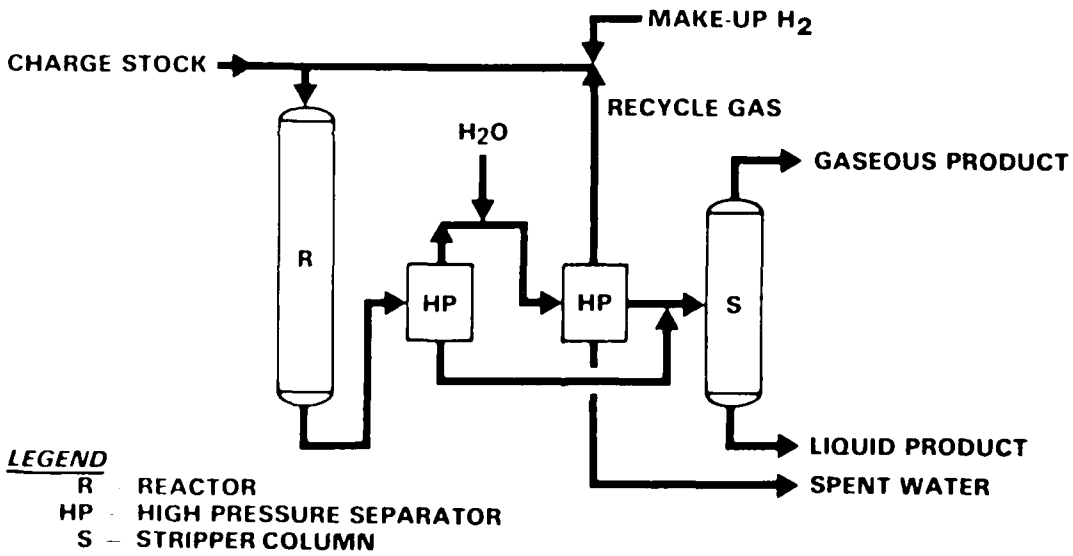
4) PROCESS CONDITIONS WERE ESTABLISHED FOR THE PRODUCTION OF LARGE SCALE SAMPLE.

FIGURE 15

# HIGH PRESSURE HYDROTREATING
## PROCESS CONDITIONS

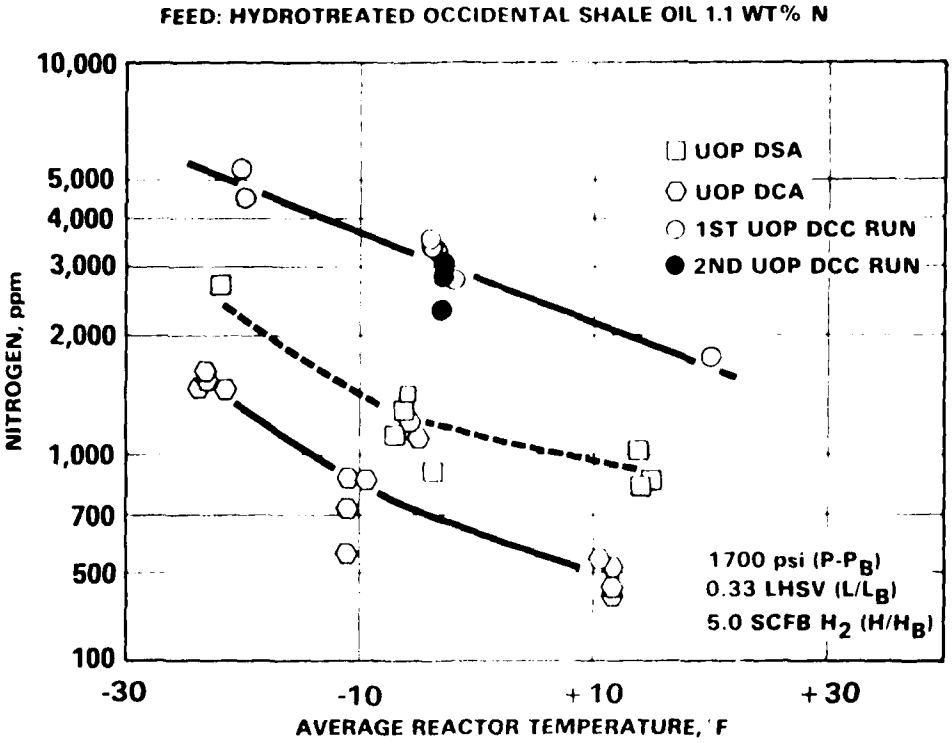
| | |
|---|---|
| PRESSURE, psi ($P$-$P_B$) | 1700 |
| LIQUID HOURLY SPACE VELOCITY ($L/L_B$): | 0.17-0.50 |
| HYDROGEN CIRCULATION, ($H/H_B$): | 5.0 |
| REACTOR TEMPERATURE, F ($T$-$T_B$): | −20 TO +50 |

FIGURE 16




# HIGH PRESSURE HYDROTREATING PILOT PLANT
## SCHEMATIC FLOW DIAGRAM

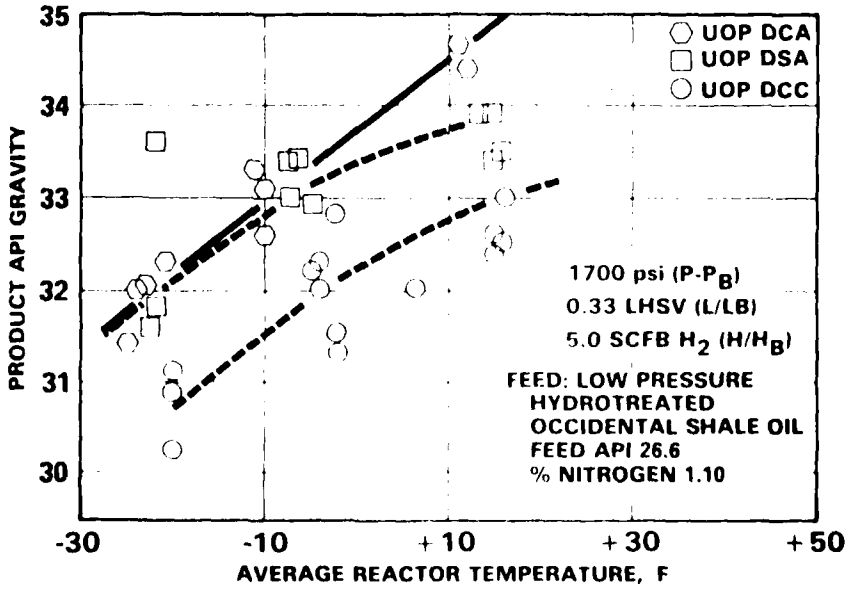
FIGURE 17




**PRODUCT NITROGEN vs. AVERAGE REACTOR TEMPERATURE**

FIGURE 18

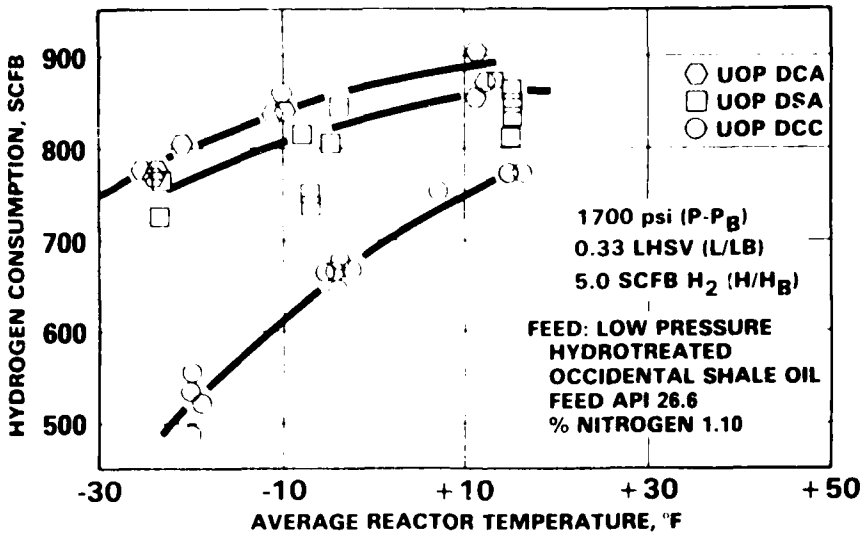
UOP 525 39




**PRODUCT API vs. AVERAGE REACTOR TEMPERATURE**

FIGURE 19

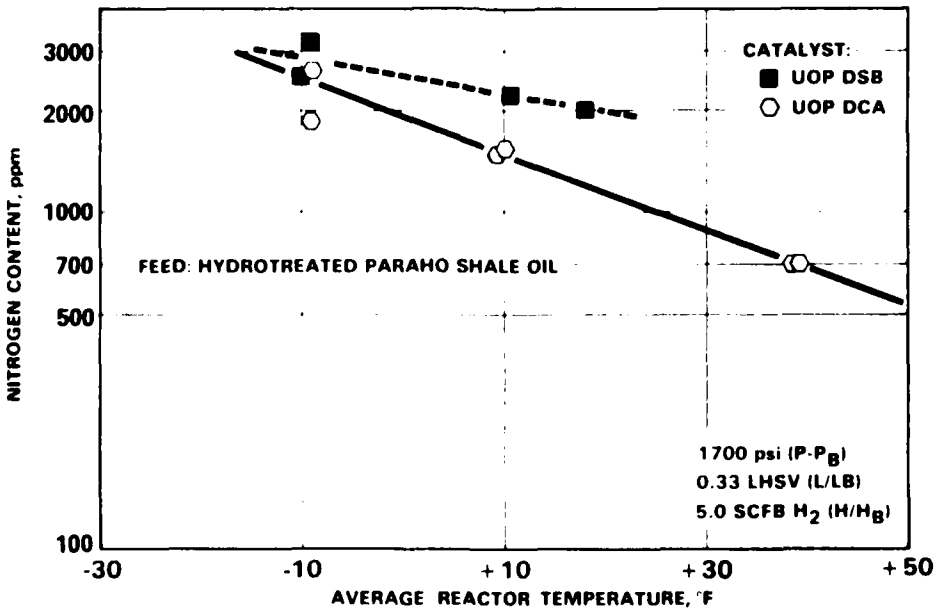
UOP 525 42B




**HYDROGEN CONSUMPTION vs. AVERAGE REACTOR TEMPERATURE**

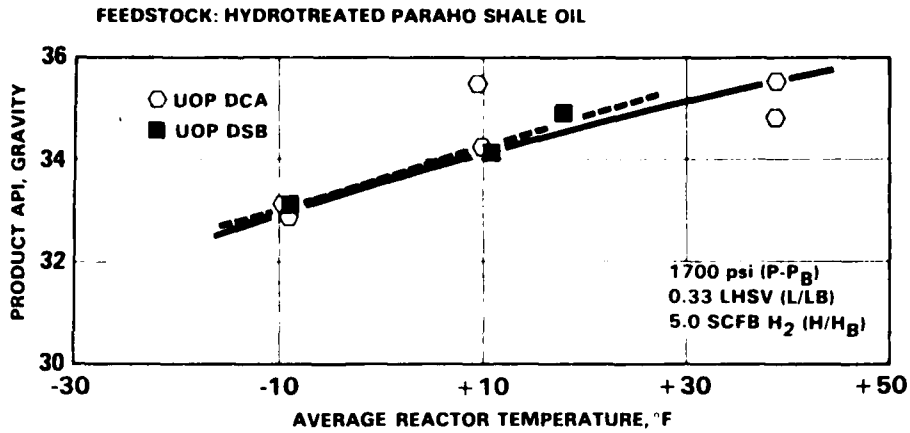
FIGURE 20

UOP 525-42A




**PRODUCT NITROGEN vs. AVERAGE REACTOR TEMPERATURE**

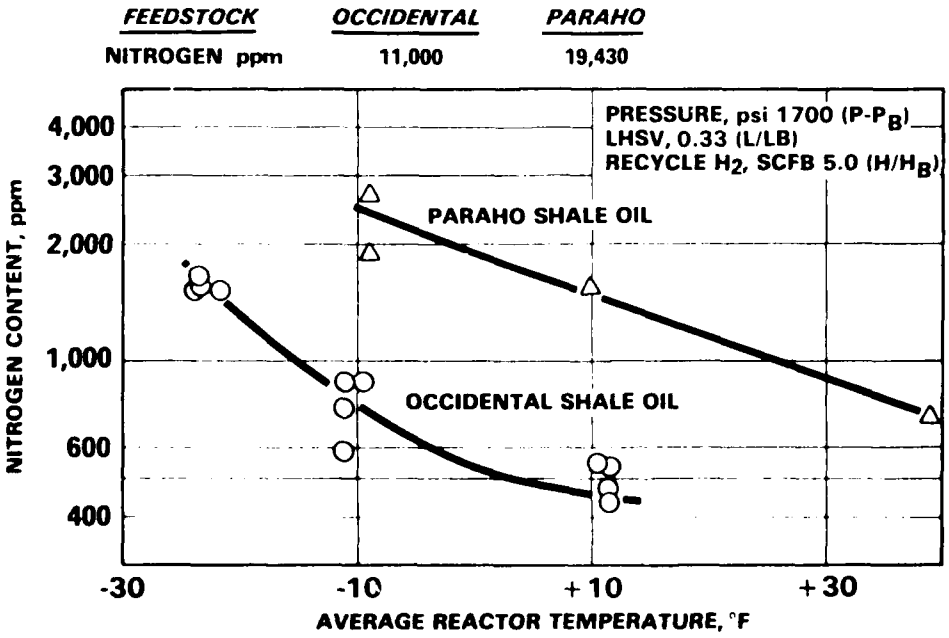
FIGURE 21




**PRODUCT GRAVITY vs. AVERAGE REACTOR TEMPERATURE**

**FIGURE 22**

UOP 525 49




**PRODUCT NITROGEN VERSUS AVERAGE REACTOR TEMPERATURE**

**CATALYST: UOP DCA**

**FIGURE 23**

UOP 525 40

# CONCLUSIONS

1. ESTABLISHED PROCESS CONDITIONS REQUIRED TO OBTAIN TARGET PRODUCT NITROGEN LEVELS

2. BASED ON CATALYST EVALUATION TEST, SELECTED UOP DCA CATALYST FOR PRODUCTION RUN

UOP 525-81

FIGURE 24

# HYDROCRACKING
## PROCESS CONDITIONS

SEPARATOR PRESSURE, psi ($P-P_B$): —150

LIQUID HOURLY SPACE VELOCITY, ($L/L_B$): 3.0

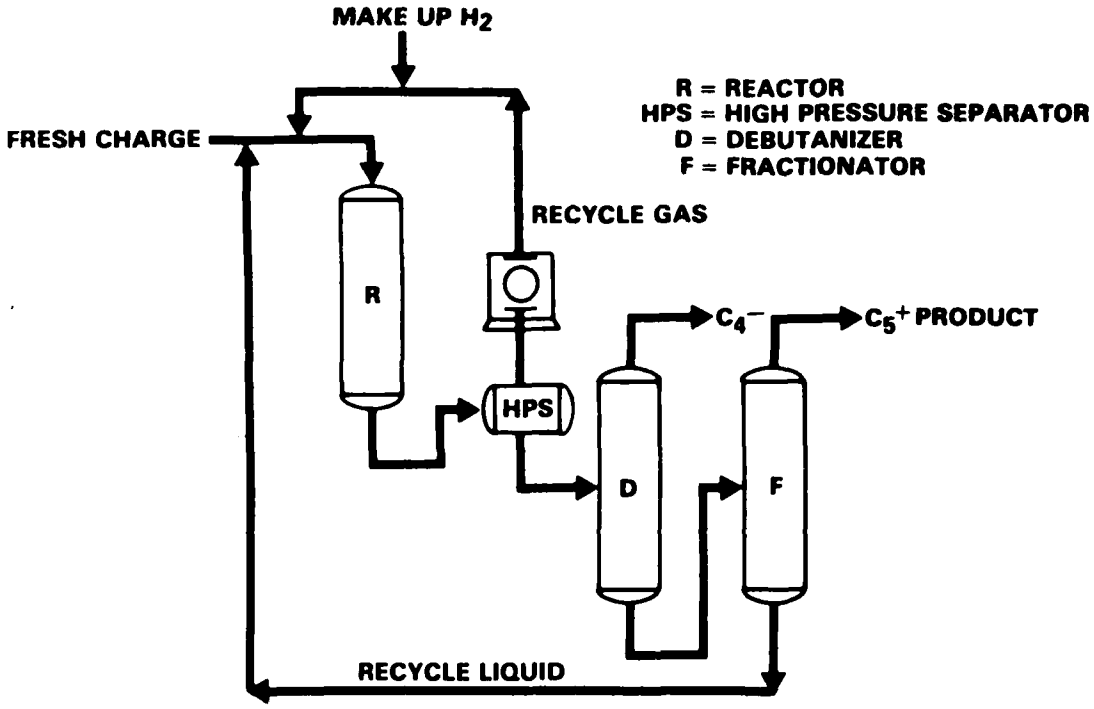
COMBINED FEED RATIO, ($C/C_B$): 1.0

HYDROGEN CIRCULATION, ($H/H_B$): 1.20

REACTOR TEMPERATURE, °F ($T-T_B$): ADJUSTED TO ACHIEVE 100% CONVERSION TO JP-8

UOP 525-23B

FIGURE 25




# PILOT PLANT SCHEMATIC – SINGLE STAGE HYDROCRACKER

FIGURE 26

UOP 525-21

## OCCIDENTAL SHALE OIL INSPECTION

| CHARGE STOCK | SHALE OIL, AS RECEIVED | L.P. HYDROTREATED SHALE OIL | H.P. HYDROTREATED SHALE OIL | H.P. HYDROTREATED SHALE OIL |
|---|---|---|---|---|
| API GRAVITY AT 60°F | 22.9 | 26.8 | 31.8 | 34.3 |
| DISTILLATION | | | | |
| IBP, °F | 376 | 286 | 245 | 255 |
| 50% | 712 | 641 | 646 | 619 |
| EP, °F | 953 | 1034 | ~1079 | 1052 |
| % OVER | 87 | 99 | 99 | |
| POUR POINT, °F | +75 | +55 | +80 | +75 |
| BROMINE NUMBER | 23.6 | 10.5 | 1.1 | 0.481 |
| SULFUR, WT-% (LECO) | 0.64 | 0.03 | <0.03 | <0.03 |
| NITROGEN, WT-% (KJELDAHL) | 1.51 | 1.10 | 0.09 | 0.01 |
| ARSENIC, ppm | 27.5 | <1 | 1 | <1 |
| CONRADSON CARBON, WT-% | 1.36 | 0.51 | <0.01 | <0.01 |
| TOTAL OXYGEN, ppm | 6,500 | 2800 | 651 | 144.2 |

UOP 525-61

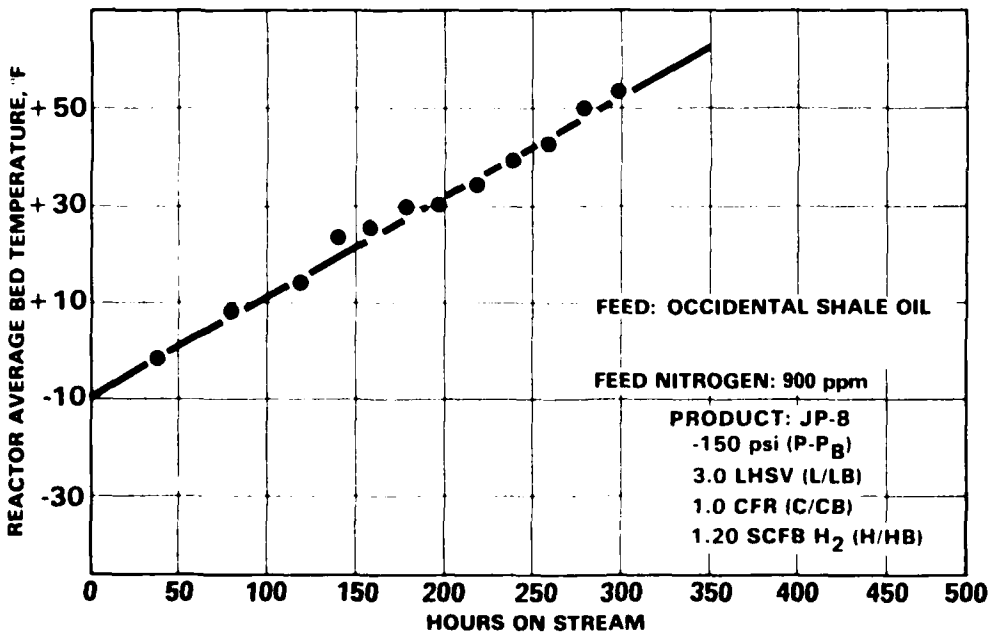
FIGURE 27

# PARAHO SHALE OIL INSPECTION

| CHARGE STOCK | SHALE OIL, AS RECEIVED | L.P. HYDROTREATED SHALE OIL | H.P. HYDROTREATED SHALE OIL |
|---|---|---|---|
| API GRAVITY AT 60°F | 19.8 | 23.0 | 33.3 |
| DISTILLATION | | | |
| IBP, °F | 408 | 311 | 250 |
| 50% | 789 | 723 | 654 |
| EP, °F | 1005 | 1090 | ~ 1085 |
| POUR POINT, °F | +85 | +85 | +85 |
| BROMINE NUMBER | 34.7 | 19.4 | 1.0 |
| SULFUR, WT-% (LECO) | 0.70 | 0.05 | <0.03 |
| NITROGEN, WT-% (KJELDAHL) | 2.19 | 1.943 | 0.07 |
| ARSENIC, ppm | 19 | <1 | <1 |
| CONRADSON CARBON, WT-% | 2.71 | 1.08 | <0.01 |
| TOTAL OXYGEN, ppm | 15,800 | 2800 | |

UOP 525 68

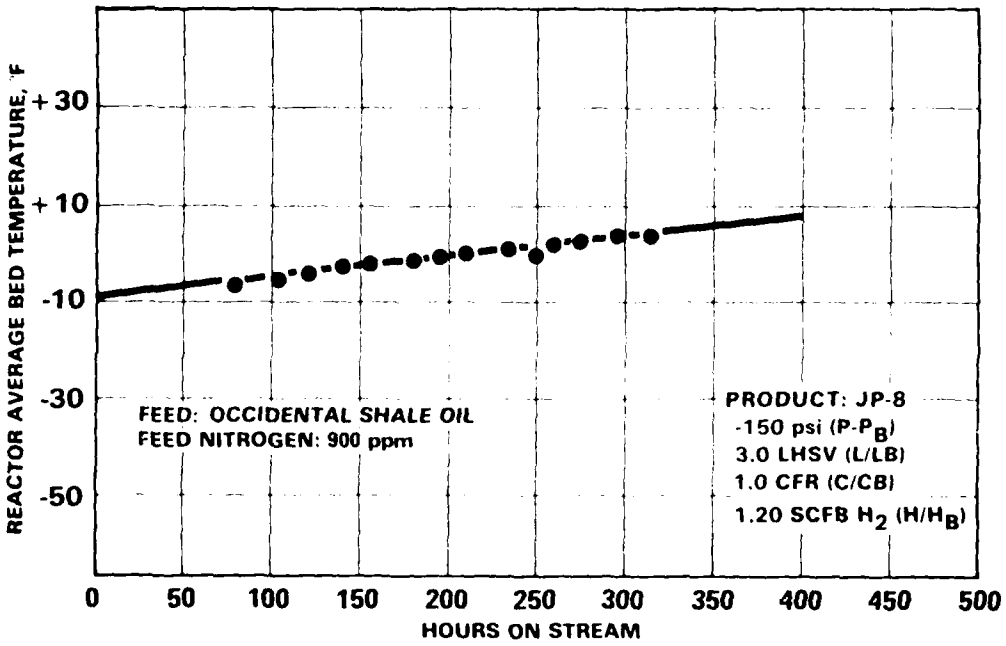
FIGURE 28




# SINGLE STAGE HYDROCRACKING

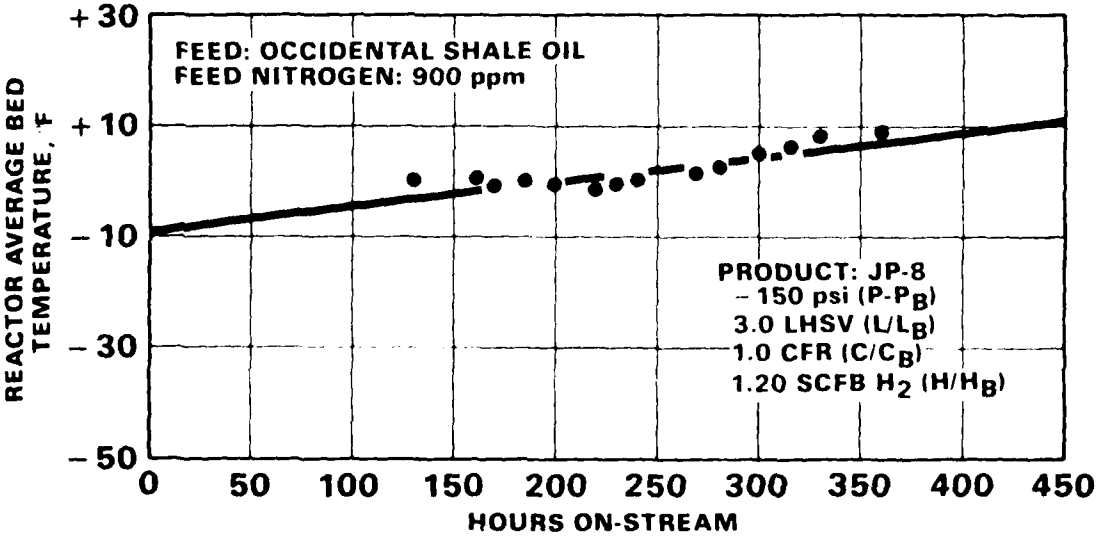
FIGURE 29

UOP 525 44



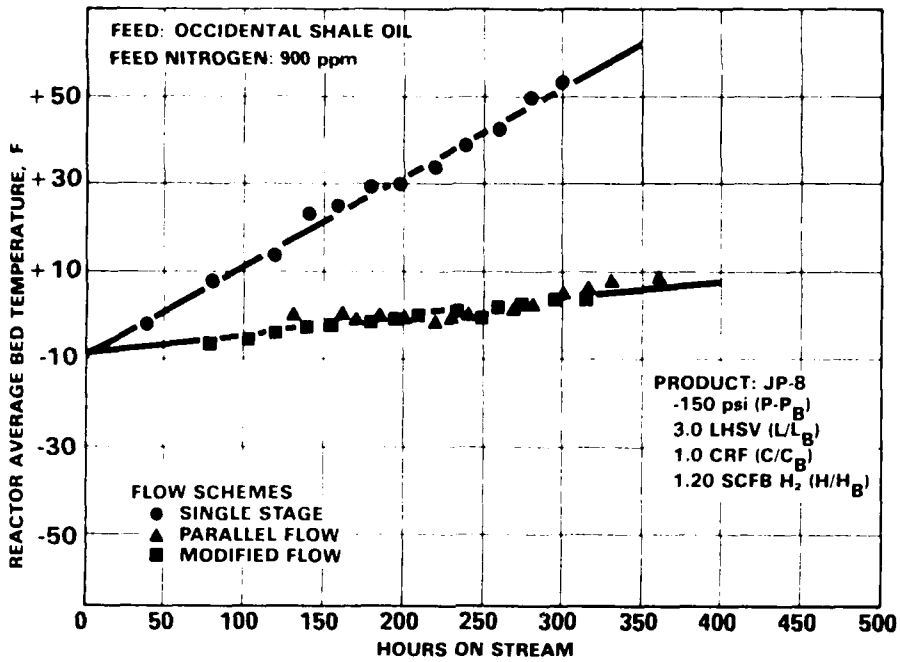

**MODIFIED FLOW HYDROCRACKING**

**FIGURE 30**



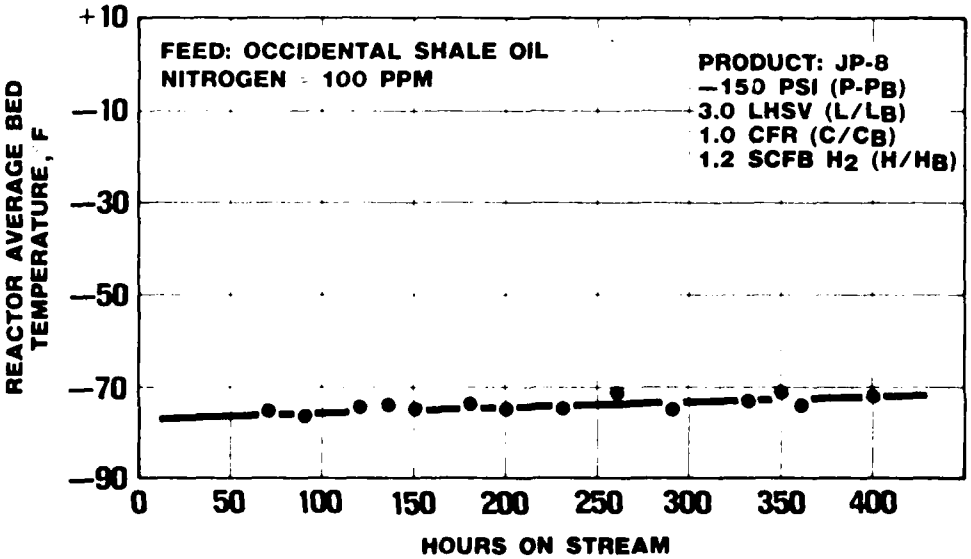

**PARALLEL FLOW HYDROCRACKING**

**FIGURE 31**



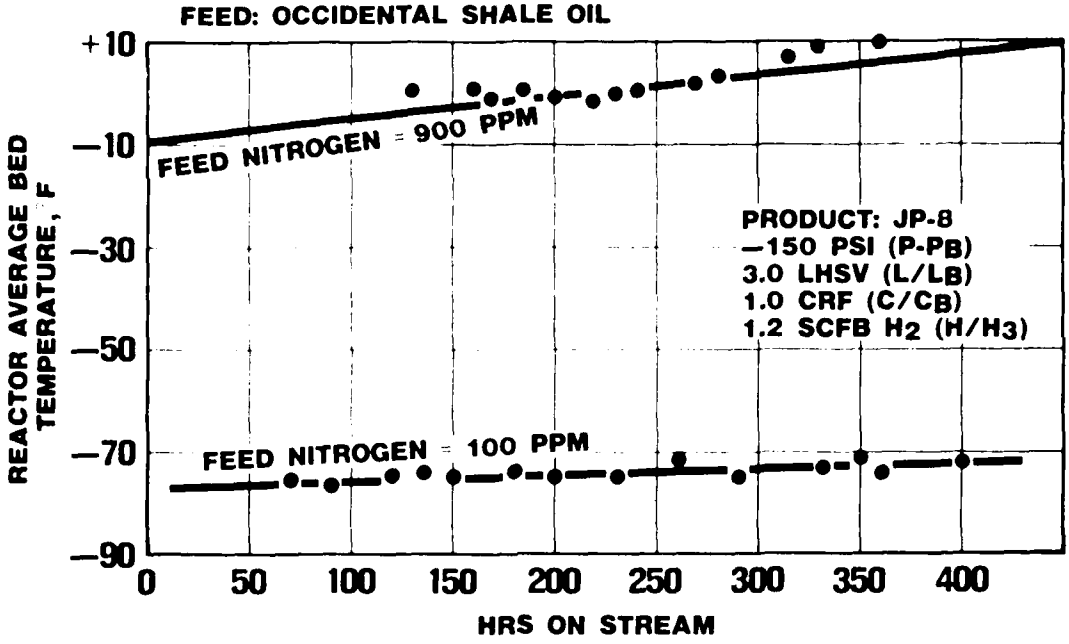

**COMPARISON OF HYDROCRACKING FLOW SCHEMES**

FIGURE 32




**PARALLEL FLOW HYDROCRACKING**

FIGURE 33




# PARALLEL FLOW HYDROCRACKING

## THE EFFECT OF FEED NITROGEN ON CATALYST STABILITY

FIGURE 34

UOP 525 94

# CONCLUSIONS

1. DEMONSTRATED THE ADVANTAGE OF MODIFIED FLOW AND PARALLEL FLOW HYDROCRACKING
2. SELECTED PARALLEL FLOW HYDROCRACKING AS OPTIMUM FLOW SCHEME
3. ESTABLISHED OPERATING CONDITIONS TO ACHIEVE MAXIMUM JET FUEL PRODUCTION FROM SHALE OIL
4. DETERMINED YIELDS HYDROGEN CONSUMPTION AND PRODUCT QUALITIES FOR JET FUEL PRODUCTION
5. DETERMINED SENSITIVITY OF HYDROCRACKER STABILITY TO FEED NITROGEN CONTENT

UOP 525 93

FIGURE 35

FIGURE 36

OVERALL MATERIAL BALANCE

JP-8 JET FUEL

| | Maximum JP-8 | | |
|---|---|---|---|
| Feed | Wt.% | Vol.% | BPSD |
| Shale Oil | 100.00 | 100.00 | 100,000 |
| Hydrogen | (4.18) | - | - |
| Total | 100.00 | - | - |
| Products | | | |
| Gasoline | 6.59 | 7.98 | 7,979 |
| Jet Fuel JP-8 | 71.16 | 81.05 | 81,047 |
| Jet Fuel JP-4 | - | - | - |
| Subtotal | 77.75 | 89.03 | 89,026 |
| By-Products | | | |
| Sulfur | 0.64 | - | - |
| Ammonia | 1.95 | - | - |
| Water | 0.72 | - | - |
| Subtotal | 3.31 | - | - |
| Material Lost in Production | 5.04 | - | - |
| Streams Utilized as Fuel | | | |
| Fuel Oil | 8.08 | 8.55 | 8,545 |
| Fuel Gas | 5.82 | - | - |
| Subtotal | 13.90 | 8.55 | 8,545 |
| Grand Total | 100.00 | - | - |

FIGURE 37

OVERALL MATERIAL BALANCE

JP-4 JET FUEL

| | Maximum JP-4 | | |
|---|---|---|---|
| | Wt.% | Vol.% | BPSD |
| **Feed** | | | |
| Shale Oil | 100.00 | 100.00 | 100,000 |
| Hydrogen | (4.10) | - | - |
| Total | 100.00 | - | - |
| **Products** | | | |
| Gasoline | - | - | - |
| Jet Fuel JP-8 | - | - | - |
| Jet Fuel JP-4 | 78.95 | 92.67 | 92,672 |
| Subtotal | 78.95 | 92.67 | 92,672 |
| **By-Products** | | | |
| Sulfur | 0.64 | - | - |
| Ammonia | 1.95 | - | - |
| Water | 0.72 | - | - |
| Subtotal | 3.31 | - | - |
| **Material lost in Production** | 4.45 | | |
| **Streams Utilized as Fuel** | | | |
| Fuel Oil | 13.29 | 14.06 | 14,055 |
| Fuel Gas | - | - | - |
| Subtotal | 13.29 | 14.06 | 14,055 |
| Grand Total | 100.00 | - | - |

FIGURE 38

UPDATED BASES FOR SHALE OIL PROCESSING

STUDY ECONOMIC EVALUATIONS

CAPITAL INVESTMENT:

- Midwest plant location adjacent to existing refinery[1]
- 100,000 BPSD crude shale oil capacity
- 2nd quarter 1980 cost base
- 100% Equity financing
- Investment timing over three-year construction period

  25% - first year

  50% - second year

  25% - third year
- 10% investment tax credit

WORKING CAPITAL:

- 21 days crude storage capacity/14 day crude inventory
- 14 days product storage capacity/7 day product inventory
- Crude valued at $30.00/BBL
- Product valued at $40.00/BBL
- Debt financed at 10%

CAPITAL RETURN:

- 15% DCF rate
- Zero salvage value
- 13 years sum of years digits depreciation

[1]This will enable credits to be taken for excess steam or fuel gas.

FIGURE 38 (CONT.)

OPERATING BASES:

- 16 year plant operating life
- 50% operating capacity 1st year - 100% thereafter
- 90% on-stream factor
- 100,000 barrel per stream day (BPSD) capacity
- All process fuel/heat requirements shall be generated internally from the original shale oil feed

OPERATING COST BASES:

- Crude shale oil - $30/BBL
- Cooling water 3¢/1000 GAL
- Electricity 3.5¢/KWHR
- Operators $12.00/manhour
- Helpers $10.50/manhour
- Supervision 25% of direct labor
- Overhead 100% of direct labor
- Federal & state taxes - 50%
- Maintenance, local taxes & insurance - 4.5% of fixed investment
- Product Values - all fuels are equal value
- By-Product values - Ammonia ($120/ST)
  Sulfur ($53/LT)

FIGURE 39

INDIVIDUAL PROCESS UNIT ESTIMATED ERECTED COST

100,000 BPSD CRUDE SHALE OIL CHARGE RATE

(MILLIONS OF DOLLARS)

| | Max. JP-8 | Max. JP-4 |
|---|---|---|
| UOP Unibon LP Hydrotreating | 42 | 42 |
| UOP Unibon HP Hydrotreating | 120 | 120 |
| HC Unibon Hydrocracking - Fractionation | 190 | 180 |
| Naphtha Hydrotreating - Platforming | 14 | - |
| Hydrogen Plant - Steam Reforming | 182 | 144 |
| Desalter | 2 | 2 |
| Amine Treating | 7 | 7 |
| Sour Water Stripper | 2 | 2 |
| Sulfur Plant | 7 | 7 |
| Total | 566 | 504 |

Basis: Midwest U.S. location
Third quarter 1980

FIGURE 40

COST OF PRODUCTION BREAKDOWN

100,000 BPSD CHARGE RATE

| | Max JP-8 | Max JP-4 |
|---|---|---|
| Operating Cost, $/BBL of Feed | 2.03 | 2.02 |
| Cost of Feed, $/BBL | 30.00 | 30.00 |
| Capital Charges for 15% DCF Return, $/BBL of Feed | 8.98 | 8.31 |
| Total Cost of Production, $/BBL of Feed | 41.01 | 40.33 |
| Total Cost of Liquid Feed Products, $/BBL | 46.06 | 43.52 |

III

# MILITARY JET FUEL FROM SHALE OIL

By

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Ashland Petroleum Research & Development

# MILITARY JET FUELS FROM SHALE OILS

H. F. Moore and W. A. Sutton
Ashland Petroleum Company

ABSTRACT: Ashland Petroleum Company began work under Contract F33615-78-C-2080 on February 15, 1980, to demonstrate the applicability of the EXTRACTACRACKING process towards production of aviation turbine fuels from whole crude shale oil. Data and results are presented for the Phase II Laboratory process variable and small sample production studies. Both in situ and above ground shale oils were processed, and a total of 9 potential turbine fuel samples provided to the Air Force.

The presentation is composed of three parts: 1) background to the contract and a review of Phase I results, 2) results from the Phase II laboratory process variable studies, and 3) properties and yields of the 9 samples provided to the Air Force.

## PART 1. BACKGROUND

Slide 1. Objectives and goals for the program as defined in the original contract documents.

Slide 2. Definition of the Phased components of this program.

Slide 3. These are the major problems encountered in processing whole crude shale oil which are the basis for this configuration of the EXTRACTACRACKING process.

Slide 4. For shale oil, the EXTRACTACRACKING process configuration results in this overall flow diagram.

Slide 5. These areas are the manner and types of response of the aforementioned problems encountered with shale oil refining.

Slide 6. Processing of shale oil in this manner results in these advantages for the EXTRACTACRACKING process when compared to processes generally considered to be state-of-the-art in shale oil refining.

Slide 7. This figure presents yield results from the Phase I effort when producing a maximum targeted JP-8 grade of turbine fuel.

Slide 8. The entire process, for the yield structure defined in Slide 7, was costed according to these primary factors.

Slide 9. The resulting finished fuel costs are shown on this slide. NOTE: These data are based on late 1978 cost estimates, and should be regarded as relative only.

PART 2. PHASE II LABORATORY PROCESS VARIABLE STUDY

Slide 10. Breakdown and task definition for the Phase II effort.

Slide 11. The first component of the Phase II effort was definition of both in situ and above ground shale oil properties. This slide presents a summary of those results, compared with a conventional (Arabian Light) and an incremental (Maya) petroleum crude oil.

Slide 12. Arsenic may well be the major problem in refining of crude shale oil in existing refineries. Note that the distribution of arsenic is across all boiling ranges, and not just limited to the heavier fractions as most metals are in petroleum stocks.

Slide 13. This figure demonstrates that, while shale oils in general have little naphtha content, they also have limited residual yields, and can for many purposes be considered as a limited combination of distillate and gas oil fractions.

Slide 14. Each processing module will be discussed separately, with key data. Note that we have defined the key element of the crude shale oil hydrotreater to be minimization of hydrogen consumption. This module, in fact, is the limiting factor in defining the hydrogen consumption for the entire process.

Slide 15. Operating conditions, therefore, for this module are set primarily by hydrogen consumption considerations. As noted here, consumption increases rapidly as the operating pressure of the unit is increased. Note that operating pressure increases also significantly increase capital cost of the unit.

Slide 16. Of further importance, increasing the operating temperature decreases the hydrogen utilization efficiency of this unit. Utilization efficiency is defined as that fraction of total hydrogen consumed which accounts for an increase in hydrogen content of the liquid products, and is therefore available, and results in, increased hydrogen content

of any finished products. While not shown here, space velocity has a similar impact, resulting in the desired situation of high specific reactor throughputs.

Slide 17. Based on these considerations, we would like to set our reactor conditions at low temperature, high throughput, and (relatively) low pressures. Since we will be extracting nitrogen compounds at a later point in the process, we would also like to maximize basic nitrogen content of the distillate materials at this point. As this slide shows, this is not only possible, but occurs essentially at the conditions which were selected based on hydrogen consumption considerations.

Slide 18. With this selection of desired operating conditions, we also must select a catalyst. As shown in this slide, and in good agreement with present knowledge in the petroleum industry, we can limit denitrogenation in this unit by using cobalt-molybdate based catalyst.

Slide 19. Since our conditions, or at least desired conditions are now defined, we must determine the overall processing results at these conditions. This slide demonstrates desulfurization resulting at these conditions for both shale oils, and in particular in comparison to petroleum stocks.

Slide 20. This slide compares denitrogenation results for these materials.

Slide 21. Finally, since we know the desired operating conditions catalyst, and anticipated results, we must define the aging parameters for these operations. As shown in this slide, a low rate of deactivation was encountered.

Slide 22. The next major module in the process is the fluid catalytic cracker. This module effectively determines the quantities of distillate products resulting from the overall plant.

Slide 23. This slide demonstrates the types of data for multiple samples derived under this program. In particular, this slide also compares FCC response of the in situ and above ground oils.

Slide 24. Slide 23 results were surprising, and against our preconceived notions; we checked the remaining data sets. These results were confirmed, with the finding that total (naphtha plus distillate) yields were not significantly different for the two oils when compared at equivalent

hydrotreating conditions. The major difference between the two oils is that the above ground material consistently produces higher coke, but lower gas, yields at equivalent conversions than the in situ material.

Slide 25. A major piece of data desired from these studies was the effect of basic nitrogen content of the feedstock on the FCC unit performance. As shown in this slide, major results are that increasing basic nitrogen content of the feedstock tends to reduce the conversion level at which the maximum (naphtha plus distillate) yield occurs, and that total yield of the desired light fractions decreases. Confirming our original statements, this slide also demonstrates the shift of operating selectivity from naphtha product to distillate product as basic nitrogen content increases.

SLide 26. This sample demonstrates the detail to which several samples were evaluated. Note in particular the redistribution in hydrogen, and the apparent degree of heteroatom removal.

Slide 27. All the data obtained as in Slide 26 were evaluated to determined if functionalities for desulfurization and denitrogenation could be isolated. There were no good correlations developed, with both sulfur and nitrogen appearing to approach limiting values rather than correlating with operating severity or feedstock properties.-

Slide 28. The final major portion of the conversion section of the EXTRACTACRACKING plant is the nitrogen extraction unit. Note that the key element here is maximizing nitrogen removal, while minimizing hydrocarbon loss, at no external hydrogen addition.

Slide 29. As it turns out, required operating conditions for this unit were strongly constrained by several factors. As shown, minimum treating rates and strengths are defined by the rapid decrease in efficiency observed.

Slide 30. The upper bound of treating strength is defined very clearly as well. As shown, above about 40 percent, excess removal of non-nitrogen types occurs in addition to difficulty in handling of these materials.

Slide 31. These studies have allowed us to concentrate on evaluating the nitrogen heterocycle types found in shale oil. We have finally defined the structure of these materials,

as shown in this slide. There is still some uncertainty as to whether the left rear corner is a motorcycle or a bicycle tire.

Slide 32. The recycle hydrotreater provides upgraded feedstock to the FCC unit.

Slide 33. The sulfur content of the FCC bottoms is more refractory to removal by hydrotreatment than the original crude shale hydrotreater sulfur content.

Slide 34. Surprisingly, this trend does not hold for the nitrogen material. There are no differences in removal rates here that are not directly attributable to catalyst type or operating conditions.

Slide 35. The guardcase hydrotreater takes extraction raffinate and upgrades it to reformer specifications.

Slide 36. Relative severity requirements were defined for each major sample produced. The M Series samples were found to be contaminated, and required relatively high operating severity. However, better product workup for the GC samples demonstrates the relative ease of processing as originally anticipated. Note that the above ground material is slightly more difficult to process to specifaction than the in situ material.

Slide 37. Freeze point modification is another unique aspect of EXTRACTACRACKING, allowing a maximum amount of turbine fuel boiling range material to be used in the turbine fuel blending process.

Slide 38. Freeze point modifications were significant for all samples. The major remaining question was the relative aging characteristics of the unit. For the in situ material, aging was gradual and within reasonable limits.

Slide 39. The above ground material, however, showed relatively high aging rates. Condition modification will be re quired when processing this material.

Slide 40. The aromatic saturation unit is provided to reduce aromatics content of the turbine fuel to essentially any level desired. Samples produced during Phase II demonstrated aromatics contents ranging from 2-30+%.

Slide 41. Due to the cost of building new refineries, the question arises as to what impact these studies could have on existing refineries. This slide demonstrates that the process as derived could easily be integrated with existing refineries with only a minor amount of new construction and/or revamp.

PART 3. PRODUCTION OF LABORATORY SAMPLES

Slide 42. Samples produced under this program were analyzed by these methods.

Slide 43. Sample M-112 was produced as a blocked-out JP-4 sample, with these results.

Slide 44. These are the properties of M-112. While the sample was missing a large quantity of light ends, note the excellent freeze point.

Slide 45. Sample M-121 was produced as a blocked-out JP-8 sample.

Slide 46. These are the properties of M-121.

Slide 47. Sample GC-1 was produced as a concurrent production mode operation for producing all grades of pertinent turbine fuels. These are the yields resulting, which are depressed due to experimentation with full-range chargestock to the FCC unit.

Slide 48. Sample GC-1 was separated into two turbine fuel fractions. This is JP-4 note the low aromatics level.

Slide 49. This is the JP-8 prepared from GC-1. The flash point was slightly off, but was not corrected since this is a relatively minor factor at laboratory production efforts.

Slide 50. Sample GC-2 was also a concurrent production run, in this case on above ground shale oil. Total yields were depressed due to experimentation in the FCC processing portion of the study.

Slide 51. JP-4 produced from GC-2. Note the aromatics level.

Slide 52. JP-5 produced from GC-2.

Slide 53. JP-8 produced from GC-2.

Slide 54. Sample M-212 was a unique sample, combining the properties of JP-4 and JP-8 grades.

Slide 55. Properties of M-212.

Slide 56. Sample M-221 was also a combined turbine fuel.

Slide 57. Properties of M-221.

Slide 58. A comparison of Phase I and potential Phase II results. The yields shown for Phase II effectively set an upper bound on potential yields, based on the Phase II data set.

MILITARY JET FUELS FROM SHALE OIL

OBJECTIVE: PROVIDE SAMPLE QUANTITIES OF AVIATION TURBINE FUEL DERIVED FROM WHOLE CRUDE SHALE OIL

GOALS:
1. PROVIDE SAMPLES OF MILITARY FUEL OF VARIABLE QUALITY.
2. COMPUTER MODEL THE PROCESSING METHOD.
3. DEVELOP A PROCESSING METHOD HAVING A MINIMUM OVERALL ENERGY EFFICIENCY OF 70%.
4. PROVIDE A PROCESSING METHOD WHICH PRODUCES A FULL SLATE OF MILITARY TRANSPORTATION FUELS.

Slide 1

MILITARY JET FUEL FROM SHALE OIL PHASES

PHASE I. PRELIMINARY PROCESS ANALYSIS

PHASE II. LABORATORY SAMPLES

PHASE III. COMPONENT TEST SAMPLES

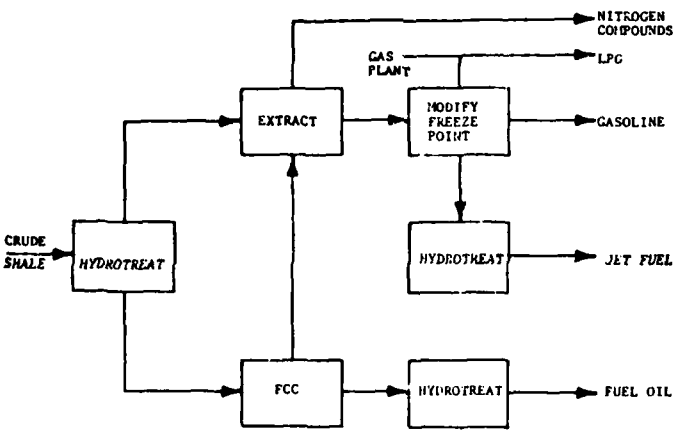
PHASE IV. OVERALL ECONOMIC OPTIMIZATION

Slide 2

MAJOR PROBLEMS IN SHALE OIL PROCESSING

- NITROGEN
- OXYGEN
- SULFUR
- ARSENIC
- NORMAL PARAFFINS
- CONJUGATED DIOLEFINS
- METALS
- TRAMP METALS AND FINES FROM RETORTING
- BOILING RANGE DISTRIBUTION

Slide 3




THE EXTRACTACRACKING(R) PROCESS

Slide 4

EXTRACTACRACKING'S ANSWER TO
SHALE OIL REFINING PROBLEMS

| PROCESS STEP | PROBLEMS ADDRESSED |
|---|---|
| • CRUDE SHALE HYDROTREATING | • SULFUR, ARSENIC, OLEFINS |
| • FLUID CATALYTIC CRACKING | • BOILING RANGE DISTRIBUTION |
| • LIQUID EXTRACTION | • NITROGEN, OXYGEN |
| • GUARDCASE HYDROTREATING | • RESIDUAL AMOUNTS OF SULFUR, NITROGEN, OXYGEN, AND ARSENIC |
| • FREEZE POINT MODIFICATION | • NORMAL PARAFFINS |
| • FINAL PRODUCT TREATING | • CONVERSION OF ANY ITEM REMAINING DELETERIOUS TO PRODUCT QUALITY |

Slide 5

ADVANTAGES OF THE EXTRACTACRACKING PROCESS

- HYDROGEN CONSUMPTION IS MINIMIZED
- CONVERSION LEVELS MAY BE VARIED READILY
- VIRGIN JET FUEL FRACTIONS ARE CONSERVED
- THE PROCESS IS RELATIVELY INSENSITIVE TO FEEDSTOCK
- ULTRA-HIGH PRESSURE EQUIPMENT IS NOT REQUIRED
- LITTLE OR NO RESIDUAL FUEL IS PRODUCED
- THE FINISHED FUEL REDUCES $NO_x$ EMISSIONS
- THERMAL STABILITY IS ATTAINED
- FREEZE POINT IS DIRECTLY CONTROLLED
- DIRECT AROMATICS CONTROL IS PROVIDED
- MOTOR GASOLINE OCTANE CAN BE VARIED WIDELY

Slide 6

OVERALL MILITARY FUEL YIELDS
JP-8 EXTRACTACRACKING

| | BPD | VOL% OF PRIME PRODUCTS | VOL% OF FEED |
|---|---|---|---|
| GASOLINE | 27,986 | 32.0 | 28.0 |
| JP-8 | 54,444 | 62.3 | 54.4 |
| BURNER FUEL | 4,997 | 5.7 | 5.0 |
| TOTAL | 87,427 | 100.0 | 87.4 |

BASIS: 100,000 BPD CRUDE IN-SITU SHALE OIL CHARGE

Slide 7

CAPITAL COST BASES
JP-8 EXTRACTACRACKING
PHASE I

- MIDWEST PLANT LOCATION
- MODIFIED GRASS ROOTS REFINERY
- SEPTEMBER, 1978, COSTS
- 100,000 BPD CRUDE, IN-SITU SHALE OIL CHANGE

Slide 8

SUMMARY PHASE I ECONOMIC RESULTS
JP-8 EXTRACTACRACKING

| | |
|---|---|
| THERMAL EFFICIENCY | 85% |
| FIXED CAPITAL INVESTMENT | 433.2MM$ |
| WORKING CAPITAL | 107.3MM$ |
| PRODUCT VALUE | $25.15/BBL |

BASIS: SHALE OIL @ $16/BBL
15% DCF RATE

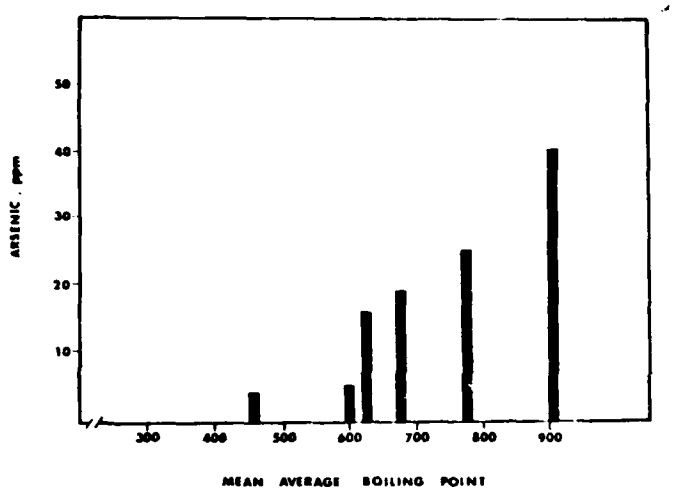
Slide 9

## Military Jet Fuel From Shale Oil
## Phase II
## Task Definition

**Task I. Evaluate Process Variables**

**Task II. Produce 500 Milliliter Fuel Samples**

Slide 10



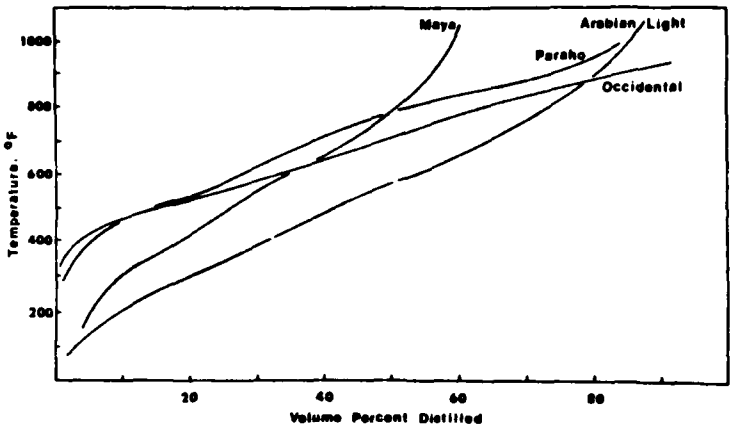

**ARSENIC CONTENT AS A FUNCTION OF BOILING RANGE FOR CRUDE OCCIDENTAL SHALE OIL**

Slide 12

CRUDE OIL COMPARISON

| ITEM | ARABIAN LIGHT | IN SITU SHALE OIL | ABOVE GROUND SHALE OIL | MEXICAN MAYA |
|---|---|---|---|---|
| GRAVITY, °API | 33.3 | 23.6 | 20.9 | 22.2 |
| K FACTOR | 11.9 | 11.6 | 11.4 | 11.6 |
| SULFUR, WT % | 1.8 | 0.53 | 0.63 | 3.4 |
| NITROGEN, WT % | - | 1.42 | 1.85 | (>0.31) |
| BASIC NITROGEN, WT % | (>0.007) | 0.86 | 1.48 | (>0.01) |
| OXYGEN, WT % | - | 1.21 | 1.04 | - |
| POUR POINT, °F | <-20 | 65 | 70 | <-20 |
| VIS @ 100°F, SUS | 46.3 | 162 | 205 | 326 |
| DISSOLVED $H_2S$, PPM | TR | 27 | 33 | 14 |
| ORGANIC CHLORIDE, PPM | 7.7 | 4 | 13 | 27 |
| BS & W, VOL % | TR | 0.1 | TR | 0.15 |
| SALT, #/1000 BBL | 0 | 2.47 | 1.98 | 12.4 |
| CARBON RESIDUE, WT % | - | 1.22 | 1.62 | 10.2 |
| TOTAL METALS, PPM | ( 13) | 68 | 106 | ( 340) |
| ACID NUMBER | - | 1.36 | 1.90 | 0.24 |

Slide 11




COMPARATIVE BOILING RANGE DISTRIBUTION

Slide 13

## Crude Shale Oil Hydrotreater

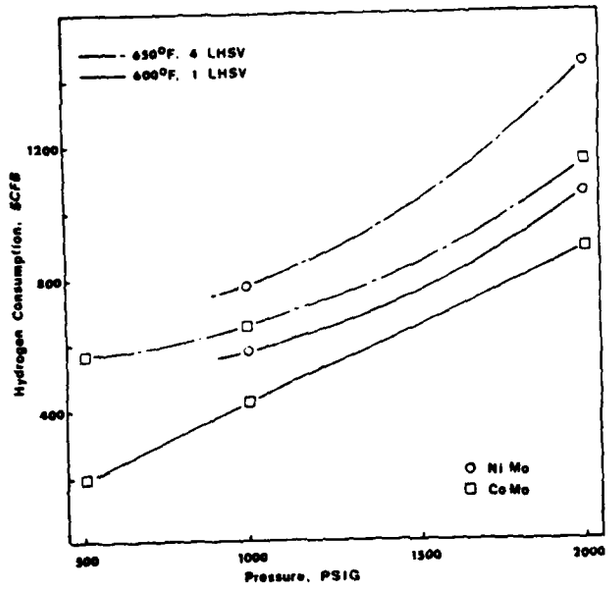
**Objectives:** Provide olefin saturation, metals removal, and desulfurization at minimum denitrogenation, hydrogen consumption, and operating severity.

**Key Element:** Hydrogen Consumption

**Parameters Evaluated:**
- Operating Severity
- Catalyst Type
- Shale Oil Type

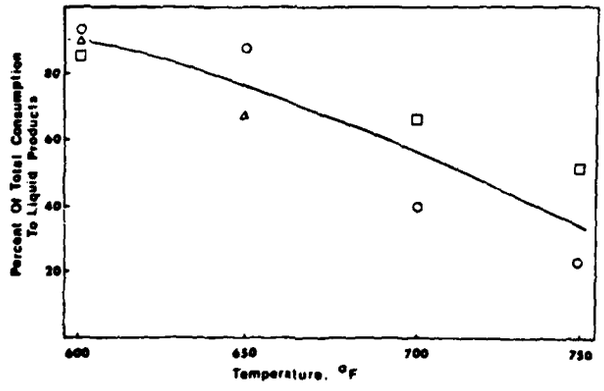
**Unique Features:**
- Low Pressure Operation
- Operating Parameters Corresponding to present Commercial Practice

Slide 14



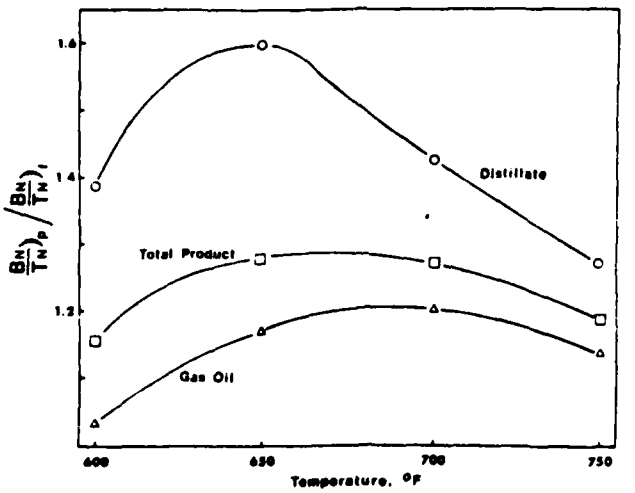

HYDROGEN CONSUMPTION TRENDS

Slide 15



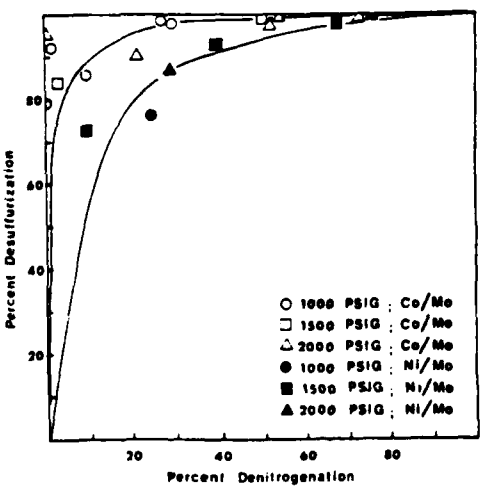

HYDROGEN CONSUMPTION EFFICIENCY

Slide 16



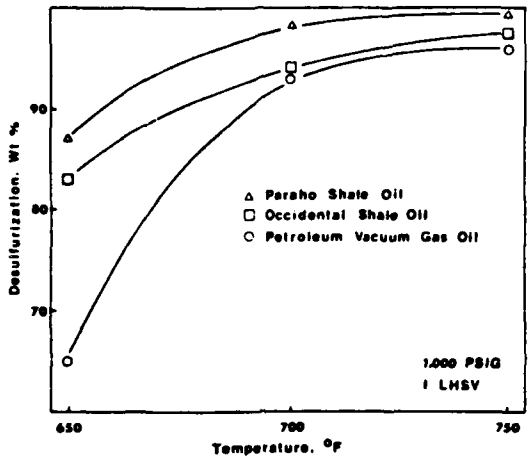

**BASIC NITROGEN GENERATION**

Slide 17




**ABOVE GROUND SHALE OIL HYDROTREATING**

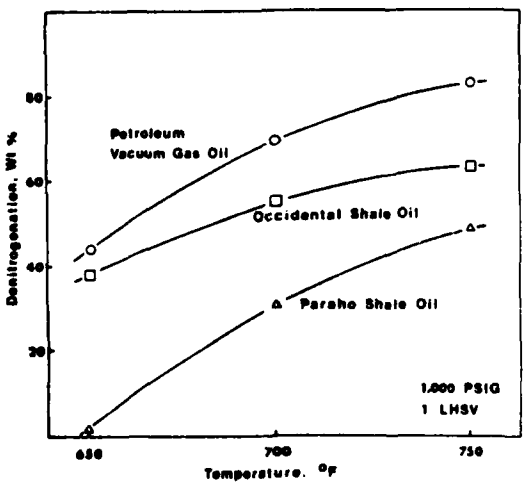
Slide 18




**DESULFURIZATION COMPARISON**

**FOR SHALE OIL AND PETROLEUM**

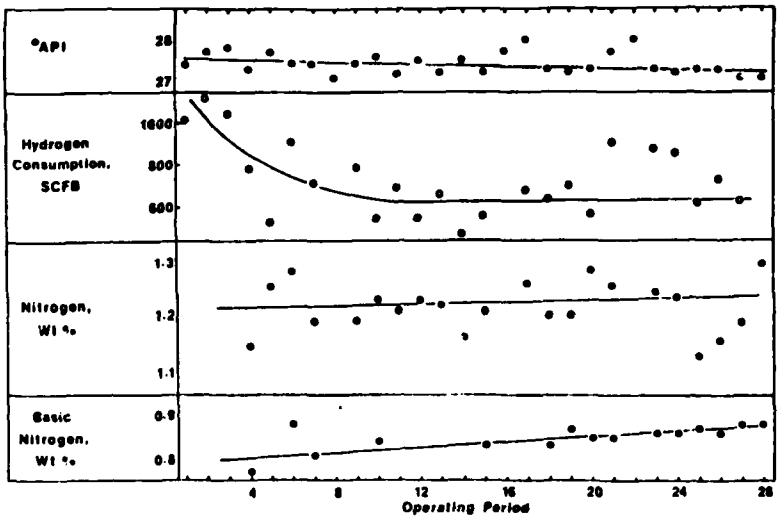
Slide 19




**DENITROGENATION COMPARISON**

**FOR SHALE OIL AND PETROLEUM**

Slide 20




CSHT AGING RESULTS FOR IN SITU SHALE OIL

Slide 21

## Fluid Catalytic Cracking

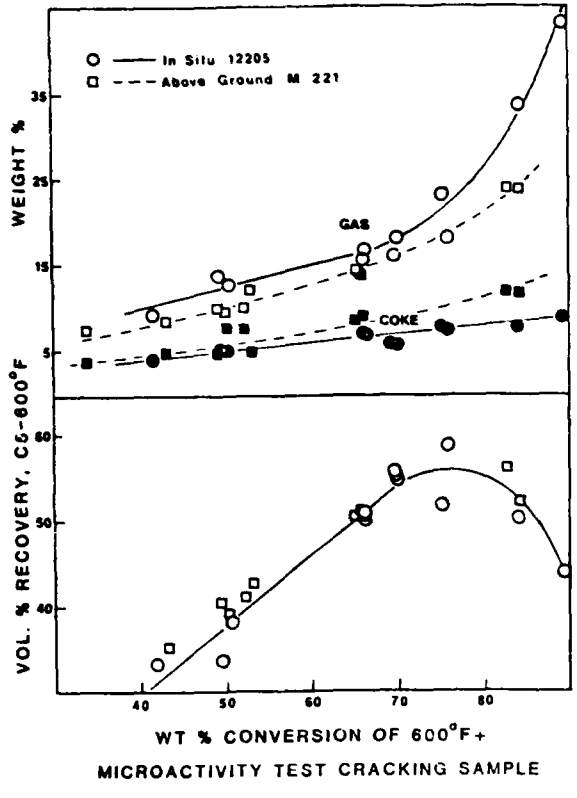
**Objectives:** Convert an economic maximum of +600°F Material into turbine fuel and gasoline boiling ranges. Provide concurrent heteroatom removal and hydrogen redistribution.

**Key Element:** Economic Maximum Distillate Production

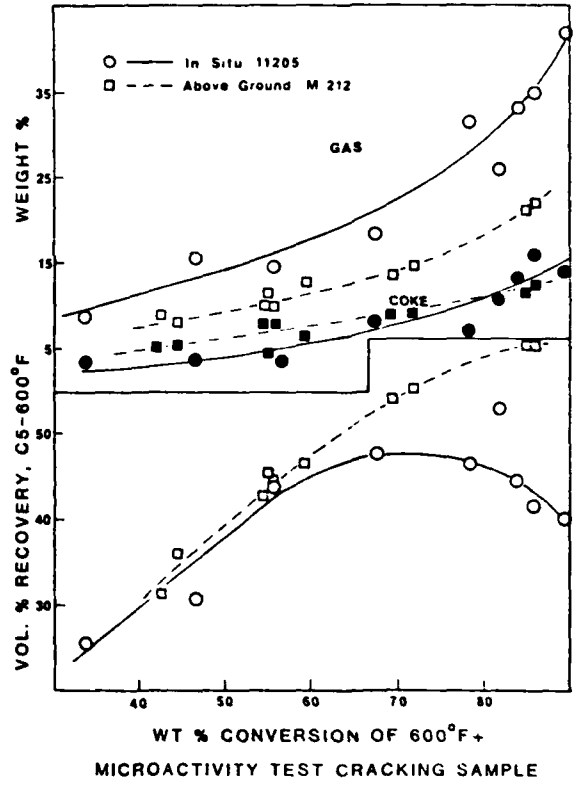
**Parameters Evaluated:**
- Operating Severity
- Hydrotreater Source Parameters
- Shale Oil Type

**Unique Features:**
- High Nitrogen Feedstocks
- Production Emphasis on Distillate plus Gasoline Ranges

Slide 22




Slide 24




Slide 23

**FLUID CATALYTIC CRACKING**
**FCR PROCESSING**
**SAMPLE M 221**

| Operating Conditions | |
|---|---|
| Temperature, °F | 1007 |
| Cat/Oil Ratio | 17.8 |
| C on Regen Cat, % | 0.01 |
| Conversion, Wt %[a] | 62.9 |
| Closure, Wt % | 98.7 |

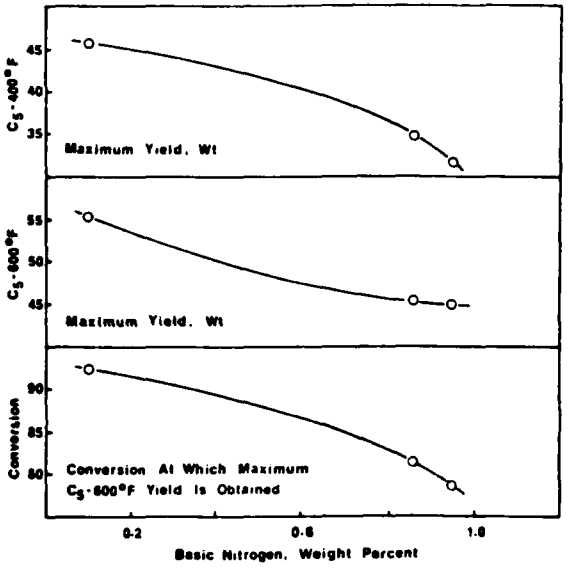
| Product Yields, Wt % | |
|---|---|
| $H_2$ | 0.22 |
| $C_1$ | 0.88 |
| $C_2$ | 1.96 |
| $C_3$ | 0.70 |
| $C_3^=$ | 2.22 |
| $iC_4$ | 0.36 |
| $nC_4$ | 0.35 |
| $C_4^=$ | 2.66 |
| $C_5$ – 600 | 33.66 |
| 600 + | 37.38 |
| Coke | 19.61 |

**Liquid Properties**

| Item | Feed | Total Product | 600°F | +600°F |
|---|---|---|---|---|
| °API | 20.9 | - | 42.4 | 13.6 |
| Carbon, %w | 87.5 | - | - | - |
| Hydrogen, %w | 10.1 | - | 12.2 | - |
| Nitrogen, %w | (2.065) | (1.370) | (1.183) | (1.828) |
| $N_{basic}$, %w | 1.311 | - | - | - |
| Sulfur, %w | 0.15 | 0.16 | 0.15 | 0.17 |
| Oxygen, %w | - | - | - | 0.197 |
| Ramsbottom C, %w | 1.04 | - | - | 2.04 |
| Aromatics, %w | - | - | - | - |
| GHV, Btu/lb | - | - | - | - |
| Distillation, Wt % (°F) by | | | - | - |
| IBP | 594 | 122 | 133 | 491 |
| 2 | 600 | 169 | 148 | 531 |
| 10 | 640 | 282 | 209 | 601 |
| 30 | 725 | 480 | 284 | 662 |
| 50 | 804 | 629 | 343 | 723 |
| 70 | 873 | 721 | 414 | 797 |
| 90 | 958 | 846 | 520 | 892 |
| 98 | 1001 | 930 | 590 | 963 |
| EP | 1013 | 956 | 620 | 999 |

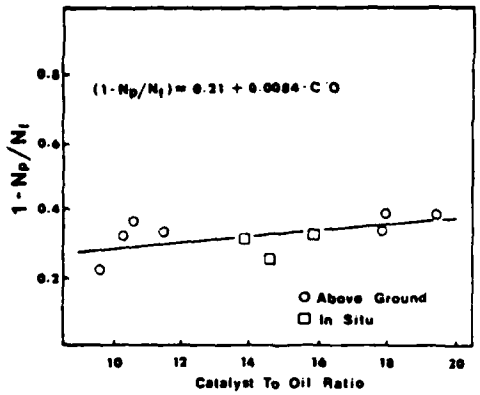
a – Based on the specified cut point above

Slide 26




**FCC YIELD MAXIMA DEPENDENCE ON FEEDSTOCK BASIC NITROGEN CONTENT FOR IN SITU SHALE OIL**

Slide 25




**DENITROGENATION DURING FLUID CATALYTIC CRACKING**

Slide 27

## Nitrogen Extraction

**Objectives:** Remove significant quantities of nitrogen compounds without external hydrogen addition

**Key Element:** Maximum Nitrogen Removal at Minimum Hydrocarbon Loss

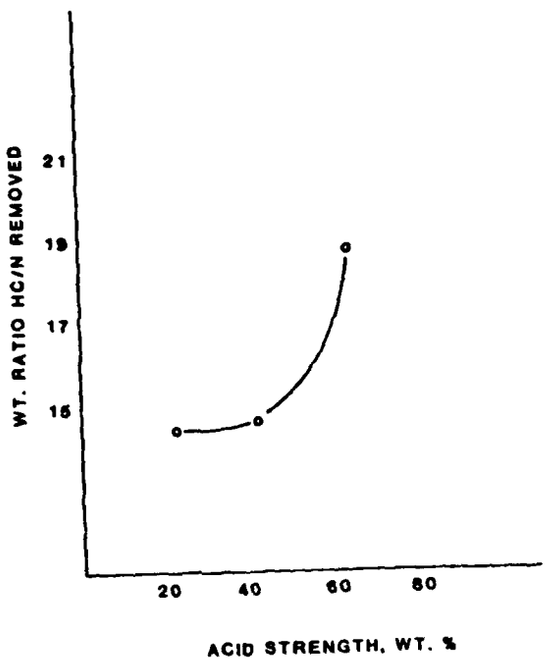
**Parameters Evaluated:**
- Feedstock Genesis
- Acid Strength
- Acid Dosage
- Temperature, Viscosity

**Unique Features:**
- Nitrogen Removal Without Hydrogen Addition
- Processing of High Olefin Stocks

Slide 28

RATIO OF HYDROCARBON TO NITROGEN REMOVAL

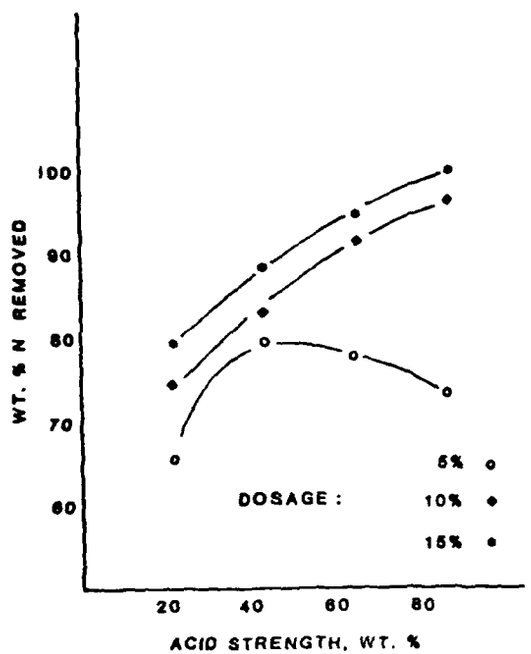
IN CONTINUOUS COUNTERCURRENT EXTRACTION



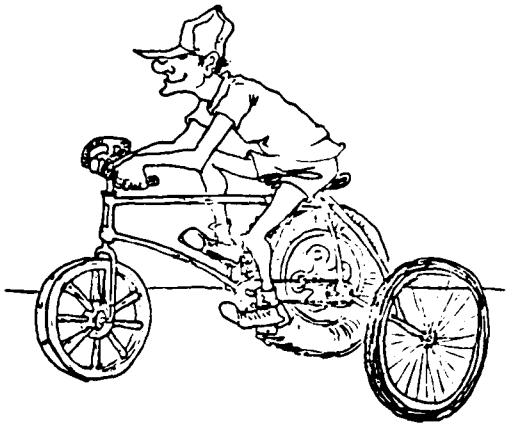

Slide 30

BATCH EXTRACTION

OF BASIC NITROGEN




Slide 29



**A Real Heterocycle!**

Slide 31

## Recycle Oil Hydrotreating

**Objectives:** Upgrade heavy FCC products to improve recycle crackability.

**Key Element:** Product Response to Cracking

**Parameters Evaluated:**
- Feedstock Source
- Operating Severity

**Unique Features:**
- Hydrotreatment prior to recycle
- Conditions correspond to present commercial practice.

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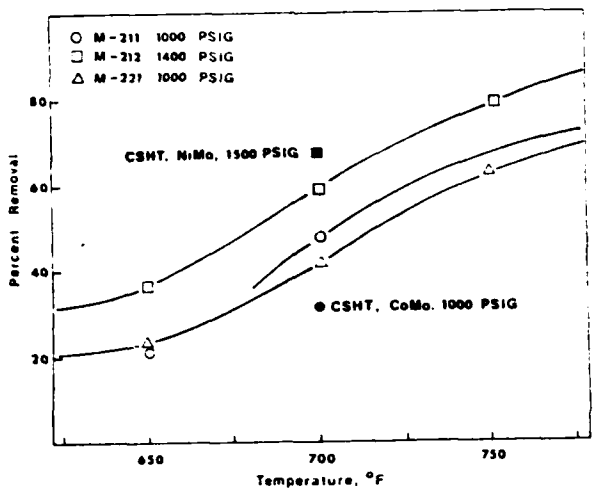
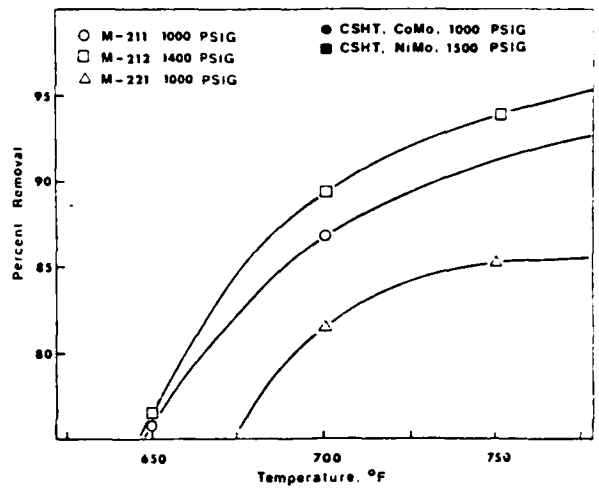



CYCLE OIL HYDROTREATING
ABOVE GROUND SHALE OIL
TEMPERATURE DEPENDENCE OF
DENITROGENATION AT 1 LHSV

Slide 34




CYCLE OIL HYDROTREATING
ABOVE GROUND SHALE OIL
TEMPERATURE DEPENDENCE OF
DESULFURIZATION AT 1 LHSV

Slide 33

## Guardcase Hydrotreating

**Objectives:** Process the extraction raffinate to a quality suitable for further upgrading; remove final traces of heteroatoms, metals, etc., as necessary.

**Key Element:** Product Suitable For Use as Reformer Charge

**Parameters Evaluated:**
- Feedstock Source
- Operating Severity

**Unique Features:**
- Feedstock end point

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## Apparent Minimum Severity Requirements Guardcase Hydrotreating

| Shale Oil Type | Sample Number | Feed Nitrogen Wt % | Temperature °F | Pressure PSIG | LHSV $Hr^{-1}$ |
|---|---|---|---|---|---|
| In Situ | M-112 | 0.24 | 700 | 1200 | 0.6 |
| | M-121 | 0.23 | 700 | 1200 | 0.65 |
| | GC-1 | 0.20 | 650 | 1000 | 1.0 |
| Above Ground | M-211 | 0.36 | 700 | 1200 | 0.94 |
| | M-212 | 0.45 | 725 | 1200 | 0.93 |
| | M-221 | 0.34 | 700 | 1200 | 0.49 |
| | GC-2 | 0.26 | 650 | 1200 | 0.96 |

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## Freeze Point Modification

**Objectives:** Reduce the freeze point of the guardcase products to maximize the quantity of the desired turbine fuel fractions. Concurrently, upgrade the produced gasoline (if any) octane number.

**Key Element:** High end point reforming

**Parameters Evaluated:**
- Feed Source
- Boiling Range
- Operating Severity

**Unique Features:**
- High end point reforming
- Concurrent freeze point depression and octane improvement.

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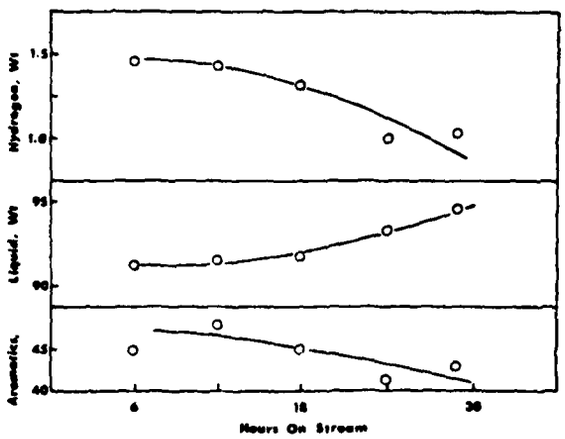
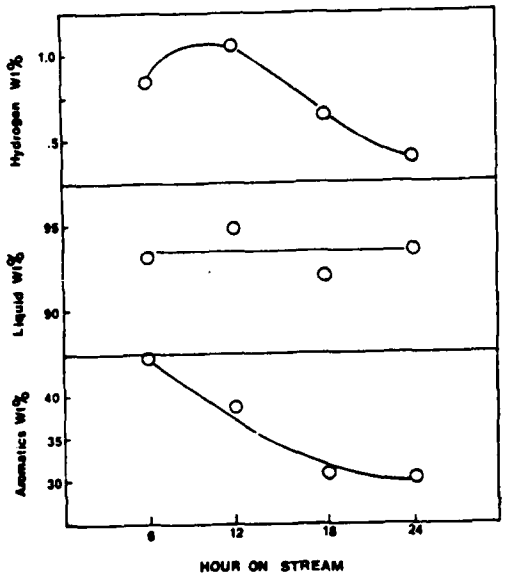



**ACCELERATED AGING RESPONSE**

**OF SAMPLE GC-1**

(Normalized Data)

Slide 38




ACCELERATED AGING RESPONSE
OF SAMPLE GC-2

(Normalized Data)

Slide 39

## Aromatic Saturation

**Objectives:** Reduce turbine fuel aromatics content to acceptable levels.

**Key Element:** Aromatic saturation to less than 25%

**Parameters Evaluated:** • Feed Source

**Unique Features:** • Application to this use

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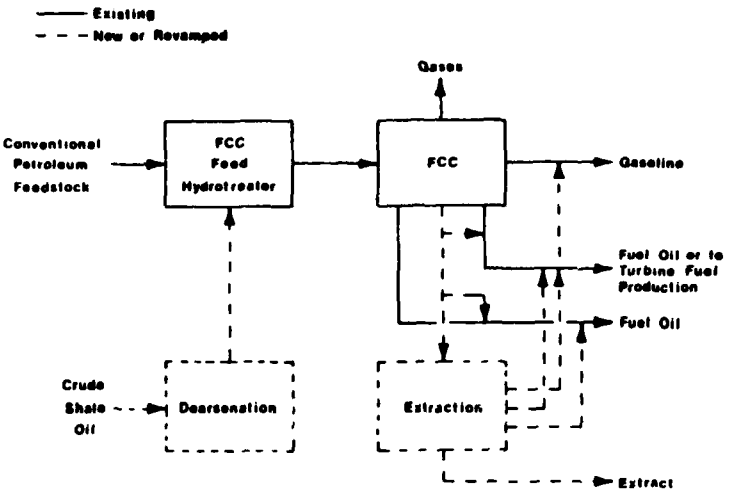


**AN EXAMPLE OF INTEGRATING EXTRACTACRACKING® WITH AN EXISTING PETROLEUM REFINERY**

Slide 41

## Aviation Turbine Fuel Test Methods

| Description | Method |
|---|---|
| Gravity, API | ASTM—D287 |
| Hydrogen | ASTM—D3701 |
| Aromatics | ASTM—D1319 |
| Freeze Point | ASTM—D2386 |
| Reid Vapor Pressure | ASTM—D323 |
| Flash Point | ASTM—D56 |
| Distillation | ASTM—D86 |
| Heat of Combustion | ASTM—D3338 |

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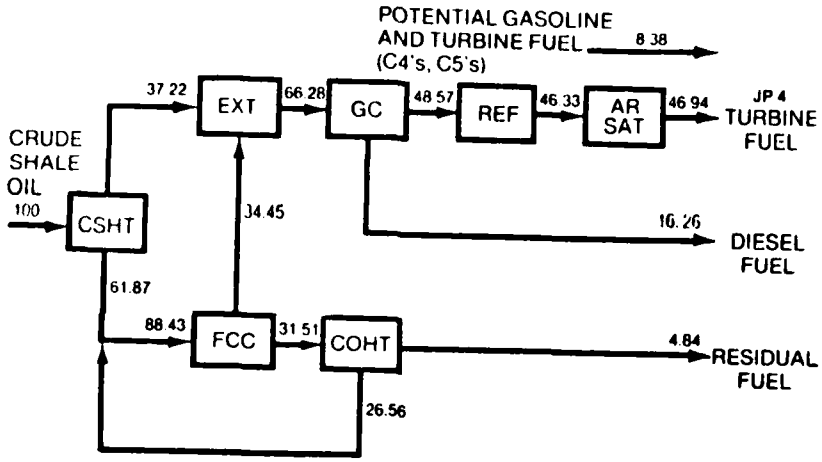


SAMPLE M-112
Target: JP-4

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## Aviation Turbine Fuel From Crude Shale Oil Phase II

| | | |
|---|---|---|
| Sample No. | M-112 | |
| Fuel Type | JP-4 | |
| Shale Source | In Situ | Specifications |
| Gravity, API | 46.7 | 45-57 |
| Hydrogen, Wt% | 14.6 | 13.6 min |
| Saturates, Vol% | 80.9 | |
| Olefins, Vol% | 0.8 | |
| Aromatics, Vol% | 18.3 | 25.0 max |
| Freeze Point, °F | −81 | −72 max |
| RVP, PSI | | 2-3 |
| Flash Point, °F | | |
| Heat of Combustion, BTU/# | 18,584 | 18,400 min |
| Distillation, °F | | |
| IBF | 218 | |
| 10% | 226 | |
| 20% | 314 | |
| 50% | 379 | |
| 90% | 454 | |
| FBP | 490 | |
| Residue | 1.0 | |
| Loss | 1.0 | |

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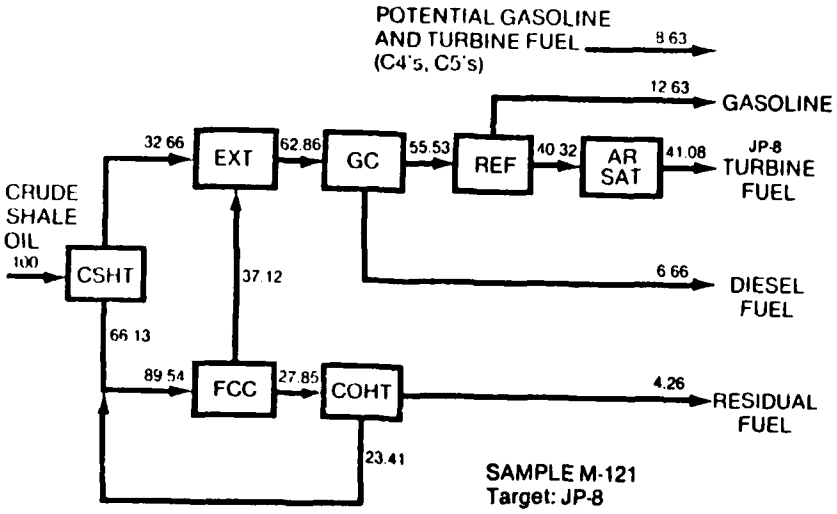
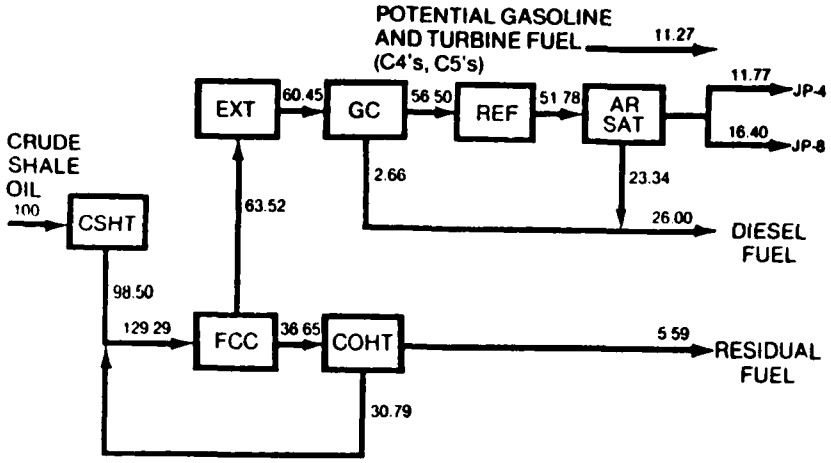



Slide 45

## Aviation Turbine Fuel From Crude Shale Oil Phase II

| Sample No. | M-121 | |
|---|---|---|
| Fuel Type | JP-8 | |
| Shale Source | In Situ | Specifications |
| Gravity, API | 41.4 | 37-51 |
| Hydrogen, Wt% | 13.8 | 13.6 min |
| Saturates, Vol% | 78.6 | |
| Olefins, Vol% | 1.0 | |
| Aromatics, Vol% | 20.4 | 25.0 max |
| Freeze Point, °F | −64 | −58 max |
| RVP, PSI | | |
| Flash Point, °F | 132 | 100 min |
| Heat of Combustion, BTU/# | 18,542 | 18,400 min |
| Distillation, °F | | |
| IBP | 340 | |
| 10% | 373 | |
| 20% | 387 | |
| 50% | 422 | |
| 90% | 475 | |
| FBP | 498 | |
| Residue | 1.0 | |
| Loss | 1.0 | |

Slide 46




SAMPLE GC-1
Concurrent Fuel Production

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## Aviation Turbine Fuel From Crude Shale Oil Phase II

| Sample No. | GC1-4 | |
|---|---|---|
| Fuel Type | JP-4 | |
| Shale Source | In Situ | Specifications |
| Gravity, API | 52.6 | 45-57 |
| Hydrogen, WT% | 14.6 | 13.6 min |
| Saturates, Vol% | 94.5 | |
| Olefins, Vol% | 0.7 | |
| Aromatics, Vol% | 4.8 | 25.0 max |
| Freeze Point, °F | —90 | —72 max |
| RVP, PSI | 1.5 | 2-3 |
| Flash Point, °F | | |
| Heat of Combustion, BTU/# | 18,769 | 18,400 min |
| Distillation, °F | | |
| IBF | 156 | |
| 10% | 228 | |
| 20% | 253 | |
| 50% | 304 | |
| 90% | 387 | |
| FBP | 412 | |
| Residue | 1.0 | |
| Loss | 1.0 | |

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## Aviation Turbine Fuel From Crude Shale Oil Phase II

| Sample No. | GC 1-8 | |
|---|---|---|
| Fuel Type | JP-8 | |
| Shale Source | In Situ | Specifications |
| Gravity, API | 44.8 | 37-51 |
| Hydrogen, Wt% | 14.1 | 13.8 min |
| Saturates, Vol% | 88.9 | |
| Olefins, Vol% | 0.8 | |
| Aromatics, Vol% | 10.3 | 25.0 max |
| Freeze Point, °F | −64 | −58 max |
| RVP, PSI | | |
| Flash Point, °F | 96 | 100 min |
| Heat of Combustion, BTU/# | 18,637 | 18,400 min |
| Distillation, °F | | |
| IBP | 286 | |
| 10% | 321 | |
| 20% | 336 | |
| 50% | 373 | |
| 90% | 458 | |
| FBP | 506 | |
| Residue | 1.0 | |
| Loss | 0.5 | |

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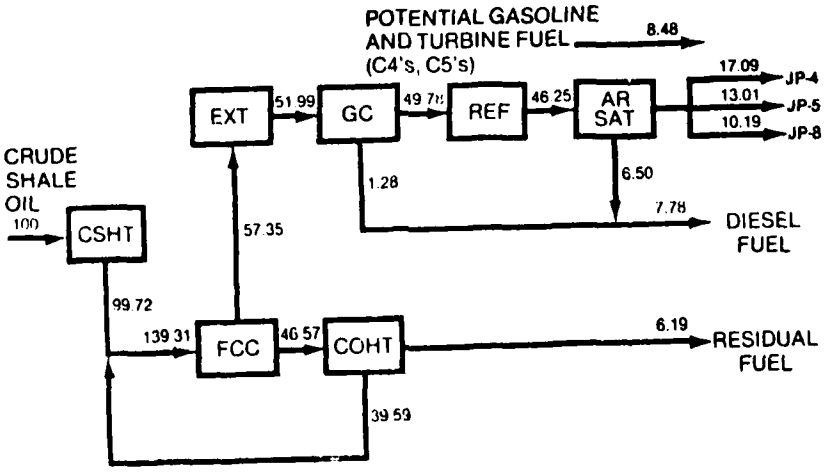


SAMPLE GC-2
Concurrent Fuel Production

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## Aviation Turbine Fuel From Crude Shale Oil Phase II

| | | |
|---|---|---|
| Sample No. | GC 2-4 | |
| Fuel Type | JP-4 | |
| Shale Source | Above Ground | |
| Gravity, API | 54.3 | Specifications 45-57 |
| Hydrogen, Wt% | 14.9 | 13.6 min |
| Saturates, Vol% | 97.9 | |
| Olefins, Vol% | 0.4 | |
| Aromatics, Vol% | 1.7 | 25.0 max |
| Freeze Point, °F | −90 | −72 max |
| RVP, PSI | 2.1 | 2.3 |
| Flash Point, °F | | |
| Heat of Combustion, BTU/# | 18,820 | 18,400 min |
| Distillation, °F | | |
| IBP | 152 | |
| 10% | 228 | |
| 20% | 247 | |
| 50% | 285 | |
| 90% | 359 | |
| FBP | 412 | |
| Residue | 1.0 | |
| Loss | 1.0 | |

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## Aviation Turbine Fuel From Crude Shale Oil Phase II

| | | |
|---|---|---|
| Sample No. | GC2-5 | |
| Fuel Type | JP-5 | |
| Shale Source | Above Ground | |
| Gravity, API | 43.3 | Specifications 36-48 |
| Hydrogen, WT% | 14.2 | 13.5 min |
| Saturates, Vol% | 92.4 | |
| Olefins, Vol% | 0.7 | |
| Aromatics, Vol% | 6.9 | 25.0 max |
| Freeze Point, °F | −68 | −51 max |
| RVP, PSI | | |
| Flash Point, °F | 146 | 140 min |
| Heat of Combustion, BTU/# | 18,648 | 18,300 min |
| Distillation, °F | | |
| IBP | 356 | |
| 10% | 380 | |
| 20% | 388 | |
| 50% | 405 | |
| 90% | 439 | |
| FBP | 452 | |
| Residue | 1.0 | |
| Loss | 0.5 | |

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## Aviation Turbine Fuel From Crude Shale Oil Phase II

| | | |
|---|---|---|
| Sample No. | GC2-8 | |
| Fuel Type | JP-8 | |
| Shale Source | Above Ground | |
| | | Specifications |
| Gravity, API | 43.6 | 37-51 |
| Hydrogen, Wt% | 14.2 | 13.6 min |
| Saturates, Vol% | 92.1 | |
| Olefins, Vol% | 0.8 | |
| Aromatics, Vol% | 7.1 | 25.0 max |
| Freeze Point, °F | —60 | —58 max |
| RVP, PSI | | |
| Flash Point, °F | 130 | 100 min |
| Heat of Combustion, BTU/# | 18,659 | 18,400 min |
| Distillation, °F | | |
| IBP | 338 | |
| 10% | 367 | |
| 20% | 377 | |
| 50% | 407 | |
| 90% | 466 | |
| FBP | 502 | |
| Residue | 1.0 | |
| Loss | 0.5 | |

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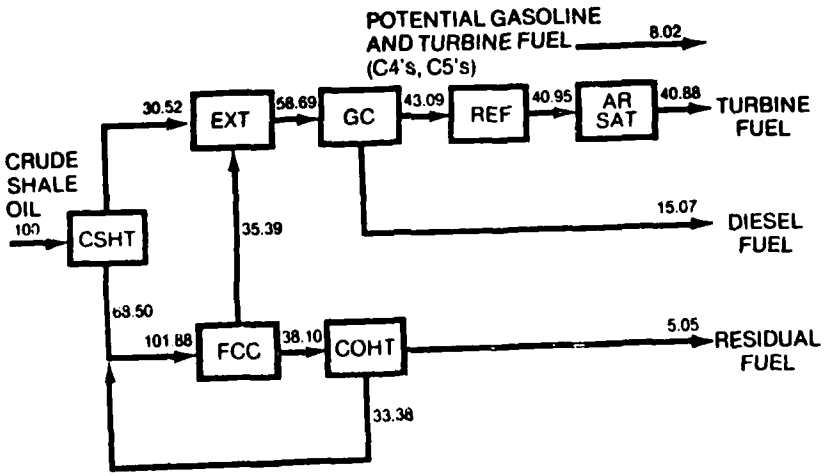


SAMPLE M-212
Target: Broad-range Turbine Fuel

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## Aviation Turbine Fuel From Crude Shale Oil Phase II

| | |
|---|---|
| Sample No. | M-212 |
| Fuel Type | *Broad Range* |
| Shale Source | Above Ground |
| Gravity, API | 44.6 |
| Hydrogen, Wt% | 14.0 |
| Saturates, Vol% | 74.7 |
| Olefins, Vol% | 1.0 |
| Aromatics, Vol% | 24.3 |
| Freeze Point, °F | −64 |
| RVP, PSI | |
| Flash Point, °F | |
| Heat of Combustion, BTU/# | 18,546 |
| Distillation, °F | |
| IBP | 241 |
| 10% | 309 |
| 20% | 336 |
| 50% | 398 |
| 90% | 466 |
| FBP | 500 |
| Residue | 1.0 |
| Loss | 1.0 |

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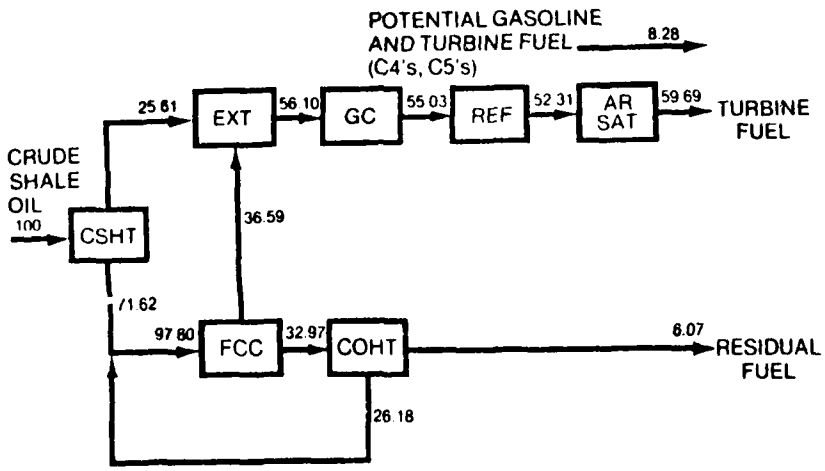


SAMPLE M-221
Target: Broad-range Turbine Fuel

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## Aviation Turbine Fuel From Crude Shale Oil Phase II

| | |
|---|---|
| Sample No. | M-221 |
| Fuel Type | Broad Range |
| Shale Source | Above Ground |
| Gravity, API | 43.3 |
| Hydrogen, Wt% | 13.6 |
| Saturates, Vol% | 66.0 |
| Olefins, Vol% | 1.0 |
| Aromatics, Vol% | 33.0 |
| Freeze Point, °F | —54 |
| RVP, PSI | |
| Flash Point, °F | |
| Heat of Combustion, BTU/# | 18,474 |
| Distillation, °F | |
| IBP | 225 |
| 10% | 299 |
| 20% | 330 |
| 50% | 402 |
| 90% | 496 |
| FBP | 536 |
| Residue | 1.0 |
| Loss | 1.0 |

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## Comparison of Potential Yields from Phases I and II

BASIS: 100,000 BPD IN SITU SHALE OIL

| Net Products | Yield Estimate, Volume Percent | |
|---|---|---|
| | Phase I | Phase II |
| Propane | 0.6 | 2.8 |
| Propylene | 7.0 | 5.6 |
| I Butane | 2.1 | 4.2 |
| n Butane | 1.0 | 2.5 |
| Butylenes | 4.9 | 2.9 |
| Gasoline | 20.1 | 24.4 |
| Turbine Fuel | 54.4 | 51.8 |
| Diesel Fuel | 0.0 | 7.1 |
| Residual Fuel | 5.0 | 2.6 |
| Total | 95.1 | 103.9 |

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IV

# SUNTECH'S ANHYDROUS HYDROGEN CHLORIDE EXTRACTION PROCESS FOR MANUFACTURING MILITARY FUELS FROM RAW SHALE OIL

By

H. E. Reif, J. P. Schwedock,

and A. Schneider

Suntech, Inc.

# SUNTECH'S ANHYDROUS HYDROGEN CHLORIDE EXTRACTION PROCESS FOR MANUFACTURING MILITARY FUELS FROM RAW SHALE OIL

H. E. Reif, J. P. Schwedock, and A. Schneider
SUNTECH, INC.

## Summary

This Phase II report incorporates pilot plant data generated for preparing a design basis for manufacturing military fuels from raw shale oil. Three different processing schemes are presented and are compared with estimates made in Phase I. Plant capacities and product yields are not optimized at this time.

The high nitrogen, oxygen, and arsenic contents of raw shale oil present special problems not encountered in refining conventional petroleum. Considerable effort was expended in selecting and evaluating non-proprietary catalysts for use in the various catalytic processing units. Main hydrotreater catalyst aging tests were performed. A six-month run using both Occidental and Paraho shale oils was carried out. An additional run of one month's duration was made at high severity with Occidental shale oil. HCl treating was selected as the most effective of three extraction processes for removing organic nitrogen from hydrotreated shale oil distillates. Depth of hydrogenating was varied to yield sufficient HCl extract in order to balance overall refinery hydrogen requirements. Hydrocracking was incorporated into the processing scheme to maximize yields of military fuels. Modification of Suntech's Hydrocracking Model was required to fit the non-proprietary catalyst's denitrogenation, hydrogenation, and cracking activity parameters.

Using material produced in our pilot plant program, five 500-ml. samples of military turbine fuels of varying characteristics were prepared for laboratory testing.

A set of tables and figures have been prepared which outline pertinent information relative to the various processing steps involved, along with preliminary economic evaluations based on guidelines furnished by the U. S. Air Force. Uncertainties and conclusions are stated.

TABLE I Suntech's processing concept is described and also shown schematically in Figure 1.

Figure 1 The schematic flow diagram for refining raw shale oil using Suntech's anhydrous HCl extraction is shown. The slate of military fuels produced is optional and they meet or exceed current specifications.

TABLE II Occidental is a higher grade of raw shale oil than Paraho based on boiling range, nitrogen, sulfur, and hydrogen contents. Both shale oils contain significant quantities of arsenic.

Figure 2 The flow diagram of a conventional raw shale oil hydrotreating and distillation operation is shown. A vacuum still is used to produce a gas oil fraction with a 1000°F. end point. The waxy nature of the 1000°F.$^+$ bottoms precludes its use in the HCl treating step due to the formation of emulsions.

TABLE III The use of less severe conditions to process whole Occidental shale oil increases the nitrogen content in the effluent in order to produce sufficient extract for hydrogen manufacture. The less severe operating conditions result in lower hydrogen consumption and a lower $C_4^+$ product yield. Note that the use of a guard case R-1 is necessary to remove arsenic from the feed, as well as to hydrogenate olefins and aromatics. R-2 catalyst life is expected to be 12 months, twice the life predicted in Phase I.

Figure 3 A two-reactor isothermal pilot plant was employed to determine catalyst aging characteristics. The catalyst aging curve shows that after the loss of the initial high activity characteristic of fresh catalysts, the temperature required in the R-2 catalyst bed to hydrotreat whole Occidental shale oil to 5000 ppm total nitrogen in the product remained essentially constant. Almost four months of successful life-testing were accumulated with Occidental shale oil. The R-1 guard reactor catalyst bed was kept at an average temperature of 650°F.

Figure 4 Using the same catalyst loading that had accumulated almost four months of life with Occidental shale oil, an additional two-month life test with Paraho shale oil was completed. Since the Paraho feed contained 2.13 wt.% total nitrogen compared to the 1.46 wt.% total nitrogen content found in Occidental shale oil, a 50°F. increase in catalyst temperature was required to yield product containing 5000 ppm total nitrogen. During this period the catalyst aged about 10°F. Based on the stable aging characteristics of the catalyst in R-2, a life expectancy of 1 year is projected; for R-1 we project a 6-month catalyst life.

Finally, a month-long run was made employing the relatively severe operating conditions of 825-850°F., 2800 psig total pressure, and a liquid hourly space velocity of one. Here the results duplicated those obtained in our subcontract with HRI by

producing less than 5 ppm total nitrogen in the reactor effluent. During this period of severe operation, some catalyst activity loss was apparent.

TABLE IV — Significant quantities of ammonia and hydrogen sulfide are produced during the hydrogenation.

TABLE V — Nitrogen, sulfur, and aromatic content increase with increasing boiling range. Very little material is found boiling below 250°F. in the hydrotreated product.

Figure 5 — The purpose of the naphtha hydrotreater is to clean up the feedstock to meet product specifications. The effluent is passed through a stripper before blending into final products.

TABLE VI — Due to the higher levels of nitrogen present in our feed to the naphtha hydrotreater, hydrogen consumption is up considerably from Phase I predictions.

TABLE VII — Inspections are shown on the 180-490°F. feed and product streams.

TABLE VIII — Note that the inspection on the feed characterizes its entire boiling range, 180-550°F. The inspection on the product characterizes the JP-8 product, that is the 290-550°F. fraction.

TABLE IX — HCl treating is more efficient in removing nitrogen compounds from heavy distillate than either DMF or methanol extraction.

Figure 6 — Pilot plant HCl treating was carried out batchwise. Due to the smooth operation of these runs, we feel that the process can be readily adapted to continuous operation and achieve similar results.

TABLES X & XII — Higher levels of nitrogen present in the long range gas oil feed require greater HCl addition than called for in Phase I. Raffinate yields for Occidental are down, while the extract yield is considerably higher than for the Paraho case in Phase I. Considerable amounts of chlorides remain in both the raffinate and decomposed adduct.

TABLE XI — Lost in the water wash of the raffinate are 64 BPSD of raffinate and 24,690 lbs./SD of anhydrous HCl.

TABLE XIII — Nitrogen and chloride concentrations in the recovered raffinate and extract phases are slightly higher than observed in the JP-4 operation.

Figure 7 — The single stage hydrocracker is shown. The products taken off the final product distillation tower are given. Extinction recycle is optional.

TABLES XIV & XVI — Originally, we intended to use a proprietary hydrocracking catalyst with which we have had experience. We were not permitted to use this catalyst for shale oil applications, and have chosen non-proprietary Catalyst "B" instead. Operating temperatures and pressures are up slightly from Phase I; however, the liquid hourly space velocity in the R-2 hydrocracker has been increased from 1.0 to 2.0.

TABLE XV — Ammonium chloride formed during the R-1 hydrotreating operation is taken out with the injection of water before the high pressure separator. High yields of JP-4 jet fuel are obtained, with the 490°F. bottoms being recycled to extinction.

TABLE XVII — High yields of JP-8 jet fuel are obtained, with the 550°F. bottoms being recycled to extinction. Significant quantities of $C_4$-290°F. material are also produced which will be used as a gasoline blend stock. Ammonium chloride is taken out with the injection of water after the R-1 hydrotreater.

TABLE XVIII — This case is similar to the maximum JP-4 operation, with the exception that there is no recycle oil to the R-2 hydrocracker. In addition to JP-4 jet fuel, diesel fuel #2, and a 675 F.$^+$ bottoms fuel oil are produced. Since there is no attempt made to add recycle oil to the R-2 hydrocracker, chemical consumption of hydrogen is significantly lower than in the maximum JP-4 case.

TABLES XIX & XX — Specification JP-4, JP-8, DF-2, and $C_4$-290 F. gasoline blendstock can be produced by Suntech's process to upgrade raw Occidental shale oil. Note that essentially complete removal of nitrogen and sulfur is obtained. The blended heavy fuel consists of the 1000 F.$^+$ bottoms from the vaccuum distillation tower blended with the 675 F.$^+$ fuel oil derived in the JP-4 plus other fuels operation. Some nitrogen and sulfur remain in the blended heavy fuel.

TABLE XXI — Material balance summaries are shown for the three cases to be examined:

(a) Maximum JP-4 Production.
(b) Maximum JP-8 Production.
(c) JP-4 Plus Other Fuels Production

TABLE XXII — Inspections and analyses of laboratory production samples of JP-4 derived from raw Occidental shale oil are presented. The very low freeze point of the 100% hydrocrackate sample demonstrates that catalytic hydrocracking of the HCl raffinate is a powerful method of meeting jet fuel freeze point specifications. The hydrocrackate can be used by itself or as a blending component for depressing freeze points of other marginal components.

TABLE XXIII Inspections and analyses of laboratory production samples of JP-8 derived from raw Occidental shale oil are shown. Note that the 100% hydrocrackate sample had a low flash point of 75°F. This is the result of a distillation error in which too low an initial cut point was taken. This is not a serious problem, as it can be easily corrected by taking a higher initial cut point during the final distillation.

TABLE XXIV Guidelines for developing Suntech's Phase II economics are given. Note that a 1st Quarter 1980 cost base is used instead of the September 1978 base used in preparing Phase I economics. Crude shale oil is valued at $30/Bbl. (vs. $16/Bbl. in Phase I) and all product fuels are equally valued at $40/Bbl. (vs. $21/Bbl. in Phase I).

TABLE XXV Estimated plant capacities and investments are presented. The main hydrotreater consists of two parallel trains with the effluents fed to a single atmospheric and vacuum distillation plant. The gas oil hydrocracker also consists of two parallel trains with the effluents distilled in a single fractionator. Improved processing information, the use of a different feedstock, and increasing the total nitrogen content in the main hydrotreater effluent from 2000 to 5000 ppm result in lower plant investments than predicted in Phase I. As in Phase I, the main hydrotreater and the TPO hydrogen plant account for the majority of the processing facility costs.

TABLE XXVI Direct plus indirect manufacturing costs vary from 3.91 to 3.99 $/Bbl. of liquid product. Total plant investments range from $841 million for the JP-4 plus other fuels case to $859 million for maximum JP-4 production. Total product costs including the adjustedcrude costs are $1.01/gal. of product for maximum JP-4; $1.03/gal. of product for maximum JP-8; and $1.04/gal. of product for the JP-4 plus other fuels case. Optimization studies have not been performed for this evaluation.

TABLE XXVII Results of the three processing routes are summarized. Based on total energy input to the refinery, 86.8 volume % jet fuel is produced when maximizing JP-4; 52.8 volume % jet fuel when maximizing JP-8; and 65.3 volume % jet fuel in the JP-4 plus other fuels case. The plant investment for a conventional petroleum fuels refinery of similar capacity is approximately 4000 $/SDB.

Plant investments for the three shale oil refineries are between 7643 to 7809 $/SDB. The higher costs result from the need to hydrotreat 100% of the crude to the processing units and the need to manufacture all of the hydrogen required. The major portion of this required hydrogen is produced by partial oxidation, which is considerably more expensive than steam reforming.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge E. J. Janoski, A. Macris, and J. J. vanVenrooy for their contributions in bringing the Phase II program to a successful completion.

## LIST OF SYMBOLS AND ABBREVIATIONS

### SYMBOLS

| | |
|---|---|
| ¢/Gal. | Cents per Gallon |
| $/B | Dollars per Barrel |
| $/CD | Dollars per Calendar Day |
| # PSD | Pounds per Stream Day |

### ABBREVIATIONS

| | |
|---|---|
| AGO | Atmospheric Gas Oil Fraction |
| BPCD | Barrels per Callendar Day |
| BPSD | Barrels per Stream Day |
| BTU's | British Thermal Units |
| DMF | n,n-Dimethylformamide |
| FOE | Fuel Oil Equivalent |
| $H_2$ | Hydrogen Gas |
| HCl | Anhydrous Hydrogen Chloride Gas |
| HP Sep | High Pressure Separator |
| $H_2S$ | Hydrogen Sulfide Gas |
| LHSV | Liquid Hourly Space Velocity |
| LP Sep | Low Pressure Separator |
| LT/SD | Long Tons per Stream Day |
| N | Nitrogen |
| NA | Not Available |
| $NH_3$ | Ammonia Gas |
| $O_2$ | Oxygen Gas |
| R-1 | First Reactor |
| R-2 | Second Reactor |
| S | Sulfur |
| ppm | Parts per Million by Weight |
| SCF $H_2$/SD | Standard Cubic Feet Hydrogen per Stream Day |
| ST/SD | Short Tons per Stream Day |
| TBP | True Boiling Point Distillation |
| TPO | Texaco Partial Oxidation Process |
| VGO | Vacuum Gas Oil Fraction |
| WTD | Weighted |
| WWT Plant | Waste Water Treating Plant (Chevron) |

TABLE I. SUNTECH CONCEPT FOR UPGRADING AND REFINING RAW SHALE OIL INTO AVIATION TURBINE FUELS

1. HYDROTREAT WHOLE SHALE OIL TO PARTIALLY REDUCE TOTAL NITROGEN CONTENT.

2. DISTILL HYDROTREATED PRODUCT INTO APPROPRIATE FRACTIONS FOR ADDITIONAL PROCESSING.

3. REHYDROTREAT LIGHT DISTILLATE FRACTION TO MEET PRODUCT SPECIFICATIONS.

4. TREAT WIDE BOILING DISTILLATE FRACTION WITH ANHYDROUS $HCL$ TO LOWER NITROGEN CONTENT IN RAFFINATE.

5. THERMALLY DECOMPOSE $HCL$ EXTRACT TO RECOVER ANHYDROUS $HCL$. GENERATE HYDROGEN BY PARTIAL OXIDATION OF NITROGEN-RICH EXTRACT FRACTION.

6. HYDROCRACK RAFFINATE FRACTION TO MAXIMIZE YIELD OF AVIATION TURBINE FUELS.

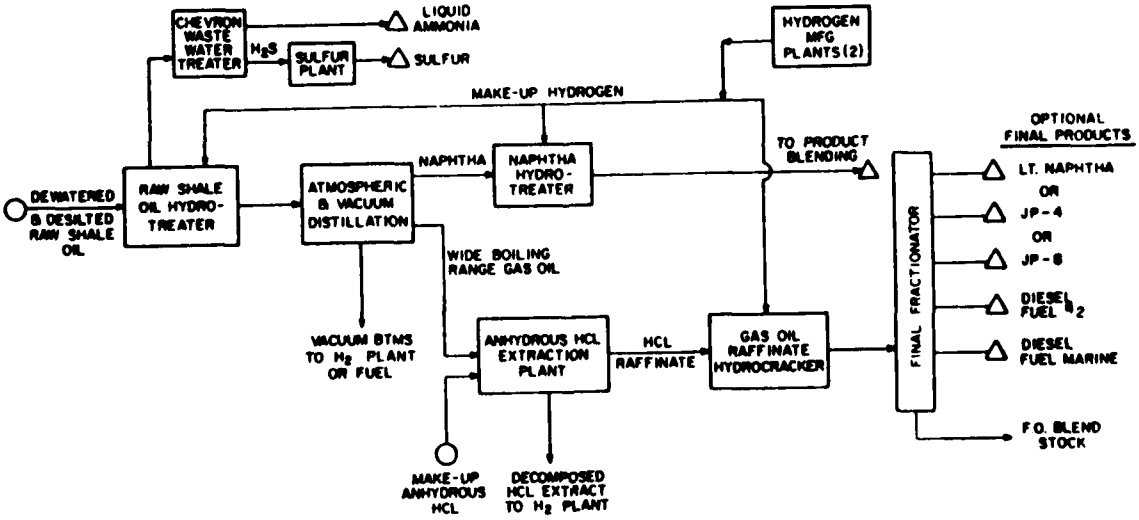


Fig. 1 SCHEMATIC FLOW DIAGRAM FOR REFINING RAW SHALE OIL USING ANHYDROUS HCL EXTRACTION

10/8/80

TABLE II. INSPECTIONS AND ANALYSES OF RAW SHALE OIL

| RAW SHALE OIL | PARAHO | OCCIDENTAL |
|---|---|---|
| INSPECTION DATA | | |
| API @ 60°F | 20.6 | 23.0 |
| SPECIFIC GRAVITY 60/60 | 0.9303 | 0.9160 |
| VISCOSITIES, KV | | |
| @ 100°F | 60 cs | 32.3 cs |
| @ 210°F | 5.38 cs | 4.82 cs |
| DISTILLATION, °F | D1160 | D2887 |
| IBP | 133 | 296 |
| 10 VOL.% | 508 | 459 |
| 30 " | 687 | 558 |
| 50 " | 798 | 605 |
| 70 " | 918 | 768 |
| 90 " | 1057 | 876 |
| FBP | 1065/95% | 1071 |
| RAMSBOTTOM CARBON RES., WT.% | 1.4 | - |
| ASPHALTENES, WT.% | - | 2.4 |
| CHEMICAL COMPOSITION DATA, WT.% | | |
| CARBON | 83.83 | 84.82 |
| HYDROGEN | 11.72 | 12.04 |
| OXYGEN | 1.31 | 1.18 |
| NITROGEN (TOTAL) | 2.13 | 1.46 |
| (BASIC) | 1.31 | 0.81 |
| SULFUR | 0.75 | 0.52 |
| IRON, PPM | 90 | - |
| ARSENIC | 34 | 33 |

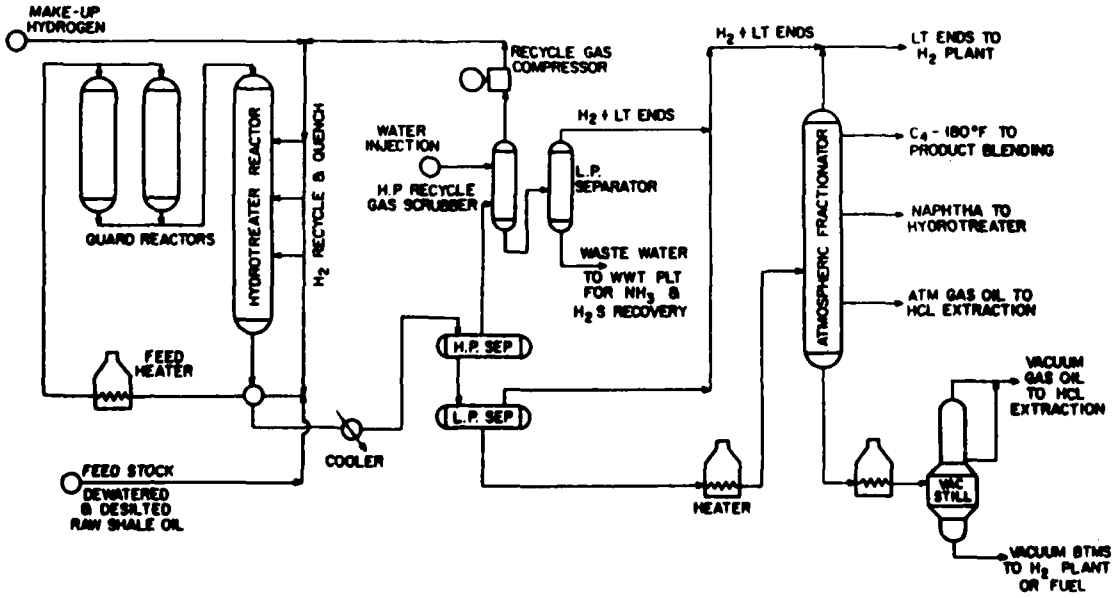


Fig. 2 SIMPLIFIED FLOW DIAGRAM OF RAW SHALE OIL HYDROTREATER AND DISTILLATION PLANTS

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TABLE III. OPERATING CONDITIONS FOR PROCESSING WHOLE OCCIDENTAL SHALE OIL

BASIS:

CHARGE RATE: 100,000 BPSD (90,000 BPCD)

OPERATING FACTOR: 0.90

CATALYSTS: NiMo ON SPHERICAL ALUMINA (R-1)
NiMo ON ALUMINA (R-2)

CATALYST LIFE: 6 MONTHS (R-1)
12 MONTHS (R-2)

REACTOR OPERATING CONDITIONS

| CASE | PHASE I (PARAHO) | PHASE II (OCCIDENTAL) |
|---|---|---|
| LHSV, V/HR/V | 0.55 | 1.0 R-1<br>1.0 R-2 |
| AVG. CATALYST TEMP., °F | | |
| R-1 | - | 625 |
| R-2 | 750 1/ | 690 |
| PRESSURE, TOTAL PSIA | 1650 | 1615 |
| $H_2$PP | 1400 | 1520 |
| RECYCLE GAS RATE, SCF/B | 4100 | 4000 |
| HYDROGEN CONSUMPTION, SCF/B | | |
| CHEMICAL | 1760 | 1100 |
| DISSOLVED | 150 | 150 |
| BLEED | 75 | 100 |
| TOTAL TO HYDROTREATER | 1985 | 1350 |
| PRODUCT DATA | | |
| TOTAL NITROGEN, PPM | 2000 | 5000 |
| SULFUR, PPM | 50 | 140 |
| $C_4$+ YIELD, VOL. % FEED | 106.96 | 103.55 |

1/ CAT. LIFE ASSUMED TO BE 6 MONTHS.

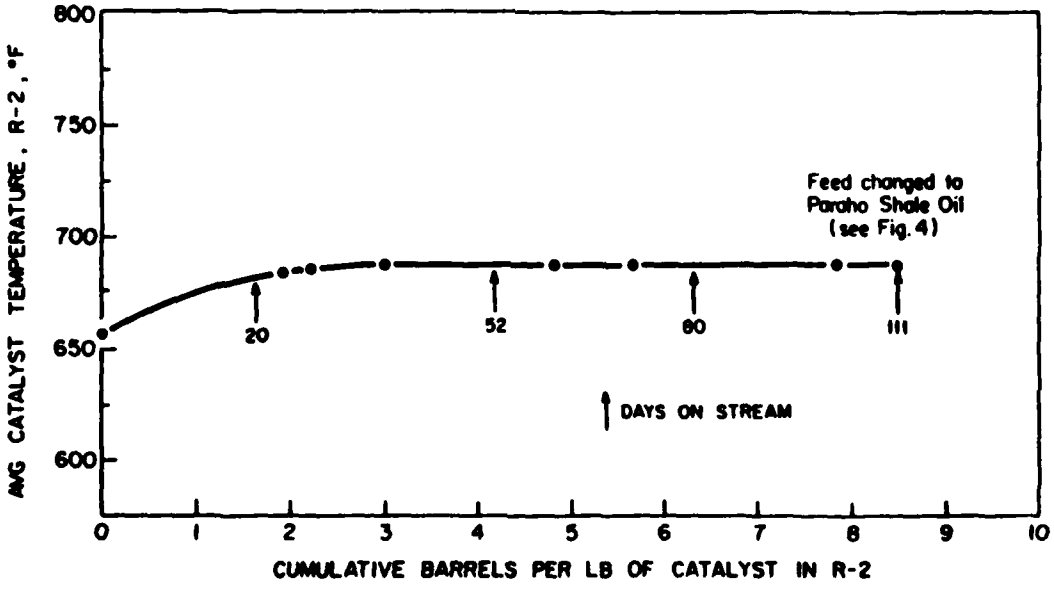


Fig. 3 CATALYST LIFE TEST FOR HYDROTREATING WHOLE OCCIDENTAL SHALE OIL
(TO 5,000 ppm $N_T$ PRODUCT)

10/8/80

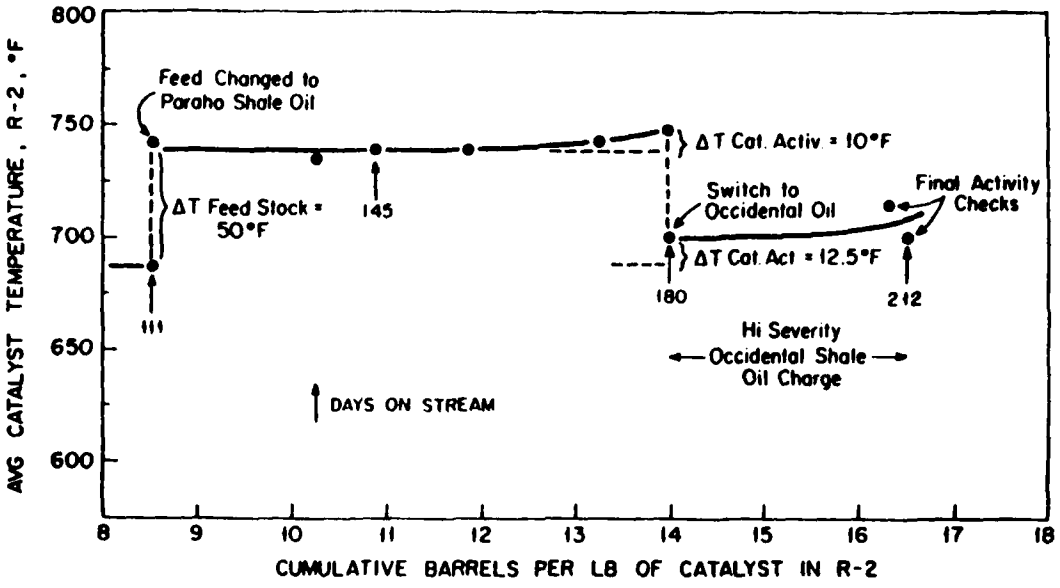


**Fig. 4 CATALYST LIFE TEST FOR HYDROTREATING WHOLE PARAHO SHALE OIL**
(TO 5,000 ppm $N_T$ PRODUCT)

10/8/80

TABLE IV. MATERIAL BALANCE SUMMARY FOR MAIN HYDROTREATER AND DISTILLATION UNITS

BASIS: 100,000 BPSD RAW OCCIDENTAL SHALE OIL
135 x $10^6$ SCF HYDROGEN PSD (110 x $10^6$ SCF $H_2$ CHEMICALLY CONSUMED PSD)
LIQUID EFFLUENT TREATED TO 5000 PPM TOTAL NITROGEN

| PRODUCTS, TBP CUT POINTS | JP-4 | JP-8 |
|---|---|---|
| AMMONIA, STPSD | 187 | 187 |
| HYDROGEN SULFIDE, SULFUR EQ. STPSD | 110 | 110 |
| UNREACTED $H_2$ SCF x $10^6$ SCF PSD | 25.0 | 25.0 |
| $C_1$-$C_3$ GASES, LBS. PSD | 385,294 | 385,294 |
| $C_4$-180°F, BPSD | 2,116 | |
| 180-490°F, BPSD | 24,141 | |
| 490-1000°F, BPSD | 73,133 | |
| $C_4$-290°F, BPSD | | 4,550 |
| 290-550°F, BPSD | | 25,561 |
| 550-1000°F, BPSD | | 69,279 |
| 1000°F+ BOTTOMS, BPSD | 4,159 | 4,159 |
| TOTAL LIQUIDS, BPSD | 103,549 | 103,549 |

TABLE V. PRODUCT INSPECTIONS ON STREAMS FROM MAIN HYDROTREATER DISTILLATION UNIT

| FRACTION | 180-490°F | 490-1000°F | $C_4$-290°F | 290-550°F | 550-1000°F | 1000°F+ BTMS. |
|---|---|---|---|---|---|---|
| API GRAVITY @ 60°F | 41.5 | 28.9 | 71.0 | 40.6 | 28.6 | 16.0 |
| DISTILLATION, °F | | | | | | |
| 1/10 | 180/290 | 490/605 | 50/145 | 290/360 | 550/606 | NA |
| 30/50 | 405/441 | 661/734 | 183/202 | 433/458 | 671/744 | - |
| 70/95 | 468/486 | 817/965 | 217/252 | 480/526 | 820/970 | - |
| EP | 490 | 1000 | 290 | 550 | 1000 | - |
| AROMATICS, WT. % | 24 VOL.% | 42 | 3 VOL.% | 25 | 45 | 50 |
| OLEFINS, VOL.% | 3 | - | - | 3 | - | - |
| TOTAL NITROGEN, PPM | 3260 | 4800 | - | 3480 | 5600 | 7900 |
| SULFUR, PPM | 65 | 140 | - | 80 | 150 | 1220 |

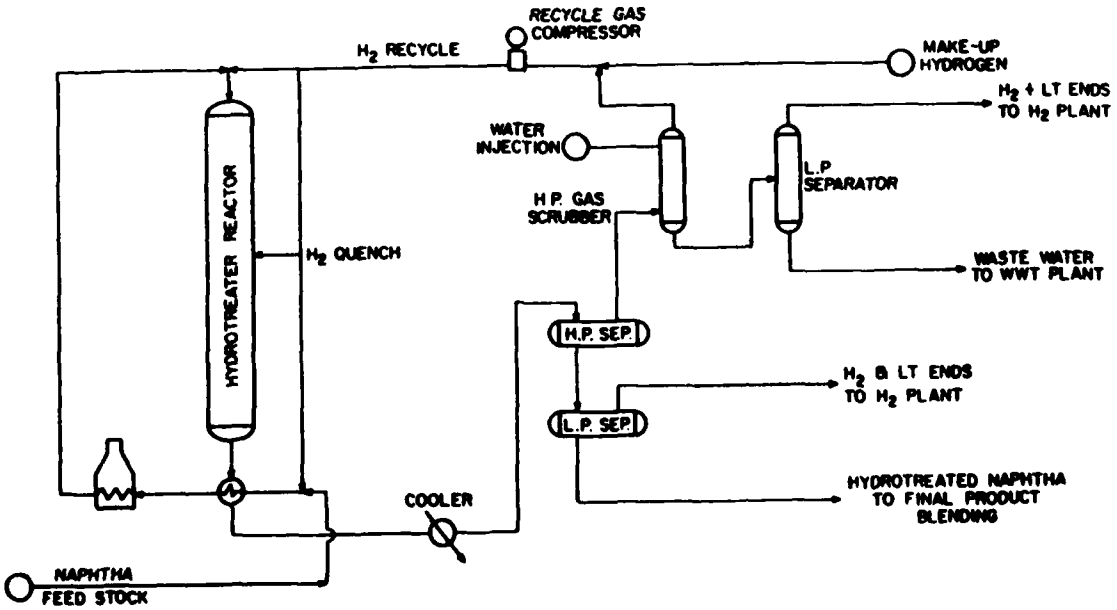


Fig. 5 SCHEMATIC FLOW DIAGRAM OF NAPHTHA HYDROTREATER

10/10/80

TABLE VI OPERATING CONDITIONS FOR NAPHTHA HYDROTREATER

OPERATING FACTOR: 0.91 PHASE I, 0.90 PHASE II

CATALYST: NiMo ON ALUMINA

CATALYST LIFE: 2 YEARS

REACTOR OPERATING CONDITIONS:

| CASE | PHASE I MAX.JP-4 | PHASE II MAX.JP-4 | PHASE I MAX.JP-8 | PHASE II MAX. JP-8 |
|---|---|---|---|---|
| FEEDSTOCK TBP BOILING RANGE, °F | 180-450 | 180-490 | 180-535 | 180-550 |
| TOTAL NITROGEN, PPM | 620 | 3260 | 690 | 3480 |
| LHSV, V/HR/V | ~2.0 | 2.0 | ~2.0 | 2.0 |
| AVG. CATALYST TEMP., °F | ~725 | 750 | ~725 | 750 |
| TOTAL PRESSURE, PSIA | 1215 | 1500 | 1215 | 1500 |
| $H_2$PP | 1100 | 1400 | 1100 | 1400 |
| RECYCLE GAS RATE, SCF/B | 4500 | 4000 | 4500 | 4000 |
| HYDROGEN CONSUMPTION, SCF/B | | | | |
| CHEMICAL | 78 | 350 | 96 | 400 |
| DISSOLVED | 40 | 50 | 40 | 50 |
| TOTAL TO HYDROTREATER | 118 | 400 | 136 | 450 |
| PRODUCT | | | | |
| TOTAL NITROGEN, PPM | 4 | 8 | 4 | 8 |
| SULFUR, PPM | NIL | 2 | NIL | 2 |
| $C_4$+ YIELD, VOL.% FEED | 101.28 | 101.66 | 100.97 | 102.24 |

TABLE VII. MATERIAL BALANCE SUMMARY FOR NAPHTHA HYDROTREATER

JP-4 OPERATION

BASIS: 24,141 BPSD OF 180-490°F NAPHTHA FRACTION
9.66 x $10^6$ SCF HYDROGEN PSD (8.45 x $10^6$ SCH $H_2$ CHEMICALLY CONSUMED)

PRODUCTS

| | |
|---|---|
| AMMONIA, STPSD | 13.7 |
| HYDROGEN SULFIDE, SULFUR, EQ,STPSD | 0.2 |
| UNREACTED $H_2$ x $10^6$ SCF PSD | 1.21 |
| $C_1$-$C_3$ GASES, LBS PSD | 13.956 |
| $C_4$-180°F, BPSD | 1,207 |
| 180-490°F BPSD | 23,335 |
| TOTAL CUT | 24,542 |

INSPECTIONS ON 180-490°F CUT

| | FEED | PRODUCT |
|---|---|---|
| API GRAVITY @ 60°F | 41.5 | 42.3 |
| AROMATICS, VOL. % | 24.3 | 15.0 |
| OLEFINS, VOL. % | 3.0 | 1.4 |
| TOTAL NITROGEN, PPM | 3260 | 8.0 |
| SULFUR, PPM | 65 | 2.0 |

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TABLE VIII MATERIAL BALANCE SUMMARY FOR NAPHTHA HYDROTREATER

JP-8 OPERATION

BASIS: 27,995 BFSD OF 180-550°F KEROSINE FRACTION
12.60 x $10^6$ SCF HYDROGEN PSD (11.20 x $10^6$ SCF $H_2$ CHEMICALLY CONSUMED)

| PRODUCTS | |
|---|---|
| AMMONIA, STPSD | 17.0 |
| HYDROGEN SULFIDE, SULFUR EQ, STPSD | 0.3 |
| UNREACTED $H_2$ x $10^6$ SCF PSD | 1.40 |
| $C_1$-$C_3$ GASES, LBS. PSD | 16,185 |
| $C_4$ - 290°F, BPSD | 4,937 |
| 290-550°F, BPSD | 23,685 |

INSPECTIONS ON FEED AND PRODUCT

| | 180-550°F FEED | 290-550°F PRODUCT |
|---|---|---|
| API GRAVITY @ 60°F | 40.6 | 41.6 |
| AROMATICS, VOL. % | 25.0 | 15.0 |
| OLEFINS, VOL. % | 3.2 | 1.4 |
| TOTAL NITROGEN, PPM | 3480 | 8.0 |
| SULFUR, PPM | 80 | 2.0 |

TABLE IX. EVALUATION OF NITROGEN EXTRACTION PROCESSES

1. DMF AND METHANOL APPEAR TO BE ABOUT EQUAL FOR EXTRACTING NITROGEN COMPOUNDS FROM LIGHT DISTILLATES ( < 700°F E.P.) DERIVED FROM MILDLY HYDROTREATED OCCIDENTAL SHALE OIL.

2. THESE SOLVENTS WOULD BE USEFUL FOR REMOVING NITROGEN COMPOUNDS IN THE JP-4 THROUGH DF-2 BOILING RANGE. ABOVE 700°F, THESE SOLVENTS APPEAR TO BE MARGINAL.

3. SOLVENT EXTRACTION TO REMOVE NITROGEN COMPOUNDS FROM 700°F+ FRACTIONS OF HYDROTREATED SHALE OIL FOR UPGRADING FEEDSTOCKS FOR HYDROCRACKING, CATALYTIC CRACKING AND LUBE MANUFACTURE WOULD BE INEFFECTIVE.

4. HCL TREATMENT OF 450-1000°F DISTILLATE FRACTIONS OF HYDROTREATED SHALE OIL WAS MORE EFFECTIVE FOR REMOVAL OF NITROGEN CONTAINING COMPOUNDS THAN SOLVENT EXTRACTION.

THEREFORE, HCL EXTRACTION IS THE PROCESS OF CHOICE FOR REMOVING NITROGEN COMPOUNDS FROM HIGH BOILING FRACTIONS OF MILDLY HYDROTREATED SHALE OIL.

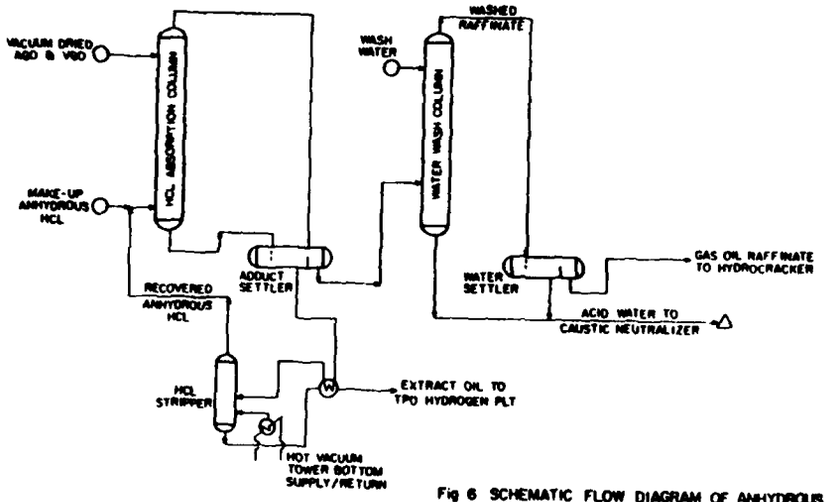


Fig 6 SCHEMATIC FLOW DIAGRAM OF ANHYDROUS HCL EXTRACTION PLANT

10/10/80

TABLE X. MAXIMUM JP-4 - $HCL$ TREATING FOR REMOVING NITROGEN FROM HYDROTREATED SHALE OIL (5000 PPM)

| CASE | PHASE I | PHASE II |
|---|---|---|
| HYDROTREATED FEED | | |
| TBP BOILING RANGE, °F | 450-1000 | 490-1000 |
| API GRAVITY | 31.9 | 28.9 |
| TOTAL NITROGEN, PPM | 2000 | 4800 |
| SULFUR, PPM | 55 | 140 |
| AROMATICS AND POLARS, WT.% | 26 | 42 |
| REACTOR CONDITIONS ($HCL$ TREATMENT) | | |
| RESIDENCE TIME, MINUTES | ~10 | 30 |
| INLET TEMP., °F | 100 | 100 |
| OUTLET TEMP., °F | 105 | 110 |
| TOTAL PRESSURE, PSIG | ~1 | 1 |
| $HCL$ ADDITION, LBS/100 LBS. FEED | 0.98 | 2.68 |
| SETTLING TIME, MINUTES | ~15 | 30 |
| RAFFINATE PHASE DATA | | |
| YIELD, WT.% OIL CHARGED | 97.0 | 86.2 |
| API GRAVITY | 32.5 | 30.7 |
| TOTAL NITROGEN, PPM | 720 | 700 |
| SULFUR, PPM | 30 | 17 |
| AROMATICS AND POLARS, WT.% | 24.0 | 34 |
| CHLORIDE, PPM | 200 | 700 |

(CONT'D.)

TABLE X (CONT'D.)

MAXIMUM JP-4 (CONT'D.)

| | PHASE I | PHASE II |
|---|---|---|
| HCL ADDUCT DECOMPOSITION CONDITIONS | | |
| RESIDENCE TIME, MINUTES | ~5 | 30 |
| TEMPERATURE, °F | 575 | 575 |
| TOTAL PRESSURE, PSIG | 1 | 1 |
| HCL RECOVERY, WT.% REACTED | 96.2 | 95.93 |
| DECOMPOSED ADDUCT (HCL-FREE BASIS) | | |
| YIELD, WT.% OIL CHARGED | 3.0 | 13.9 |
| API GRAVITY | 12.5 | 16.8 |
| TOTAL NITROGEN, WT.% | 4.34 | 3.02 |
| SULFUR, PPM | 860 | 900 |
| AROMATICS AND POLARS, WT.% | ~90 | 89 |
| CHLORINE, PPM | 5000 | 1500 |

TABLE XI MATERIAL BALANCE SUMMARY OF ANHYDROUS HYDROGEN CHLORIDE EXTRACTION UNITS

JP-4 OPERATION

BASIS: 490-1000°F HYDROTREAT GAS OIL FEED

| | FEED | RECOVERED HCL-FREE RAFFINATE | RECOVERED EXTRACT |
|---|---|---|---|
| YIELDS | | | |
| WT.% | 100 | 86.2 | 13.9 |
| VOL.% | 100 | 87.1 | 12.8 |
| BBL/SD | 73,133 | 63,681 | 9,388 |
| INSPECTIONS & ANALYSES | | | |
| API/SP GRAV @ 60°F | 28.9/0.8823 | 30.7/0.8725 | 18.4/0.9542 |
| AROMATICS, WT.% | 42 | 34 | 89 |
| TOTAL NITROGEN, PPM | 4800 | 700 | 3.02 WT.% |
| SULFUR, PPM | 140 | 17 | 900 |
| CHLORINE, PPM | 0 | 700 | 1500 |

LOSSES: RAFFINATE = 64 BPSD
ANHYDROUS HCL = 24,690 LBS/SD

TABLE XII. MAXIMUM JP-8 - $HCl$ TREATING FOR REMOVING NITROGEN FROM HYDROTREATED SHALE OIL (5,000 PPM)

| CASE: | PHASE I | PHASE II |
|---|---|---|
| HYDROTREATED FEED | | |
| TBP BOILING RANGE, °F | 535-1000°F | 550-1000°F |
| API GRAVITY | 31.0 | 28.5 |
| TOTAL NITROGEN, PPM | 2210 | 5600 |
| SULFUR, PPM | 60 | 150 |
| AROMATICS AND POLARS, WT.% | 26.7 | 45 |
| REACTOR CONDITIONS ($HCl$ TREATMENT) | | |
| RESIDENCE TIME, MINUTES | ~10 | 30 |
| INLET TEMP., °F | 100 | 100 |
| OUTLET TEMP., °F | 105 | 110 |
| TOTAL PRESSURE, PSIG | ~1 | 1 |
| $HCl$ ADDITION, LBS/100 LBS. FEED | 1.08 | 2.70 |
| SETTLING TIME, MINUTES | ~15 | 30 |
| RAFFINATE PHASE DATA | | |
| YIELD, WT.% OIL CHARGED | 96.6 | 86.2 |
| API GRAVITY | 31.7 | 30.3 |
| TOTAL NITROGEN, PPM | 770 | 750 |
| SULFUR, PPM | 40 | 28 |
| AROMATICS AND POLARS, WT.% | 24.5 | 35 |
| CHLORINE, PPM | 220 | 750 |

(CONT'D.)

TABLE XII (CONT'D.)

MAXIMUM JP-8 (CONT'D.)

| | PHASE I | PHASE II |
|---|---|---|
| $HCl$ ADDUCT DECOMPOSITION CONDITIONS | | |
| RESIDENCE TIME, MINUTES | ~5 | 30 |
| TEMPERATURE, °F | 575 | 575 |
| TOTAL PRESSURE, PSIG | 1 | 1 |
| $HCl$ RECOVERY, WT.% REACTED | 96.55 | 95.63 |
| DECOMPOSED ADDUCT ($HCl$-FREE BASIS) | | |
| YIELD, WT.% OIL CHARGED | 3.4 | 13.9 |
| API GRAVITY | 11.3 | 16.3 |
| TOTAL NITROGEN, WT.% | 4.31 | 3.57 |
| SULFUR, PPM | 630 | 930 |
| AROMATICS AND POLARS, WT.% | ~90.0 | 89 |
| CHLORINE, PPM | 5000 | 1800 |

TABLE XIII. MATERIAL BALANCE SUMMARY OF ANHYDROUS HYDROGEN CHLORIDE EXTRACTION UNITS

JP-8 OPERATION

BASIS: 550-1000°F HYDROTREATED GAS OIL FEED

| | FEED | RECOVERED HCL-FREE RAFFINATE | RECOVERED EXTRACT |
|---|---|---|---|
| YIELDS | | | |
| WT.% | 100 | 86.2 | 13.9 |
| VOL.% | 100 | 87.1 | 12.8 |
| BBL/SD | 69,279 | 60,329 | 8,890 |
| INSPECTIONS AND ANALYSES | | | |
| API/SP GRAV @ 60°F | 28.6/0.8842 | 30.3/0.8744 | 16.3/0.9573 |
| AROMATICS, WT.% | 45 | 35 | 89 |
| TOTAL NITROGEN, PPM | 5600 | 750 | 3.57 WT.% |
| SULFUR, PPM | 150 | 28 | 930 |
| CHLORINE, PPM | 0 | 750 | 1800 |

LOSSES: RAFFINATE = 60 BPSD
ANHYDROUS HCL = 25,340 LBS/SD

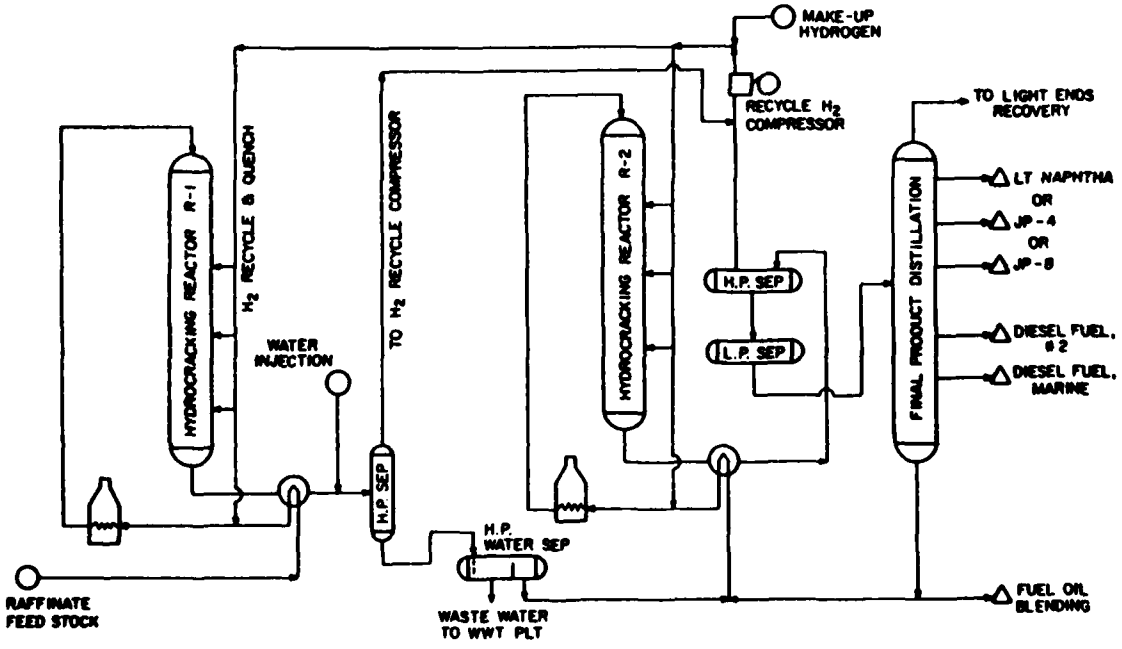


Fig. 7 SCHEMATIC FLOW DIAGRAM OF SINGLE STAGE HYDROCRACKER FOR MANUFACTURING MILITARY FUELS FROM SHALE OIL

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## TABLE XIV. MAXIMUM JP-4 OPERATING CONDITIONS FOR GAS OIL HYDROCRACKER

| CASE: | PHASE I R-1 | PHASE I R-2 | PHASE II R-1 | PHASE II R-2 |
|---|---|---|---|---|
| OPERATING FACTOR | 0.91 | | 0.90 | |
| CATALYST | PROPRIETARY | PROPRIETARY | NiMo | "B" |
| CATALYST LIFE, YEARS | 3 | 6 | 2 | 2 |
| **REACTOR OPERATING CONDITIONS:** | | | | |
| LHSV, VOL/HR/V | 1 | | 1 | 2 |
| AVERAGE CATALYST TEMP, °F | 690 | | 710 | 710 |
| TOTAL PRESSURE | 1600 | | 1700 | |
| RECYCLE GAS RATE, SCF/B | 6000 | | 6000 | |
| HYDROGEN CONSUMPTION, SCF/B | | | | |
| CHEMICAL | 1250 | | 1450 | |
| DISSOLVED | 105 | | 115 | |
| TOTAL | 1355 | | 1565 | |
| CONVERSION, VOL.% FRESH FEED | 42 | | 70 | |
| **FEEDSTOCK CHARACTERIZATION:** | | | | |
| TBP BOILING RANGE, °F | 450-1000 | | 490-1000 | |
| API GRAVITY | 32.5 | | 30.7 | |
| TOTAL NITROGEN, PPM | 720 | | 700 | |
| **PRODUCTS, VOL.% FRESH FEED** | | | | |
| $C_3$+ YIELD | 115.0 | | 114.1 | |
| JP-4 | 115.0 | | 114.1 | |

## TABLE XV. MATERIAL BALANCE SUMMARY FOR GAS OIL HYDROCRACKER JP-4 OPERATION

BASIS: 63,681 BPSD OF HCL RAFFINATE
99.66 x $10^6$ SCF HYDROGEN PSD (92.34 x $10^6$ SCF $H_2$ PSD CHEMICALLY CONSUMED)

**PRODUCTS**

| | |
|---|---|
| AMMONIUM CHLORIDE, STPSD | 10.3 |
| AMMONIA, STPSD | 5.0 |
| HYDROGEN SULFIDE, SULFIDE EQ. STPSD | 0.6 |
| UNREACTED $H_2$ x $10^6$ SCF PSD | 7.32 |
| $C_1$-$C_3$ GASES, LBS PSD | 408,529 |
| $C_4$-180°F, BPSD | 10,259 |
| 180-490°F, BPSD | 64,420 |

**INSPECTIONS ON FEED AND PRODUCT**

| | FEED | JP-4 PRODUCT |
|---|---|---|
| API GRAVITY @ 60°F | 30.7 | 54.7 |
| AROMATICS, % | 34 WT. | 15 VOL. |
| OLEFINS, VOL. % | - | 1.4 |
| TOTAL NITROGEN | 700 | 1 |
| SULFUR, PPM | 17 | 1 |

TABLE XVI. MAXIMUM JP-8 - OPERATING CONDITIONS FOR GAS OIL HYDROCRACKER

| CASE: | PHASE I R-1 | PHASE I R-2 | PHASE II R-1 | PHASE II R-2 |
|---|---|---|---|---|
| OPERATING FACTOR | 0.91 | | 0.90 | |
| CATALYST | PROPRIETARY | PROPRIETARY | NiMo | "B" |
| CATALYST LIFE, YEARS | 3 | 6 | 2 | 2 |
| REACTOR OPERATING CONDITIONS: | | | | |
| LHSV, VOL/HR/V | 1 | | 1 | 2 |
| AVERAGE CATALYST TEMP., °F | 690 | | 710 | 740 |
| TOTAL PRESSURE | 1600 | | 1700 | |
| RECYCLE GAS RATE, SCF/B | 6000 | | 6000 | |
| HYDROGEN CONSUMPTION, SCF/B | | | | |
| CHEMICAL | 1250 | | 1450 | |
| DISSOLVED | 105 | | 125 | |
| TOTAL | 1355 | | 1575 | |
| CONVERSION, VOL.% FRESH FEED | 42 | | 70 | |
| FEEDSTOCK CHARACTERIZATION | | | | |
| TBP BOILING RANGE, °F | 535-1000 | | 550-1000 | |
| API GRAVITY | 32.5 | | 30.3 | |
| TOTAL NITROGEN, PPM | 720 | | 750 | |
| PRODUCTS, VOL.% FRESH FEED | | | | |
| $C_4$+ YIELD | 114.6 | | 111.3 | |
| $C_4$-290°F B.R. | 45.9 | | 49.1 | |
| JP-8 (290-550°F B.R.) | 68.7 | | 62.2 | |

TABLE XVII. MATERIAL BALANCE SUMMARY FOR GAS OIL HYDROCRACKER

JP-8 OPERATION

BASIS: 60,329 BPSD OF HCL RAFFINATE

95.02 x $10^6$ SCF HYDROGEN PSD (87.48 x $10^6$ SCF $H_2$ PSD CHEMICALLY CONSUMED)

PRODUCTS

| | |
|---|---|
| AMMONIUM CHLORIDE, STPSD | 10.4 |
| AMMONIA, STPSD | 5.1 |
| HYDROGEN SULFIDE, SULFUR EQ., STPSD | 0.7 |
| UNREACTED $H_2$ x $10^6$ SCF PSD | 7.54 |
| $C_1$-$C_3$ GASES, LBS PSD | 661,589 |
| $C_4$-290°F, BPSD | 29,555 |
| 290-550°F, BPSD | 37,573 |

INSPECTIONS ON FEED AND PRODUCT

| | FEED | JP-8 PRODUCT |
|---|---|---|
| API GRAVITY @ 60°F | 30.3 | 43.0 |
| AROMATICS, % | 35 WT. | 16 VOL. |
| OLEFINS, VOL. % | - | 1.6 |
| TOTAL NITROGEN, PPM | 750 | 1 |
| SULFUR, PPM | 28 | 1 |

TABLE XVIII JP-4 AND OTHER FUELS - OPERATING CONDITIONS FOR GAS OIL HYDROCRACKER

| | | PHASE II | |
|---|---|---|---|
| CASE: | R-1 | | R-2 |
| OPERATING FACTOR | | 0.90 | |
| CATALYST | NiMo | | "B" |
| CATALYST LIFE, YEARS | 2 | | 2 |
| REACTOR OPERATING CONDITIONS: | | | |
| LHSV, VOL/HR/V | 1 | | 2 |
| AVERAGE CATALYST TEMP., °F | 710 | | 710 |
| TOTAL PRESSURE | | 1700 | |
| RECYCLE GAS RATE, SCF/B | | 6000 | |
| HYDROGEN CONSUMPTION, SCF/B | | | |
| CHEMICAL | | 1150 | |
| DISSOLVED | | 105 | |
| TOTAL | | 1255 | |
| CONVERSION, VOL.% FRESH FEED | | 70 | |
| FEEDSTOCK CHARACTERIZATION | | | |
| T&P BOILING RANGE, °F | | 490-1000 | |
| API GRAVITY | | 30.7 | |
| TOTAL NITROGEN, PPM | | 700 | |
| PRODUCTS, VOL.% FRESH FEED | | | |
| $C_4$+ YIELD | | 109.8 | |
| JP-4 | | 76.1 | |
| DF-2 (490-675°F B.R.) | | 25.0 | |
| FUEL OIL (675°F+ BOTTOMS | | 8.7 | |

TABLE XIX. MATERIAL BALANCE SUMMARY FOR GAS OIL HYDROCRACKER JP-4 PLUS OTHER FUELS

BASIS: 63,681 BPSD OF HCL RAFFINATE
$79.92 \times 10^6$ SCF HYDROGEN PSD ($73.23 \times 10^6$ SCF $H_2$ PSD CHEMICALLY CONSUMED)

| PRODUCTS | |
|---|---|
| AMMONIUM CHLORIDE, STPSD | 10.3 |
| AMMONIA, STPSD | 5.0 |
| HYDROGEN SULFIDE, SULFUR EQ., STPSD | 0.6 |
| UNREACTED $H_2 \times 10^6$ SCF PSD | 6.69 |
| $C_1$-$C_3$ GASES, LBS PSD | 312,950 |
| $C_4$-180°F, BPSD | 6,725 |
| 180-490°F, BPSD | 41,711 |
| 490-675°F, BPSD | 15,920 |
| 675°F, BPSD 675°F+ BOTTOMS, BPSD | 5,540 |

INSPECTIONS ON FEED AND PRODUCTS

| | FEED | JP-4 | DF-2 | 675°F+ BTMS. |
|---|---|---|---|---|
| API GRAVITY @ 60°F | 30.7 | 54.7 | 36.0 | 33.0 |
| AROMATICS, % | 34 WT. | 15 VOL. | 23 WT. | 30 WT. |
| OLEFINS, VOL.% | - | 1.4 | - | - |
| TOTAL NITROGEN, PPM | 700 | 1 | 1 | 3 |
| SULFUR, PPM | 17 | 1 | 1 | 2 |

TABLE XX. PRODUCT INSPECTIONS AND ANALYSES

| CHEMICAL AND PHYSICAL TEST DATA | JP-4 | JP-8 | 1-290°F | DF-2 | BLENDED HEAVY FUEL |
|---|---|---|---|---|---|
| API @ 60°F | 50.9 | 42.9 | 71.0 | 38.0 | 25.7 |
| DISTILLATION, °F | D 2887 | D 2887 | D-86 | D-86 | NA |
| I | 158 | 210 | 50 | 450 | - |
| 10 VOL.% | - | 310 | 145 | 480 | - |
| 20 VOL.% | 260 | 352 | 170 | 495 | - |
| 50 VOL.% | 342 | 410 | 202 | 535 | - |
| 90 VOL.% | 459 | 510 | 240 | 590 | - |
| EP | 527 | 560 | 290 | 650 | - |
| AROMATICS, % | 15 | 16 | 3 | 24 | 36 |
| OLEFINS, VOL.% | 1 | 2 | 1 | - | - |
| MERCAPTANS, WT.% | 0.0001 | 0.0003 | - | - | - |
| SULFUR, WT.% | 0.0003 | 0.0002 | NA | 0.0011 | 0.06 |
| NITROGEN (TOTAL), PPM | 5 | 3 | 1 | 3 | 3600 |
| FLASH, °F | - | 100 | - | 210 | - |
| FREEZE PT., °F | -72 | -70 | -76 | -10 | - |
| NET HT. OF COMB., BTU/LB | 18,764 | 18,610 | 19,050 | 18,730 | 18,500 |
| $H_2$ CONTENT, WT.% | 14.16 | 13.85 | NA | NA | NA |

TABLE XXI. MATERIAL BALANCE SUMMARY

BASIS: 100,000 BPSD RAW OCCIDENTAL SHALE OIL REFINERY

| | MAX. JP-4 | MAX. JP-8 | JP-4 PLUS OTHER FUELS |
|---|---|---|---|
| NET PRODUCTS, BPSD (TBP CUTS) | | | |
| $C_4$ - 290°F B.R. NAPHTHA | - | 36,608 | - |
| $C_4$ - 490°F B.R. JP-4 | 101,337 | - | 75,094 |
| 290-550°F B.R. JP-8 | - | 61,258 | - |
| 490-675°F B.R. DF-2 | - | - | 15,920 |
| 675-1000°F B.R. HEAVY FUEL | - | - | 5,540 |
| 1000°F+ BOTTOMS HEAVY FUEL | 4,159 | 4,159 | 4,159 |
| TOTAL FUELS | 105,496 | 102,025 | 100,713 |
| OTHER PRODUCTS, STPSD | | | |
| LIQUID AMMONIA | 203 | 207 | 203 |
| SULFUR | 111 | 111 | 111 |
| AMMONIUM CHLORIDE | 14 | 14 | 14 |
| LIQUID FUEL YIELDS | | | |
| TOTAL PRODUCTS AS VOL. % PROCESS FEEDS | 105.1 | 102.0 | 100.7 |
| NAPHTHA | - | 36.5 | - |
| JP-4 | 101.0 | - | 75.1 |
| JP-8 | - | 61.3 | - |
| DF-2 | - | - | 15.9 |
| HEAVY FUEL | 4.1 | 4.2 | 9.7 |
| TOTAL REFINERY INPUT (CRUDE, FUEL AND UTILITIES CONVERTED TO FOE), BPSD | 116,776 | 116,105 | 115,143 |
| TOTAL PRODUCTS AS VOL. % REFINERY INPUT | 90.3 | 87.9 | 87.5 |
| NAPHTHA | - | 31.5 | - |
| JP-4 | 86.8 | - | 65.3 |
| JP-8 | - | 52.8 | - |
| DF-2 | - | - | 13.8 |
| HEAVY FUEL | 3.5 | 3.6 | 8.4 |
| OVERALL REFINERY THERMAL ENERGY EFFICIENCY,% | 76 | 75 | 76 |

TABLE XXII. INSPECTIONS AND ANALYSES OF LABORATORY PRODUCTION SAMPLES OF JP-4 FROM RAW OCCIDENTAL SHALE OIL

| | SPEC. | CONVENTIONAL | LOW AROM. | HIGH AROM |
|---|---|---|---|---|
| COMPOSITION, VOL.% | | | | |
| HYDRO. NAPHTHA | NA | 15 | 0 | 60 |
| HYDROCRACKATE | NA | 85 | 100 | 40 |
| CHEMICAL & PHYSICAL TEST DATA | | | | |
| AROMATICS, VOL.% MAX | 25.0 | 14.6 | 4.4 | 17.0 |
| OLEFINS, VOL.% MAX | 5.0 | 1.3 | 1.4 | 2.6 |
| MERCAPTANS, WT.% MAX | 0.001 | 0.0001* | <0.0001* | 0.0001* |
| SULFUR, WT.% MAX | 0.40 | 0.0003 | 0.0003 | 0.0005 |
| NITROGEN (TOTAL), PPM | NA | 5 | <1 | 27 |
| SIMULATED DISTILLATION, °F (ASTM D 2887) | | | | |
| IBP | REPORT | 158 | 100 | 105 |
| 20 VOL.% (MAX. TEMP.) | 266 | 260 | 213 | 216 |
| 50 VOL.% (MAX. TEMP.) | 365 | 342 | 304 | 356 |
| 90 VOL.% (MAX. TEMP.) | 482 | 459 | 440 | 479 |
| EP VOL.% (MAX. TEMP.) | 608 | 527 | 540 | 598 |
| DENSITY @ 15°C, MIN/MAX | 0.751/0.802 | 0.776 | 0.753 | 0.779 |
| RVP (100°F) psi MIN/MAX | 2.0/4.0 | 1.6* | 2.2* | 2.6* |
| FREEZE PT., °F, MAX. | -72 | -72 | <-89 | -72 |
| NET HT OF COMB, MIN | 18,400 | 18,674* | 18,824* | 18,706* |
| $H_2$ CONTENT, WT.% MIN. | 13.6 | 14.16* | 14.80* | 14.24* |
| COPPER STRIP, CORROSION, MAX. | 1a | 1- | 1- | 1- |

* DATA FROM FUELS LAB, WPAFB

TABLE XXIII. INSPECTIONS AND ANALYSES OF LABORATORY PRODUCTION SAMPLES OF JP-8 FROM RAW OCCIDENTAL SHALE OIL

| | SPEC. | 100% HYDRO. NAPHTHA | 100% CRACKATE |
|---|---|---|---|
| CHEMICAL AND PHYSICAL TEST DATA | | | |
| AROMATICS, VOL. % MAX. | 25.0 | 13.2 | 17.4 |
| OLEFINS, VOL. % MAX. | 5.0 | 1.4 | 2.3 |
| MERCAPTANS, WT.% MAX. | 0.001 | 0.0001* | 0.0003* |
| SULFUR, WT.% MAX. | 0.4 | 0.0006 | 0.0003 |
| NITROGEN (TOTAL), PPM | NA | 7.3 | 1.4 |
| SIMULATED DISTILLATION, °F (ASTM D 2887) | | | |
| IBP | REPORT | 210 | 187 |
| 10 VOL.% (MAX. TEMP.) | 367 | 310 | 271 |
| 20 " " | REPORT | 352 | 313 |
| 50 " " | REPORT | 403 | 416 |
| 90 " " | REPORT | 464 | 534 |
| EP | 626 | 516 | (586) |
| FLASH, °F, MIN. | 100 | 100 | 75** |
| DENSITY @ 15°C, MIN. | 0.775 | 0.796 | 0.814 |
| MAX. | 0.840 | | |
| FREEZE PT., °F | -58 | -62 | <-76 |
| NET HT OF COMB., BTU/LB. | 18,400 | 18,639* | 18,588* |
| $H_2$ CONTENT, WT.% MIN. | 13.6 | 13.98* | 13.75 |
| COPPER STRIP CORROSION, MAX. | 1a | 1- | 1- |

* DATA FROM FUELS LAB, WPAFB

** DOES NOT MEET SPEC. DUE TO LOW IBP.

## TABLE XXIV. BASIS FOR DEVELOPING PHASE II PRELIMINARY ECONOMIC EVALUATION

**CAPITAL INVESTMENT:**

- MIDWEST PLANT LOCATION ADJACENT TO EXISTING REFINERY
- 100,000 BPSD CRUDE SHALE OIL CAPACITY
- 1ST QUARTER 1980 COST BASE
- 100% EQUITY FINANCING
- INVESTMENT TIMING OVER THREE-YEAR CONSTRUCTION PERIOD
  - 25% FIRST YEAR
  - 50% SECOND YEAR
  - 25% THIRD YEAR
- 10% INVESTMENT TAX CREDIT

**WORKING CAPITAL:**

- 21 DAYS CRUDE STORAGE CAPACITY/14 DAY CRUDE INVENTORY.
- 14 DAYS PRODUCT STORAGE CAPACITY/7 DAY PRODUCT INVENTORY.
- CRUDE VALUED AT $30.00/BBL
- PRODUCT VALUED AT $40.00/BBL
- DEBT FINANCED AT 10%

**CAPITAL RETURN:**

- 15% DCF RATE
- ZERO SALVAGE VALUE
- 13 YEARS SUM OF YEARS DIGITS DEPRECIATION

TABLE XXIV (CONT'D.)

**OPERATING BASES:**

- 16 YEAR PLANT OPERATING LIFE
- 50% OPERATING CAPACITY 1ST YEAR - 100% THEREAFTER
- 90% ON-STREAM FACTOR
- 100,000 BARREL PER STREAM DAY (BPSD) CAPACITY

**OPERATING COST BASES:**

- CRUDE SHALE OIL - $30/BBL
- ALL PROCESS HEAT REQUIREMENTS ARE GENERATED INTERNALLY
- COOLING WATER 3¢/1000 GAL
- ELECTRICITY 3.5¢/KWHR
- OPERATORS* $12.00/MANHOUR } WTD. AVG. @ $10.95
- HELPERS* $10.50/MANHOUR }
- SUPERVISION 25% OF DIRECT LABOR
- OVERHEAD 100% OF DIRECT LABOR
- FEDERAL & STATE TAXES - 50%
- MAINTENANCE, LOCAL TAXES & INSURANCE - 4.5% OF FIXED INVESTMENT
- PRODUCT VALUES - ALL FUELS ARE EQUAL VALUE
- BY-PRODUCT VALUES - AMMONIA ($120/ST)
  SULFUR ($ 53/LT)

*4.2 SHIFT POSITIONS PLUS 10% RELIEF REQUIRED FOR CONTINUOUS OPERATION

TABLE XXV. PLANT CAPACITIES AND ESTIMATED FIRST QUARTER 1980 INVESTMENTS (PHASE II)

| CASE | MAX. JP-4 | | MAX. JP-8 | | JP-4 + OTHER FUELS | |
|---|---|---|---|---|---|---|
| | CAPACITY, MBPSD | $ x $10^6$ | CAPACITY MBPSD | $ x $10^6$ | CAPACITY, MBPSD | $ x $10^6$ |
| $H_2$ PLANT (TPO), MMSCF/SD (100% $H_2$ BASIS) | 151 | 107.4 | 134 | 100.0 | 145 | 105.0 |
| $H_2$ PLANT (STEAM REFORMING), MMSCF/SD | 94 | 33.9 | 114 | 34.5 | 80 | 30.8 |
| SULFUR RECOVERY, ST/SD | 111 | 10.0 | 111 | 10.0 | 111 | 10.0 |
| WASTE WATER TREATING, ST/SD, $NH_3$ | 206 | 12.9 | 209 | 12.9 | 206 | 12.9 |
| MAIN HYDROTREATER & $H_2S$ RECOVERY, MBPSD | 100 | 166.3 | 100 | 166.3 | 100 | 166.3 |
| ATM. AND VAC. DISTN., MBPSD | 104 | 45.0 | 104 | 45.0 | 104 | 45.0 |
| DIST. HYDROTREATER, MBPSD | 25 | 31.5 | 28 | 34.4 | 25 | 31.5 |
| HCL TREATER, MBPSD | 74 | 2.4 | 61 | 2.3 | 74 | 2.4 |
| HYDROCRACKER & ATM. DISTN., MBPSD FRESH FEED | 64 | 89.5 | 61 | 87.3 | 64 | 86.1 |
| SUB TOTAL | | 498.9 | | 492.7 | | 490.0 |
| TANKAGE, MM BBLS. | 5.1 | 40.0 | 5.0 | 39.0 | 5.0 | 39.0 |
| TOTAL ON-SITES | | 538.9 | | 531.7 | | 529.0 |
| OFF-SITES (45% ON-SITES LESS TANKAGE) | | 224.5 | | 221.7 | | 220.0 |
| TOTAL CAPITAL INVESTMENT | | 763.4 | | 753.4 | | 749.0 |

TABLE XXVI. PHASE II PRELIMINARY COST COMPARISON FOR MANUFACTURING MILITARY FUELS FROM RAW OCCIDENTAL SHALE OIL

BASIS: 100,000 BPSD REFINERY CRUDE CAPACITY

| MANUFACTURING COSTS, $/CD | MAX. JP-4 | MAX. JP-8 | JP-4 AND OTHER FUELS |
|---|---|---|---|
| DIRECT LABOR | 15,538 | 15,538 | 15,538 |
| PURCHASED POWER AND COOLING WATER | 70,454 | 68,454 | 60,090 |
| CATALYST, CHEMICALS AND ROYALTIES | 42,775 | 42,873 | 40,035 |
| OVERHEAD @ 100% DIRECT LABOR | 15,538 | 15,538 | 25,538 |
| MAINT., LOCAL TAXES AND INSURANCE | 66,440 | 65,552 | 65,219 |
| DEPRECIATION (AVG. OVER 13 YEARS) | 160,885 | 158,778 | 157,850 |
| TOTAL OPERATING EXPENSES | 371,630 | 366,733 | 354,270 |
| DIRECT & INDIRECT COSTS, $/B LIQ.PRODUCT | 3.91 | 3.99 | 3.91 |
| TOTAL INVESTMENT, $ x $10^6$ | | | |
| PLANT | 763.4 | 753.4 | 749.0 |
| CATALYSTS | 17.5 | 17.3 | 15.3 |
| WORKING CAPITAL | 78.3 | 77.1 | 76.3 |
| TOTAL PLANT INVESTMENT | 859.2 | 847.8 | 840.6 |

(CONT'D.)

TABLE XXVI. PHASE II PRELIMINARY COST COMPARISON FOR MANUFACTURING MILITARY FUELS FROM RAW OCCIDENTAL SHALE OIL (CONT'D.)

BASIS: 100,000 BPSD REFINERY CRUDE CAPACITY

| ALTERNATE | MAX. JP-4 | MAX. JP-8 | JP-4 AND OTHER FUELS |
|---|---|---|---|
| PRODUCT YIELDS, BPCD | | | |
| TURBINE FUELS | 91,203 | 55,133 | 67,584 |
| OTHER FUELS | 3,743 | 36,690 | 23,057 |
| TOTAL LIQUID FUELS | 94,946 | 91,823 | 90,641 |
| MANUFACTURING COSTS, $/CD | | | |
| OPERATING EXPENSES | 371,630 | 366,733 | 354,270 |
| RETURN ON INVESTMENT @ 15% | 320,918 | 316,726 | 314,096 |
| INTEREST @ 10% | 235,397 | 232,274 | 230,301 |
| | 927,945 | 915,733 | 896,667 |
| LESS $NH_3$ AND S (CREDIT) | 898,333 | 885,641 | 869,055 |
| LIQUID FUELS, BPCD | 94,946 | 91,823 | 90,641 |
| MFG. COST, $/B PRODUCT (¢/B) | 9.46 (23) | 9.65 (23) | 9.59 (23) |
| ADJUSTED CRUDE COST, $/B (¢/B) | 32.86 (78) | 33.80 (80) | 34.00 (81) |
| TOTAL PRODUCT COST, $/B (¢/B) | 42.32 (101) | 43.45 (103) | 43.59 (104) |

TABLE XXVII. SUMMARY

| PROCESSING ROUTE FOR | MAX. JP-4 | MAX. JP-8 | JP-4 AND OTHER FUELS |
|---|---|---|---|
| PRODUCTS AS VOL.% CRUDE PROCESSED | | | |
| JET FUEL | 101.0 | 61.3 | 75.1 |
| TOTAL LIQUID PRODUCTS | 105.1 | 102.0 | 100.7 |
| PRODUCTS AS VOL.% TOTAL ENERGY INPUT (CRUDE + FUEL + UTILITIES CONVERTED TO FOE) | | | |
| JET FUEL | 86.8 | 52.8 | 65.3 |
| TOTAL LIQUID PRODUCTS | 90.3 | 87.9 | 87.5 |
| TOTAL PRODUCT COST, $/B | 42.32 | 43.45 | 43.59 |
| ¢/GAL. | 101 | 103 | 104 |
| OVERALL THERMAL EFFICIENCY, % | 76 | 75 | 76 |
| PLANT INVESTMENT, $/SDB | 7809 | 7707 | 7643 |

## TABLE XXVIII. UNCERTAINTIES

1. ARSENIC DISPOSAL

   SPENT GUARD REACTOR CATALYST CONTAINS ABOUT 15 WT.% ARSENIC ACCUMULATED DURING OPERATION. CATALYST DISPOSAL MAY BE A PROBLEM.

2. CHLORIDE CONTENT IN HCL RAFFINATE

   ADDITIONAL DATA ARE NEEDED TO MINIMIZE THE CHLORIDE CONTENT. PILOT PLANT CONCENTRATIONS HAVE VARIED FROM 70 TO 750 PPM. CHLORIDES IN THE RAFFINATE FEED COMPLICATE THE HYDROCRACKING PROCESS AND REDUCE BY-PRODUCT AMMONIA YIELD.

3. CONTINUOUS HCL TREATING PROCESS

   CONTINUOUS TREATING PROCESS NOT DEMONSTRATED IN PILOT PLANT.

4. EXTINCTION RECYCLE HYDROCRACKER BOTTOMS

   NOT DEMONSTRATED IN PILOT PLANT. IF NOT FEASIBLE, A DRAG STREAM WILL BE REQUIRED.

## TABLE XXIX. SUMMARY AND CONCLUSIONS

1. PHASE II PILOT PLANT WORK IS COMPLETE. RESULTS CONFIRM OR ARE MORE FAVORABLE THAN PHASE I ESTIMATE.

2. HIGH YIELDS OF MILITARY FUELS CAN BE PRODUCED FROM RAW SHALE OIL THAT MEET CURRENT SPECIFICATIONS BASED ON PETROLEUM. OVERALL THERMAL EFFICIENCIES OF 75-76% ARE ATTAINED BASED ON TOTAL ENERGY INPUT OF CRUDE, FUEL, AND UTILITIES CONVERTED TO FOE.

3. ECONOMICS DEVELOPED FOR A 100,000 BPSD REFINERY USING A FIRST QUARTER 1980 COST BASE AND $30 PER BBL. FOR RAW SHALE. A TOTAL PRODUCT COST OF $1.01 TO $1.04 PER GALLON IS OBTAINED DEPENDING ON REFINERY PRODUCT SLATE. PROCESS UNIT CAPACITIES AND PRODUCT DISTRIBUTION HAVE NOT BEEN OPTIMIZED IN PHASE II.

4. SHALE OIL FUELS REFINERIES ARE MORE CAPITAL INTENSIVE THAN PETROLEUM REFINERIES OF COMPARABLE SIZE BY A FACTOR OF 1.5 TO 2.

5. ACCEPTABLE PERFORMING NON-PROPRIETARY CATALYST ARE INCORPORATED IN ALL CATALYTIC UNITS.

6. DECOMPOSED HCL EXTRACT IS USED FOR HYDROGEN MANUFACTURE. THIS HIGH NITROGEN CONTENT STREAM MAY HAVE GREATER VALUE FOR ALTERNATE APPLICATIONS (ADDITIVE FOR ROAD ASPHALT).

V

# PRODUCTION OF SPECIFICATION JP-4 JET FUEL FROM GEOKINETICS SHALE OIL

By

H. E. Reif, and A. Schneider

Suntech, Inc.

# PRODUCTION OF SPECIFICATION JP-4 JET FUEL FROM GEOKINETICS SHALE OIL

H. E. Reif and A. Schneider
Suntech, Inc.

## Summary

By hydrorefining 890 barrels of Geokinetics shale oil in a continuous PDU under severe conditions, a total of 270 barrels of specification grade JP-4 jet fuel distillate was produced in an operation beset by remarkably few complications. Copper strip corrosivity in the JP-4 product early in the run was later corrected by essentially complete stripping of hydrogen sulfide from the hydrorefining reactor effluent, while failure of the JFTOT test in the early product was corrected by clay treatment. During steady state operation of the PDU both problems vanished. Preliminary estimates of plant investments and economics indicate that, for the combination of severe hydrorefining and hydrocracking whereby about 85 vol.% yields of JP-4 based on total refinery input (raw shale oil, fuel and utilities converted to FOE BPD) can be achieved, capital investments and manufacturing costs do not appear to be excessive for a shale oil refinery. Additional hydrorefining process studies under severe conditions are required to develop and optimize firm process designs, economics and product yield and quality data.

A three-month program was initiated on about 1 January 1980 by Hydrocarbon Research, Inc. under subcontract to and in conjunction with the Applied Research Division of Suntech, Inc. to produce 300 barrels of specification grade JP-4 jet fuel from Geokinetics in situ whole crude shale oil. The process involved catalytic hydrorefining of the raw shale oil with Shell 324 nickel molybdenum-on-alumina catalyst under the relatively severe temperature of 825°F at 2800 psig total pressure and a liquid hourly space velocity of one. Essentially complete removal of nitrogen occurred under these conditions and distillation of the hydrorefined product gave 30-40 vol. % yields of specification grade JP-4 jet fuel based on the raw shale oil charged to hydrorefining. HRI's equipment produced approximately 10 barrels per day of finished JP-4 jet fuel. Because of prior commitments of this equipment, HRI was obliged to suspend operations after 270 barrels of JP-4 had been produced. It is likely that the entire 300 barrles could have been produced if three additional days of running time had been available.

A set of tables and figures have been prepared (APPENDIX A) which review the processing, present an estimate of the manufacturing economics, list the uncertainties and summarize the results of the production of the 270 barrels of JP-4 jet fuel. Comments and amplification are provided below for individual Tables and Figures.

Table 1 - Geokinetics is a higher grade of raw shale oil than Paraho based on boiling range, average molecular weight and contents of hydrogen, sulfur and nitrogen.

Table 2 - Prior to the beginning of the operation in HRI's PDU, bench-scale, continuous hydrorefining studies were carried out at HRI on Geokinetics raw shale oil using the Shell 324 catalyst. As received from HRI, a JP-4 sample prepared by distillation of a product of bench-scale hydrorefining contained 39 ppm of nitrogen. The low Reid vapor pressure of the sample was due to loss of butane during handling of the hydrorefined product. Gas analysis at HRI indicated that sufficient butanes are produced during hydrorefining to yield JP-4 with the specified Reid vapor pressure. This sample, however, also failed the copper strip corrosion and JFTOT tests. At Suntech a procedure for percolation of the JP-4 product through an acidic clay at commercially feasible dosages of clay was then developed which resulted in passing of the JFTOT test by the sample. The copper strip corrosion test is not affected by percolation through clay. We now know that failure of this test is due to incomplete stripping of hydrogen sulfide from hydrorefining reactor effluents before they come into contact with air.

Figure I -

Table 3 - Both shipments of JP-4 amounting to 270 barrels met all specifications. Note that 1% of external butane had to be added to meet Reid vapor pressure requirements.

Table 4 - We have seen samples of 480°F+ bottoms from the PDU operation containing as much as 109 ppm of total nitrogen and 22 wt.% aromatics. The variations in characteristics of the bottoms are probably attributable to aging of the hydrorefining catalyst system and, ultimately, to the absence of a separate guard case.

Figure II - This is Suntech's flow diagram of a conventional, raw shale oil hydrorefining and distillation operation. Note the presence of a vacuum still to produce a 1000°F+ bottoms fraction. Generally bottoms fractions of this sort are excluded from a subsequent hydrocracking step.

Table 5 - The operating conditions and product characteristics of hydrorefining Paraho whole crude shale oil projected in Suntech's Phase I Base Case Study are compared with the operating conditions actually used and the product characteristics actually found in hydrorefining of Geokinetics raw shale oil in the PDU at HRI. The chemical consumption of hydrogen projected to be significantly larger for the Paraho case than was actually observed in the Geokinetics case results from the more hydrogen deficient nature of the raw Paraho shale oil.

Figure III - A schematic flow diagram of Suntech's Phase I Base Case shows it to consist of a relatively severe hydrorefining of raw Paraho shale oil followed by an acid wash of the total liquid hydrorefined product. Note that the 850°F+ distillation bottoms is sent to Texaco Partial Oxidation to produce a portion of the hydrogen needed in the hydrorefining reactor. Hydrocracking is not used in this case.

Figure IV - A schematic flow diagram of the hydrorefining of raw Geokinetics shale oil as practiced at HRI shows the direct production of specification JP-4 jet fuel as a "straight-run" fraction and a 480°F+ waxy bottoms material. As will be shown in the next two charts, hydrocracking of the 480°F+ waxy bottoms is significantly cheaper than conventional hydrocracking, if the waxy bottoms feed to the hydrocracking operation can be routinely produced to contain less than 30 ppm of total nitrogen.

Figure V - Typically, a two-reactor (R-1 hydrotreater, R-2 hydrocracker), single stage hydrocracker with extinction recycle is required for processing feedstock containing more than 30 ppm of total nitrogen into high yields of JP-4 jet fuel.

Figure VI - A single reactor (R-1 hydrocracker), single stage hydrocracking operation with extinction recycle will be feasible for processing 480°F+ bottoms containing less than 30 ppm of total nitrogen into high yields of JP-4 jet fuel.

Table 6 - The three cases to be examined here and in subsequent charts are:

a) Suntech's Phase I Base Case for hydrorefining, acid washing and distillation to produce "straight-run" JP-4 jet fuel from raw Paraho shale oil

b) The Suntech-HRI process for severe hydrorefining and distillation to produce "straight-run" JP-4 jet fuel from raw Geokinetics shale oil

c) Suntech process for hydrorefining, distillation and hydrocracking to produce high yields of JP-4 jet fuel from raw Geokinetics shale oil

Table 7 - These charts present the guidelines for developing Suntech's Phase I economics and are used in the subsequent charts for comparing the three cases specified above in connection with Table 6.

Table 8 - This chart presents preliminary estimates based on September 1978 costs of plant investments for the three cases mentioned above. Comparing Suntech's Phase I Base Case with the Suntech-HRI case for producing "straight-run" JP-4 jet fuel, it is seen that the major reason for the smaller total capital cost for the latter case is the associated smaller investment in hydrogen producing and distillation facilities.

The capital investment cost for hydrocracking equipment makes the hydrocracking case for maximizing jet fuel production more expensive than the cases which do not involve this additional oepration. Although maximizing JP-4 jet fuel requires the generation of significantly larger daily volumes of hydrogen than Suntech's Phase I Base Case, it is interesting that the capital costs for generating hydrogen in both cases are essentially the same. This results from the generation of larger proportions of hydrogen by steam reforming than by the Texaco Partial Oxidation process in the hydrocracking case as compared with Suntech's Phase I Base Case. Hydrocracking produces significantly larger quantities of $C_1$-$C_3$ light gases than hydrorefining, and hydrogen generation by steam reforming of light gases is inherently cheaper than by the Texaco Partial Oxidation of high-boiling fractions.

Table 9 - Mainly because of the utilities purchased for the hydrocracking step, total daily operating expenses for the case to maximize JP-4 jet fuel are significantly larger than those of the other two cases. Hydrocracking is apparently very energy intensive.

Adjusted crude cost in dollars per barrel is defined:

$$\frac{\text{vol. shale oil in (process feed and fuel)}}{\text{vol. products out}} \times \text{price per barrel of shale oil}$$

Note that by the Phase I ground rules utilities such as electricity are considered to be available by purchase from external sources and therefore do not enter into the calculation of the adjusted crude cost. Inclusion of purchased utilities in the fraction

$$\frac{\text{vol. shale oil in (process feed and fuel)}}{\text{vol. products out}}$$

would relate the fraction to the thermal efficiency of the process and would further increase the adjusted crude cost.

Table 9 - The Suntech-HRI process for producing JP-4 jet fuel from raw Geokinetics shale oil turns out to have the cheapest cost per barrel of total fuel products, whereas the Phase I Base Case for producing JP-4 jet fuel by hydrorefining Paraho whole crude shale oil and the case involving maximum yields of JP-4 jet fuel from raw Geokinetics shale oil by hydrocracking have essentially the same cost per barrel of total fuel products. It is noteworthy that the higher capital and manufacturing costs in the latter case are offset by the sizeable increase in daily volume of total liquid products. This increase in volume results from the incorportation of hydrogen in the total liquid products during the hydrocracking operation. That hydrocracking simultaneously to maximize JP-4 jet fuel yields and total liquid product volumes appears to be economically advantageous in this case derives from the generation of hydrogen more cheaply from $C_1$-$C_3$ gases from hydrocracking than from the Texaco Partial Oxidation of heavy liquids. This advantage may be magnified in the manufacture of JP-8 (and JP-5) instead of JP-4 jet fuel since with the kerosene types of jet fuel perhaps all of the hydrogen could be generated from $C_1$-$C_4$ gases plus the light naphtha formed during hydrocracking.

The costs in the chart are based on September 1978 costs and on $16 per barrel raw shale oil. Assuming June 1980 labor and investment costs and $25 per barrel of raw shale oil, an additional $12.60/barrel or $0.30/gallon must be added to each case for the total fuel product costs at the bottom of the chart.

## APPENDIX A

### PURPOSE OF PROGRAM

1. TO PREPARE 300 BBL. OF SPECIFICATION JP-4 FROM GEOKINETICS SHALE OIL BY THE BEST MEANS AVAILABLE.

2. PREPARATION SHOULD BE AS CLOSE TO CONTEMPLATED COMMERCIAL PROCESSING AS FEASIBLE.

3. DELIVERY OF SAMPLE IN TIME TO MEET AIR FORCE COMBUSTION TESTING PROGRAM FOR SYNTHETIC FUELS.

TABLE I - INSPECTIONS AND ANALYSES OF RAW SHALE OILS USED FOR MAKING PROCESS ESTIMATES

| SOURCE | PARAHO | GEOKINETICS |
|---|---|---|
| INSPECTION DATA | | |
| API @ 60°F | 20.6 | 26.8 |
| DISTILLATION, ASTM D1160 CORRECTED TO 1 ATM., °F | | |
| IBP/5 | 173/456 | 345/457 |
| 10/30 | 508/687 | 469/566 |
| 50 | 798 | 655 |
| 70/90 | 918/1057 | 785/880 |
| EP | 1063 @ 95% | 975 @ 95.5% |
| RAMSBOTTOM CARBON RESIDUE, WT.% | 1.4 | |
| ASH, WT.% (ASTM D482) | 0.03 | 0.03 |
| AVERAGE MOLECULAR WEIGHT | 326 | 280 |
| CHEMICAL COMPOSITION, WT.% | | |
| CARBON | 83.83 | 84.48 |
| HYDROGEN | 11.72 | 11.69 |
| SULFUR | 0.75 | 0.48 |
| TOTAL NITROGEN | 2.13 | 1.86 |
| OXYGEN | 1.31 | 1.79 |
| ARSENIC | 34 ppm | 20 ppm |
| IRON | 90 ppm | 60 ppm |

TABLE 2 - BENCH SCALE UNIT
JP-4 PRODUCT ANALYSIS[1]

| | JP-4 SPECIFICATION | AS RECEIVED | CLAY TREATED[2] |
|---|---|---|---|
| API @ 60°F | 45-57 | 49.9 | 49.9 |
| DISTILLATION, ASTM D-86 | | | |
| IBP, °F | REPORT | 163 | |
| 10 | REPORT | 245 | |
| 20 | 293 | 284 | |
| 50 | 374 | 359 | |
| 90 | 473 | 430 | |
| E.P. | 518 | 470 | |
| RESIDUE, V.% | 1.5 MAX. | 1.0 | |
| LOSS, V.% | 1.5 MAX. | 1.0 | |
| SULFUR, WT.% | 0.40 MAX. | 0.0124 | 0.0122 |
| MERCAPTANS, WT.% | 0.001 MAX. | - | - |
| NITROGEN, PPM | NA | 39 | 3 |
| OLEFINS, V.% | 5.0 MAX. | 3.5 | 2.1 |
| AROMATICS, V.% | 25.0 MAX. | 9.3 | 8.2 |
| FREEZE PT., °F | -72 MAX. | -74 | |
| Cu STRIP CORROSION, MAX. | 1B | 2C | |
| RVP, PSIA, MIN-MAX | 2-3 | 1.2 | |
| HEATING VALUE | | | |
| NET BTU/LB. MIN. | 18,300 | 18,700 | |
| JFTOT | | | |
| ΔP, MM Hg, MAX. | 25 | 250 | 0 |
| DEPOSIT CODE, MAX. | 3 | 4 | 0 |

1/ NiMO CATALYST, LHSV = 1.0, T = 825°F, $P_T$ = 2500 PSIG, $H_2$/OIL = 4000 SCF $H_2$ BBL./FEED.

2/ CLAY DOSAGE = 250 BBL./TON

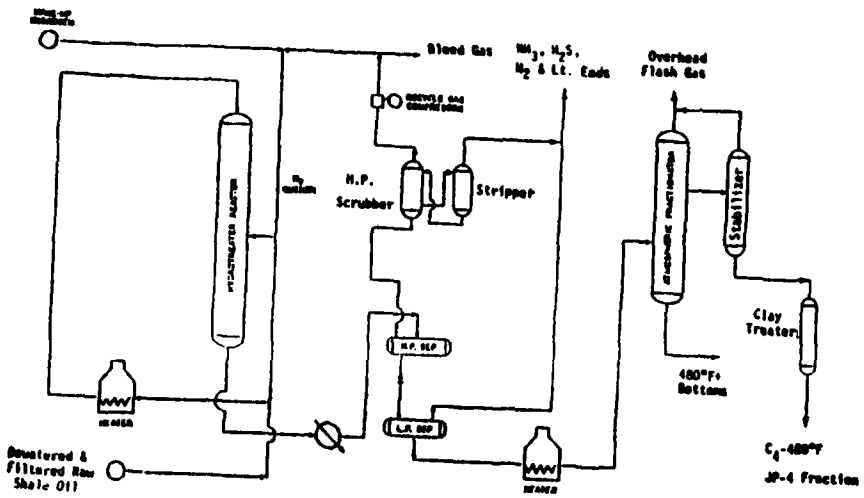



FIGURE 1 - SCHEMATIC FLOW DIAGRAM of HRI's PDU FOR HYDROTREATING GEOKINETICS SHALE OIL

TABLE 3 - JP-4 PRODUCT ANALYSIS

| | JP-4 SPECIFICATION | FIRST SHIPMENT | SECOND SHIPMENT |
|---|---|---|---|
| API @ 60°F | 45-57 | 50.2* | 49.8 |
| DISTILLATION, ASTM D-86 | | | |
| IBP, °F | REPORT | 129 | 140 |
| 10 | REPORT | 246 | 246 |
| 20 | 293 | 285 | 282 |
| 50 | 374 | 357 | 355 |
| 90 | 473 | 442 | 432 |
| E.P. | 518 | 506 | 494 |
| RESIDUE, V.% | 1.5 MAX. | 1 | 1 |
| LOSS, V.% | 1.5 MAX. | 1 | 1 |
| SULFUR, WT.% | 0.40 MAX. | 0.0006 | 0.0016 |
| MERCAPTANS, WT.% | 0.001 MAX. | | < 2 PPM |
| NITROGEN, PPM | NA | 3 PPM | < 1 PPM |
| OLEFINS, V.% | 5.0 MAX. | 1.6 | 2.0 |
| AROMATICS, V.% | 25.0 MAX. | 7.3 | 10.4 |
| FREEZE PT., °F | -72 MAX. | -76* | -76 |
| Cu STRIP CORROSION, MAX. | 1B | 1B | 1A |
| RVP, PSIA, MIN-MAX | 2-3 | 2.6 | 2.3* |
| HEATING VALVE | | | |
| NET BTU/LB. MIN. | 18,300 | 18,736 | 18,696 |
| JFTOT | | | |
| Δ°, MM HG, MAX. | 25 | 0 | 0 |
| DEPOSIT CODE, MAX. | 3 | 0 | 0 |

* HRI ANALYSIS

TABLE 4 - INSPECTIONS AND ANALYSIS OF GEOKINETICS FEED AND BOTTOMS PRODUCT

| | GEOKINETICS FEEDSTOCK | 480°F+ BOTTOMS FROM HYDROTREATING |
|---|---|---|
| API GRAVITY @ 60°F | 26.8 | 37.7 |
| DISTILLATION, °F (ASTM D1160) | | |
| IBP | 345 | 465 |
| 5 v. % | 437 | 482 |
| 10 | 469 | 500 |
| 20 | 520 | 530 |
| 50 | 655 | 600 |
| 70 | 785 | 665 |
| 90 | 880 | 765 |
| EP/VOL.% | 975/95.5 | 820/95.0 |
| AROMATICS, WT.% | | 16.3 |
| SULFUR, WT.% | 0.48 | 4 PPM |
| NITROGEN, WT.% | 1.66 | 4 PPM |
| ARSENIC, PPM | 20 | < 1 |

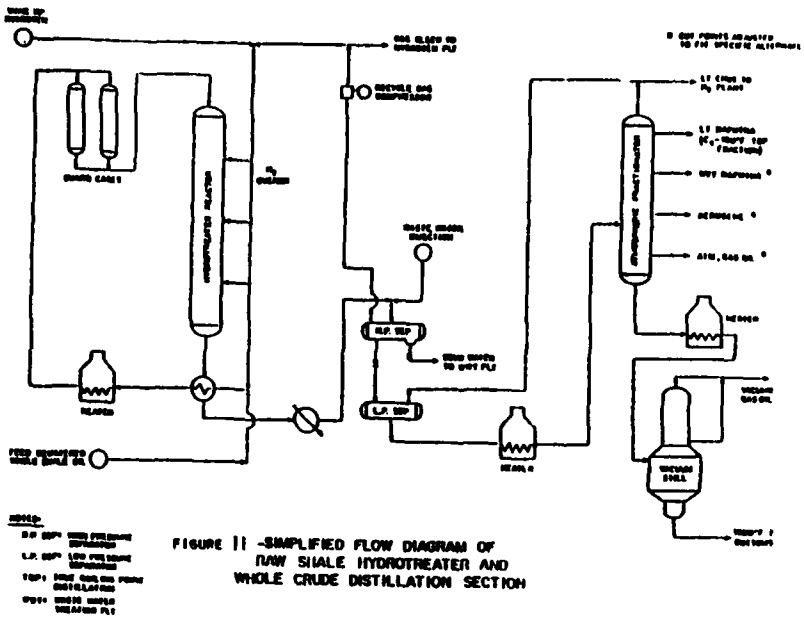


FIGURE 11 -SIMPLIFIED FLOW DIAGRAM OF RAW SHALE HYDROTREATER AND WHOLE CRUDE DISTILLATION SECTION

TABLE 5 - ESTIMATED OPERATING CONDITIONS FOR WHOLE SHALE OIL HYDROTREATER

CHARGE RATE: 110,000 BPSD (100,000 BPCD)
OPERATING FACTOR: 0.91
CATALYST: Ni Mo on ALUMINA
CATALYST LIFE: 6 MONTHS

REACTOR OPERATING CONDITIONS

| CASE | PHASE I BASE* | GEOKINETICS ALTERNATE |
|---|---|---|
| LHSV, V/Hr/V | 0.4 | 1.0 |
| AVG. CATALYST TEMP., °F | 760 | 825 |
| PRESSURE, TOTAL PSIA | 1,880 | 2800 |
| $H_2$PP | 1,600 | 2600 |
| RECYCLE GAS RATE, SCF/B | 4,100 | 6000 |
| HYDROGEN CONSUMPTION, SCF/B | | |
| CHEMICAL | 2,250 | 1700 |
| DISSOLVED | 150 | 250 |
| BLEED | 75 | 200 |
| TOTAL TO HYDROTREATER | 2,475 | 2,150 |
| PRODUCT | | |
| TOTAL NITROGEN, PPM | 300 | 3 |
| SULFUR, PPM | 25 | 100 |
| $C_4$+ YIELD, VOL.% FEED | 108.56 | 102.5 |
| JP-4 FRACTION | 29.3 | 38.7 |
| BOTTOMS | 79.3 | 63.8 |
| | 108.6 | 102.5 |

* PARAHO SHALE OIL

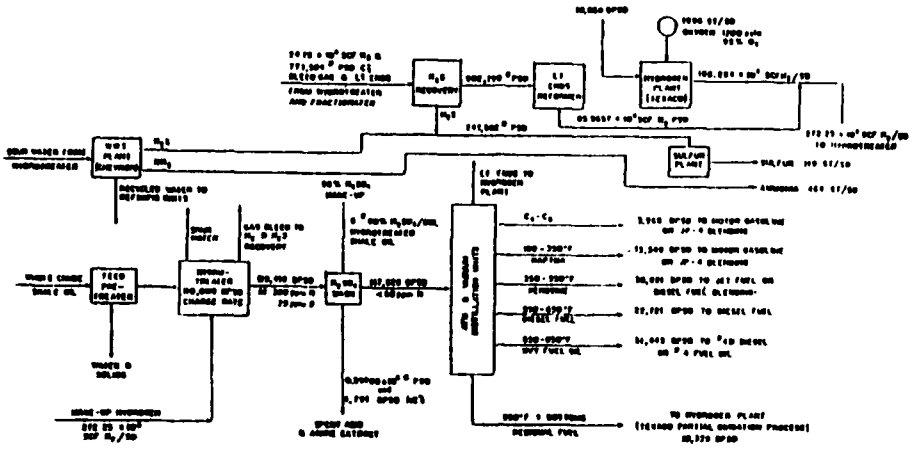


FIGURE III - REFINING FLOW PARAFO SHALE OIL

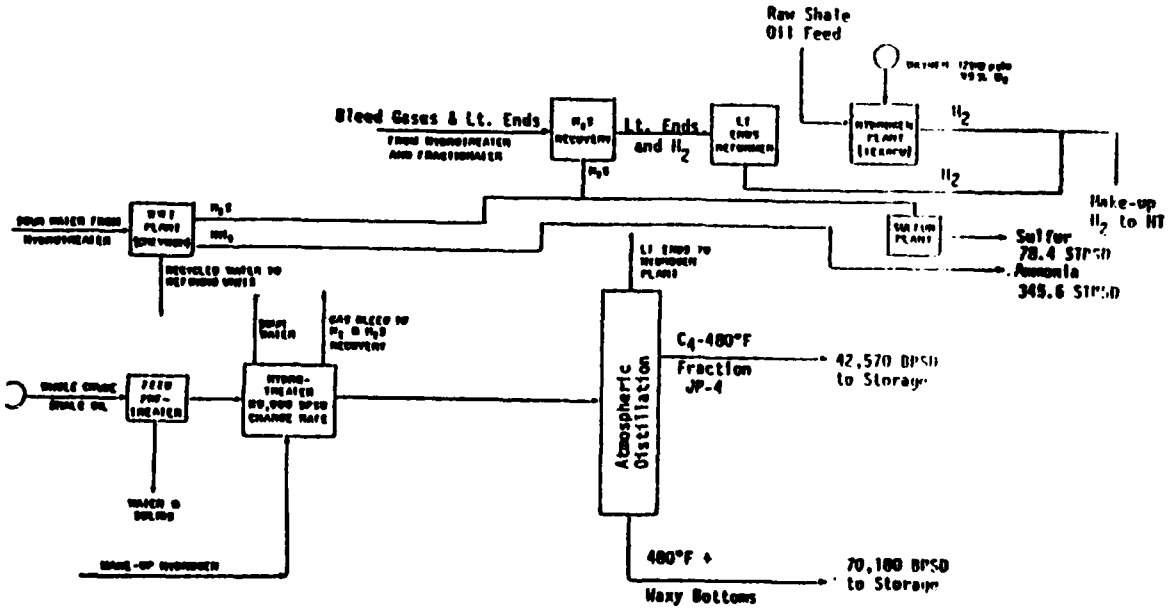
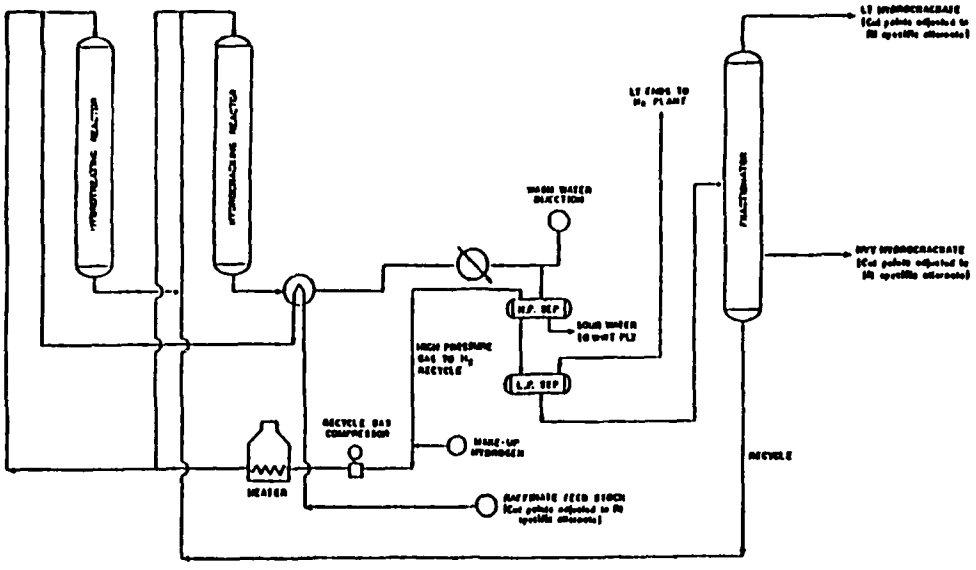
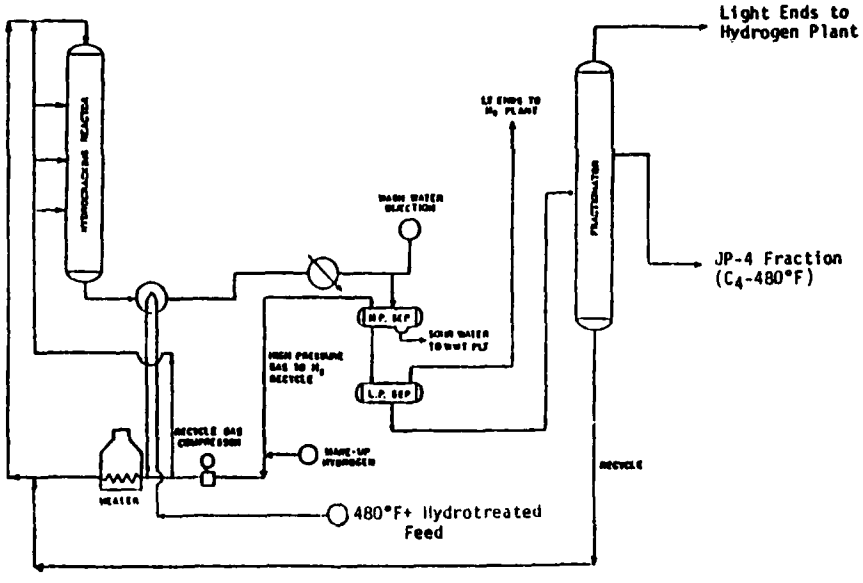



FIGURE IV - REFINING GEOKINETICS SHALE OIL
VIA HYDROTREATING




NOTES:
H.P. SEP: HIGH PRESSURE SEPARATOR
L.P. SEP: LOW PRESSURE SEPARATOR
WWT PLANT: WASTE WATER TREATING PLT

FIGURE V - SCHEMATIC FLOW DIAGRAM OF SINGLE STAGE HYDRO-CRACKER WITH EXTINCTION RECYCLE FOR MANUFACTURING TURBINE FUELS FROM SHALE OIL RAFFINATES




NOTES:
H.P. SEP: HIGH PRESSURE SEPARATOR
L.P. SEP: LOW PRESSURE SEPARATOR
WWT PLANT: WASTE WATER TREATING PLT

FIGURE VI - SCHEMATIC FLOW DIAGRAM OF SINGLE STAGE HYDRO-CRACKER WITH EXTINCTION RECYCLE FOR MANUFACTURING TURBINE FUELS FROM SHALE OIL

TABLE 6 - MATERIAL BALANCE SUMMARY - MAXIMIZING JP-4 FROM WHOLE CRUDE SHALE OIL

| BASIS: 110,000 BPSD FEED RATE | PARAHO BASE | GEOKINETICS $H/H_2$ ONLY | GEOKINETICS $H/H_2$ & H/C |
|---|---|---|---|
| TOTAL HYDROGEN, $SCFX10^6$ | 272.25 | 221.38 | 318.32 |
| NET PRODUCTS, BPSD (TBP CUTS) | | | |
| JP-4 FRACTION | 32,268 | 42,570 | 120,651 |
| OTHER FUELS (400° F+.) | 75,032* | 70,180 | 0 |
| TOTAL | 107,300 | 112,750 | 120,651 |
| OTHER PRODUCTS, STPSD | | | |
| AMMONIA | 464 | 346 | 346 |
| SULFUR | 119 | 78 | 78 |
| LIQUID FUEL PRODUCTS YIELDS | | | |
| TOTAL PRODUCTS AS VOL.% FEED | 97.6 | 102.5 | 109.7 |
| JP-4 AS VOL.% FEED | 29.3 | 37.8 | 109.7 |
| TOTAL REFINERY INPUT (CRUDE, FUEL AND UTILITIES CONVERTED TO FOE BPSD) | 120,393 | 129,948 | 137,433 |
| TOTAL PRODUCTS AS VOL.% REFINERY INPUT | 89.1 | 90.2 | 87.8 |
| JP-4 | 26.8 | 34.1 | 87.8 |

*450-650°F FRACTION

TABLE 7 - BASIS FOR DEVELOPING PHASE I ECONOMICS

GENERAL

1. CAPITAL AND OPERATING COST ESTIMATES FOR EACH REFINING SCHEME BASED ON: A) IN-HOUSE DATA. B) LITERATURE SOURCES.

2. PROCESSING SCHEMES NOT OPTIMIZED AT PRESENT DUE TO LACK OF DATA AT THIS TIME.

3. NO ALLOWANCES FOR TRANSPORTING RAW SHALE OIL TO REFINERY OR FINISHED PRODUCTS FROM REFINERY.

PLANT COSTS

LOCATION: MID WEST
TYPE: GRASS ROOTS (ADJACENT TO EXISTING REFINERY)
COST BASE: SEPTEMBER 1978
FEED: WHOLE RAW SHALE OIL
TANKAGE: 30 DAYS STORAGE CAPACITY FOR RAW SHALE OIL AND PRODUCTS
CRUDE RATE: 100,000 BPCD
UTILITIES: AVAILABLE AT PLANT SITE AT COSTS SPECIFIED:
ELECTRICITY
STEAM
FUEL
COOLING WATER

TABLE 7

BASIS FOR DEVELOPING PHASE I ECONOMICS (CONT'D.)

OVERHEAD: 100% DIRECT LABOR (FRINGE BENEFITS, OVERHEAD, GENERAL AND ADMINISTRATIVE AND CONTROL LABORATORY COSTS).

MAINTENANCE, LOCAL TAXES AND INSURANCE: 4.5% ESTIMATED ERECTED PLANT COSTS

START-UP COSTS: 5% ESTIMATED ERECTED PLANT COSTS.

CRUDE SHALE OIL: $16.00 PER BBL. AT PLANT SITE

PRODUCT VALUES: FUELS EQUAL ($21.00/BBL. FOR WORKING CAPITAL

BY-PRODUCTS - AMMONIA - $120/SHORT TON

SULFUR - $53/LONG TON

UTILITIES:

FUEL - $2.50 PER $10^6$ NET BTU'S (FOE BBL. @ 6.0 X $10^6$ NET BTU'S)

ELECTRICITY - 3.5¢ PER KW HOUR

COOLING WATER - 3¢ PER 1,000 GALLONS

SATURATED STEAM - 600 PSIG @ $3.90/1,000 LBS.
250 PSIG @ $3.30/1,000 LBS.
50 PSIG @ $2.50/1,000 LBS

CATALYSTS AND CHEMICALS: AT COST

ROYALTIES: RUNNING BASIS

TABLE 7

BASIS FOR DEVELOPING PHASE I ECONOMICS (CONT'D.)

CAPITAL RECOVERY

EQUITY FINANCING: 100%

RETURN ON INVESTMENT: 15% DISCOUNTED CASH FLOW AFTER TAXES

PLANT LIFE: 16 YEARS WITH ZERO SALVAGE VALUE

DEPRECIATION: 13 YEARS SUM OF YEARS DIGITS

FEDERAL PLUS STATE TAX RATE: 50%

INVESTMENT TAX CREDIT: 10% OF CAPITAL INVESTMENT

WORKING CAPITAL: 30 DAYS INVENTORY OF CRUDE ($16/BBL) AND 30 DAYS PRODUCT ($21/BBL)

DEBT FINANCING: 10% ANNUAL INTEREST RATE

OPERATING COSTS:

DIRECT LABOR

OPERATORS: $9.90/HR.
HELPERS: $6.90/HR.
} WTD. AVG. $8.80/HR.

SUPERVISION: 25% OF LABOR COSTS

NOTE: 4.2 SHIFT POSITIONS PLUS 10% RELIEF REQUIRED FOR CONTINUOUS OPERATION.

TABLE 8 - PRELIMINARY ESTIMATES OF PLANT INVESTMENTS (JP-4)

SEPTEMBER 1978

| CASE | PHASE I BASE CAPACITY | PHASE I BASE $ x $10^6$ | HIGH SEVERITY ALT. BASE CAPACITY | HIGH SEVERITY ALT. BASE $ x $10^6$ | HIGH SEVERITY ALT.- MAX. JP-4 CAPACITY | HIGH SEVERITY ALT.- MAX. JP-4 $ x $10^6$ |
|---|---|---|---|---|---|---|
| $H_2$ (PARTIAL $O_2$) MMSCF/D | 106 | 107.4 | 101 | 79.1 | 135 | 91.3 |
| $H_2$ (STEM REF) MMSCF/D | 86 | 28.8 | 120 | 35.2 | 182 | 45.1 |
| SULFUR RECOVERY, ST/SD | 119 | 11.5 | 78 | 10.0 | 78 | 10.0 |
| WASTE WATER TRTG. STRM/SD | 464 | 22.3 | 346 | 19.3 | 346 | 19.3 |
| MAIN HYDROTREATER AND $H_2S$ RECOV. MB/SD | 110 | 160.0 | 110 | 160.0 | 110 | 160.0 |
| ATM. AND VAC. DISTN, MB/SD | 118 | 36.8 | | | | |
| MAIN ATM. DISTN, MB/SD | | | 118 | 26.4 | 118 | 26.4 |
| HYDROCRACKER, MB/SD | | | | | 70 | 89.1 |
| ACID WASH, MB/SD | 120 | 0.5 | | | | |
| SUB TOTAL | | 367.3 | | 330.0 | | 491.2 |
| TANKAGE, MM BBLS. | 6.9 | 49.4 | 6.9 | 49.4 | 7.2 | 51.5 |
| TOTAL ONSITES | | 416.7 | | 379.4 | | 492.7 |
| OFFSITES (45% ONSITES - TANKAGE) | | 165.3 | | 148.5 | | 198.5 |
| TOTAL CAPITAL COST | | 582.0 | | 527.9 | | 691.2 |

TABLE 9 - PRELIMINARY COST COMPARISON FOR MANUFACTURING JP-4 FROM WHOLE CRUDE SHALE OIL

BASIS: 100,000 BPCD CRUDE TO HYDROTREATER

| | COSTS IN DOLLARS PER CALENDAR DAY* | | |
|---|---|---|---|
| | BASE | ALT. W/HT | ALT. W/HT AND HC |
| DIRECT LABOR | 8,976 | 8,184 | 10,296 |
| PURCHASED UTILITIES | 177,400 | 176,330 | 318,202 |
| CATALYSTS, CHEMICALS & ROYALTIES | 87,960 | 34,873 | 57,054 |
| OVERHEAD @ 100% DIRECT LABOR | 8,976 | 8,184 | 10,296 |
| MAINT, LOCAL TAXES & INSURANCE | 51,374 | 46,775 | 60,704 |
| DEPRECIATION (AVG. OVER 13 YRS) | 122,655 | 111,254 | 145,669 |
| TOTAL OPERATING EXPENSES | 457,341 | 385,600 | 602,261 |

* SEPTEMBER 1978 BASE

TABLE 9 - PRELIMINARY COST COMPARISON FOR MANUFACTURING JP-4 FROM WHOLE CRUDE SHALE OIL (CONT'D.)

| | COSTS IN DOLLARS PER CALENDAR DAY* | | |
|---|---|---|---|
| | BASE | ALT. W/WT | ALT. W/WT AND HC |
| TOTAL INVESTMENT, $ x $10^6$ | | | |
| PLANT | 582.0 | 527.9 | 681.2 |
| CATALYSTS, ETC. | 9.9 | 5.5 | 10.8 |
| WORKING CAPITAL | 112.1 | 113.9 | 119.6 |
| TOTAL | 704.0 | 647.3 | 821.6 |
| JP-4 YIELD, BPCD | 29,364 | 38,739 | 109,792 |
| MANUFACTURING COSTS, $/CD | | | |
| OPERATING EXPENSES | 457,391 | 385,600 | 602,261 |
| RETURN ON INVESTMENT @ 15% | 243,247 | 219,205 | 288,485 |
| INTEREST @ 10% | 192,873 | 177,393 | 225,086 |
| TOTAL (LESS $NH_3$ + S) | 893,485 | 782,147 | 1,115,830 |
| | (857,842) | (740,626) | (1,074,329) |
| LIQUID PRODUCTS (FUELS), BPCD | 97,843 | 102,602 | 109,792 |
| MFG. COST, $/B PRODUCT | 8.58 | 7.22 | 9.79 |
| ADJUSTED CRUDE COST, $/B | 17.77 | 17.12 | 16.98 |
| TOTAL FUEL PRODUCT COST $/B (¢/GAL.) | 26.35 (63) | 24.34 (58) | 26.77 (64) |

* SEPTEMBER 1978 BASE

TABLE 10

UNCERTANTIES

1. MAIN HYDROTREATER CATALYST LIFE.

   6 MONTHS LIFE ASSUMED IN ECONOMICS. ONLY ONE MONTH OF OPERATION DEMONSTRATED IN PDU AT HRI. NO GUARD CASE USED AND FEEDSTOCK HEATED TO 700°F BEFORE ENTERING MAIN REACTOR. PROPOSED OPERATION FEEDSTOCK HEATED TO 600-625°F, ENTERS GUARD CASE, OLEFINS SATURATED AND As AND Fe REMOVED BEFORE ENTERING MAIN REACTOR.

2. HYDROCRACK 480°F+ BOTTOMS TO EXTINCTION.

   PROBABLY ASSUMPTIONS ARE SAFE BUT NOT DEMONSTRATED. YIELDS AND PRODUCT QUALITIES ARE ESTIMATED. INCLUSION OF HYDROCRACKER WOULD PERMIT MILDER OPERATING CONDITIONS IN MAIN HYDROTREATER. ADDITIONAL DATA ARE NEEDED TO BALANCE OPERATIONS. A FULL SLATE OF DISTILLATE FUELS WOULD BE POSSIBLE WITH A HYDROCRACKER (JP-8, #2 DIESEL AND MARINE DIESEL)

3. OTHER FUELS FROM 480°F+ HYDROTREATED BOTTOMS

   FRACTION WAXY, WOULD LIKELY NEED ADDITIONAL PROCESSING TO MAKE ACCEPTABLE PRODUCTS HEAVIER THAN JP-4.

4. CATALYTIC CRACKING 480°F+ BOTTOMS

   INSPECTIONS AND ANALYSIS INDICATE THIS MATERIAL WOULD BE AN EXCELLENT FCC FEED FOR MANUFACTURING GASOLINE AND #2 FUEL OIL. CATALYTIC CRACKING DATA ARE NEEDED TO CONFIRM YIELDS.

5. APPLICABILITY FOR PROCESSING OTHER SHALE OILS

   OCCIDENTAL AND PARAHO SHALE OILS CONTAIN MORE NITROGEN, SULFUR AND ARSENIC THAN GEOKINETIC, THEREFORE, GREATER REACTOR SEVERITY WOULD BE REQUIRED TO EQUAL THE HYDROTREATED PRODUCT QUALITY OBTAINED WITH GEOKINETICS FEED. HENCE, CATALYST LIFE WOULD BE SHORTER. FOR THE HYDROTREATER/HYDROCRACKER OR FCC, PROCESSING ROUTES, DATA ARE NEEDED TO EVALUATE TRADE-OFFS.

## TABLE 11

**SUMMARY**

1. 270 BARRELS (11,355 GAL.) OF SPECIFICATION JP-4 TURBINE FUEL WAS PRODUCED BY SEVERELY HYDROTREATING GEOKINETICS SHALE OIL. REID VAPOR PRESSURE OF THE JP-4 FRACTION (I-480°F) RAN ABOUT 1.4 PSIA. 1% N-BUTANE WAS ADDED TO MEET SPECIFICATION RVP (2.0 MIN. - 3.0 MAX.). SOME BUTANE WAS PROBABLY LOST IN THE PDU OPERATION WHICH NORMALLY WOULD BE RECOVERED IN A COMMERCIAL OPERATION.

2. A TOTAL OF 890 BARRELS (36,400) OF SHALE OIL WAS PROCESSED THRU HRI'S PROCESS DEVELOPMENT UNIT. JP-4 YIELD AVERAGED ABOUT 35 VOL.% OF CHARGE. DURING THE RUN, ONE SHUTDOWN OCCURRED ABOUT 2 WEEKS AFTER START-UP DUE TO PLUGGING IN THE FRESH FEED HEATER COIL. ANALYSIS OF THE DEPOSITS SHOWED 65% ASH (45 WT.% IRON AND 6 WT.% ARSENIC). BY THE END OF THE RUN (NEARLY 3 WEEKS LATER), PRESSURE DROP HAD INCREASED AGAIN OVER THE HEATER COIL AND THE REACTOR REQUIRING A REDUCTION IN FEED RATE.

3. PROBLEMS MEETING BOTH JFTOT AND COPPER STRIP CORROSION TESTS WERE ENCOUNTERED WITH THE INITIAL JP-4 PRODUCTION IN BOTH THE BENCH SCALE AND PDU RUNS. CLAY TREATING CORRECTED THERMAL STABILITY (JFTOT) PROBLEMS. COPPER STRIP CORROSION PROBLEMS WITH THE PRODUCT FROM THE BENCH SCALE UNIT WERE ATTRIBUTED TO TRACE QUANTITIES OF $H_2S$ REMAINING IN THE LIQUID PRODUCT. 1700 GALLONS OF JP-4 PRODUCED INITIALLY IN THE PDU FAILED THE COPPER STRIP CORROSION TEST. THE ADDITION OF 5 PPM BENZOTRIAZOLE CORRECTED THIS DEFICIENCY. DURING STEADY STATE OPERATIONS OF THE PDU, THESE PROBLEMS VANISHED.

4. A PRELIMINARY PROCESS DESIGN BASIS WAS PREPARED FOR DEVELOPING ROUGH PLANT INVESTMENTS AND ECONOMICS (GEOKINETICS SHALE OIL) FOR COMPARISON WITH THE PHASE I BASE CASE (PARAHO SHALE OIL). ALTHOUGH THESE ESTIMATES HAVE MANY UNCERTAINTIES, THE RESULTS INDICATE THAT THE HYDROTREATING/HYDROCRACKING COMBINATION WOULD GIVE HIGH YIELDS OF JP-4, ABOUT 85 VOL.% OF TOTAL REFINERY INPUT (CRUDE, FUEL AND UTILITIES CONVERTED TO FOE BPD). CAPITAL INVESTMENT AND MANUFACTURING COSTS DO NOT APPEAR TO BE EXCESSIVE FOR A SHALE OIL REFINERY.

5. ADDITIONAL PROCESS DATA (HYDROTREATING CATALYST LIFE, CATALYTIC CRACKING AND HYDROCRACKING) ARE NEEDED TO DEVELOP AND OPTIMIZE FIRM PROCESS DESIGNS, ECONOMICS, PRODUCT YIELDS AND QUALITIES TO INSURE THAT SEVERE HYDROTREATING IS A VIABLE PROCESS OPTION.

VI

# AIR FORCE FUEL MAINBURNER/TURBINE EFFECTS PROGRAMS

By

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# AIR FORCE FUEL MAINBURNER/TURBINE EFFECTS PROGRAMS[1]

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## Introduction

In 1979 a multiyear program was initiated within the Air Force entitled, "The Aviation Turbine Fuel Technology Program" (ATFTP). The objective of this effort is to provide for the necessary test validation of a jet fuel which will result in adequate fuel availability and lower aircraft system life cycle cost than for the current Air Force standard jet fuel, JP-4. One of the first evaluations to be conducted within this program is the determination of fuel property effects on aircraft gas turbine engine mainburners and turbines. The scope and specific objectives of this program are discussed herein.

The broad objective of the ATFTP, the wide range of aircraft gas turbine engine types in the Air Force inventory, and the wide variations in the use of these systems necessitated a careful selection of the engines to be used in this evaluation. Initially, six engines were chosen: J57, J79, J85, F100, TF30, and TF39. These six engines represent products from the two largest manufacturors of military aircraft gas turbine engines. They represent fighter, trainer, transport, and bomber engine systems. They contain both types of major combustion systems, cannular and annular. They span system pressure ratios from 7:1 to 22:1. Finally, they span combustion design technology of approximately 20 years. The pertinent features of the systems and estimates of their numbers and rates of usage relative to the Air Force fleet of engines is provided in Table 1.

## Test Program

In the Summer of 1979 two awards were made to conduct the mainburner/turbine evaluations. General Electric (GE) and Pratt and Whitney (PW) received the awards. The primary objectives of both programs are identical. For each system the combustor is to be evaluated for its sensitivity to variations in fuel properties over its entire design operating range. This evaluation is to include the fuel effects on ignition and flame stability limitations throughout its flight envelope, combustion efficiency and gaseous emissions levels at the major static operating

[1] This program has been described in part at a NASA Symposium, April 16-17, 1980 (Reference 1); It has also been described in a paper submitted to the American Society of Mechanical Engineers for publication in conjunction with the 1981 Gas Turbine Conference (Reference 2).

points, smoke emissions, and any changes in predicted combustor liner life. The turbine is also to be extensively evaluated.

For the turbine three factors are considered important. First, increases in turbine metal temperature due to increased thermal radiation from the combustor as a function of fuel properties will be assessed. Second, changes in the temperature distribution at the combustor exit/turbine inlet plane due to fuel property variations will be evaluated. Finally, changes in the amount or distribution of particulates exiting the combustor and impacting the turbine will be documented as a function of fuel changes. These measurements will be utilized to assess the impact of fuel property variations on turbine life. The final objective is to determine each system's sensitivity to fuel properties under transient conditions, such as rapid accelerations or decelerations.

By the time final awards were made to GE and PW the two programs differed in the approaches and scope. In the GE program the bulk of the combustor and turbine data would be obtained in standard combustor component test rigs. Special rigs would be used to assess long term phenomena such as fuel nozzle fouling and turbine blade erosion. Limited engine testing in which both combustor and turbine components would be instrumented will supplement the rig test generated data base. In addition the engine test will be used to perform the transient evaluations. The GE program test matrix is provided in Table 2.

The TF30 was eliminated from consideration as the Navy has a similar effort underway with this engine. The PW program on the J57 (combustion system similar to the TF33) and the F100 will be conducted exclusively in standard combustor component test rigs and in a turbine erosion rig. The test matrix for this program appears in Table 3. The numbers that appear within the matrix of Table 3 refer to the number of test fuels ran in each particular test. For instance, six (6) test fuels were used to evaluate changes in combustor dome and liner temperatures in the J57 (TF33), single can, high pressure rig.

Test Fuels

The test fuel properties of interest for the two mainburner/turbine programs are similar to those considered in earlier evaluations of the J79 (Ref. 3) and the F101 (Ref. 4) combustion systems. The major changes are in the emphasis of certain properties rather than the selection. Properties considered of primary interest to the durability or performance of the mainburner and turbine components are fuel hydrogen content, fuel volatility, and fuel viscosity. Parameters of reduced significance are the fuel aromatic content, the distribution of aromatic types within the fuel, and the final boiling point of the fuel.

Hydrogen content has been a useful parameter in correlating high pressure test data. Combustor liner temperature (and, therefore, combustor life) and exhaust smoke correlate well with this fuel property. Fuel volatility, represented by the 10% recovery temperature during distillation, and fuel

viscosity are effective parameters in correlating both the combustion emissions during low pressure operation and the ignition and stability characteristics of combustion systems.

The distribution of aromatic types within a fuel and the fuel's end point have not been useful in correlating any combustion data on the J79 and F101 work. However, this data base is not considered sufficiently large to warrant eliminating these parameters from further consideration. Therefore, these properties are retained in these current combustion efforts but less emphasis is placed upon them in the fuel formulation.

The selection of test fuels for GE and PW programs has been an iterative process between the Aero Propulsion Laboratory and the contractors. In each program six fuels were identified for evaluation in the major component test rigs. Specialty test rigs, such as fuel nozzle fouling and turbine erosion rigs, are handled separately in that fuel selection is based on the specific needs of the rig to simulate desired conditions. Two of the six fuels were identified at the outset of the program. Petroleum derived JP-4 is to be used as a baseline. Shale oil derived JP-4 is to be used as a test fuel. This shale fuel was selected to support a supplemental objective of the program. This objective is to evaluate a specification fuel refined from shale oil crude in a commercially viable procedure. This test fuel was produced by Hydrocarbon Research Incorporated under subcontract to Suntech, Inc.

The four remaining test fuels for each program were selected by the contractors with final approval being given by the government. The approach taken by GE has been to use a subset of the test fuels used in their earlier programs (References 3 and 4), supplemented with a low hydrogen content diesel fuel. The complete list of the GE test fuels is provided in Table 4. This list includes JP-8 which is used as a specialty fuel in the fuel nozzle fouling test.

The PW fuel selection is more extensive in that four fuels are provided for ignition tests and a second set of four fuels are used in the tests of idle through full power conditions. Conventional and shale-derived JP-4 are used in all tests. The pertinent properties of the PW test fuels are listed in Table 5. Fuels 1 through 8 have been prepared by Suntech Group, Inc., under subcontract to PW. They differ from blended fuels typically used in these programs in that they are prepared from actual refinery process streams. They are not combinations of specification fuels and component additives.

## Preliminary Results

At this writing nearly all testing has been completed within both programs. Some of the data has been evaluated and correlated with dominant fuel properties. While these results must be considered preliminary (as the data has not all been checked for self consistency), it would be useful to present some of the correlations involving the shale oil JP4 at this time.

The shale oil derived JP4 exhibited very little deviation from the petroleum derived JP4 in terms of its physical properties and those few chemical properties that are routinely determined for such test fuels. The most notable difference was that the room temperature viscosity of the shale fuel was about 30% higher than that of the petroleum fuel. This property manifests itself in the quality of the fuel spray exiting the fuel nozzle. Other physical properties being held constant, increasing fuel viscosity tends to degrade the fuel spray quality, presumably by increasing the mean diameter of the fuel droplets. This change can be expressed in terms of the Sauter Mean Diameter (SMD), a calculated parameter accounting for the fuel density, surface tension, and viscosity. There are different expressions for determining the SMD based on the type of fuel nozzle being considered. In Figure 1 the SMD, normalized by the SMD of the petroleum JP4, is used to correlate the carbon monoxide emissions from the J79 and TF39 rig tests at the simulated idle test point. The shale fuel, with a higher viscosity than the baseline, generates greater CO emissions. However, these levels are consistent with what could be predicted with the fuel's higher viscosity.

This same parameter is used in Figure 2 to correlate the altitude limits at which the TF39 can be relit. Again the difference in fuel viscosity causes a deviation from baseline performance; but the change is consistent with the fuel property difference.

The fuel hydrogen content of the shale fuel was very close to that of the petroleum baseline. The parameter most often examined with respect to this fuel property is the metal temperature of the combustor liner. Two sets of data are offered in this regard. In Figure 3 measurements of the inner liner temperature rise of the J79 have been plotted against fuel hydrogen content. These measurements come from several thermocouples affixed to the liner. The peak measurement is a single reading (less the inlet gas temperature). The average data is the mathematical average of all the readings on the inner liner (again, less the inlet gas temperature). In Figure 4 a similar plot is made of the TF33 temperature data. In this figure, however, the liner temperature rise values are normalized by dividing by the temperature rise across the combustor. In both figures the shale fuel and the petroleum baseline behave similarly. Their hydrogen contents are very close and their affect on the temperature of both combustor liners are nearly the same.

Summary

The full set of data from the programs can be expected by the summer of 1981. From the data that has been correlated the shale fuel will likely behave in a manner predictable by an analysis of its major physical and chemical properties. The shale oil JP4 refined for these two test programs was very similar to a petroleum JP4 used as the baseline. As expected, the shale JP4 performed very similar to the baseline except where a major deviation in properties occurred (such as the viscosity). In this situation the shale fuel follows trends established by other test fuels and other test programs.

## References


1. "Aircraft Research and Technology for Future Fuels", NASA Lewis Research Center Symposium, Publication 2146, April 1980.

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3. Gleason, C. C., et al, "Evaluation of Fuel Character Effects on J79 Engine Combustion System", AFAPL-TR-79-2015, June 1979.

4. Gleason, C. C., et al, "Evaluation of Fuel Character Effects on the F101 Engine Combustion System", AFAPL-TR-79-2018, June 1979.


TABLE 1: TEST ENGINES

| | TYPE | COMBUSTOR SYSTEM | PRESSURE RATIO | APPLICATION | % OF AF ENGINES | % of FLEET HOURS |
|---|---|---|---|---|---|---|
| G.E. | J-79 | CANNULAR | 13.4/1 | F4 | 12.5 | 9.9 |
| | J-85 | ANNULAR | 7.4/1 | T38, F5 | 10.7 | 10.7 |
| | TF39 | ANNULAR | 22.4/1 | C5A | 1.1 | 1.1 |
| P & W | TF30 | CANNULAR | 21.8/1 | F14, F111 | 3.1 | 2.3 |
| | F100 | ANNULAR | 20/1 | F15, F16 | 8.2 | 1.0 |
| | J-57/TF33 | CANNULAR | 12/1 | B52, KC135, C141 | 31.7 | 42.4 |
| | | | | | 67.3 | 67.4 |

TABLE 2

## FUEL MAINBURNER/TURBINE EFFECTS TEST SCOPE (GE)

| TEST VEHICLE | Combustor Dome and Liner Temperature | Smoke and Gaseous Emissions | Combustor Exit Temp Distribution | Combustor Stability at Idle | Cold Day Ground Start | Altitude Relight and Stability | Fuel Nozzle Plugging | Carbon Deposition | Transient Response | Turbine Material Erosion | Turbine Stator Heat Load | Fuels to be Tested |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| J79 Single Combustor High Pressure Rig | X | X | | | | | | X | | | | 3 |
| J85 Full Annular Combustor High/Low Pressure Rig | X | X | X | X | X | X | | X | | | | 6 |
| TF33 Full Annular Combustor Atomspheric-Pressure Rig | | | X | X | | | | | | | | 3 |
| TF39 360 Sector Combustor High Pressure Rig | X | X | | | | | | X | | | | 6 |
| TF39 60° Sector Combustor Low Pressure Rig | | | | | X | X | | | | | | 6 |
| J79/J85/TF39 Fuel Nozzle Fouling Rig | | | | | | | X | | | | | 2 |
| J79/J85/TF39 Turbine Material Erosion Rig | | | | | | | | | | X | | 1 |
| J79 Engine | X | X | | | | | | | X | | X | 2 |
| J85 Engine | X | X | | | | | | X | X | | X | 6 |
| TF39 Engine | X | X | | | | | | | X | | X | 2 |

TABLE 3

## FUEL MAINBURNER/TURBINE EFFECTS TEST SCOPE (P&W)

| TEST VEHICLE | Combustor Dome and Liner Temperatures | Smoke and Gaseous Emissions | Combustor Exit Temp Distribution | Combustor Stability and Altitude Relight | Standard and Cold Day Ground Start | Carbon Deposition | Transient Response | Turbine Material Erosion |
|---|---|---|---|---|---|---|---|---|
| J57 (TF33) Single Can Hi Pressure Rig | 6 | 6 | 6 | | | 3 | 6 | |
| J57 (TF33) Multiple Can Full Ann/Lo Press Rig | | | | 6 | 6 | | | |
| F100 30° Sector Rig | 6 | 6 | 6 | 6 | 6 | 3 | 6 | 2 |
| Lo Press Turbine Rig | | | | | | | | 2 |

TABLE 4

## GENERAL ELECTRIC TEST FUELS' PROPERTIES, ESTIMATED

| TEST FUEL TYPE | $\%H_2$ | IBP | DISTILLATION, K 20% RECOVERY | EP | VISCOSITY cSt 300K |
|---|---|---|---|---|---|
| CONVENTIONAL JP-4 | 14.5 | 294 | 362 | 610 | 0.9 |
| CONVENTIONAL JP-8 | 13.9 | 398 | 469 | 589 | 2.1 |
| JP-4/2040 | 12.1 | 302 | 390 | 583 | 1.1 |
| JP-4/2040 | 13.1 | 298 | 378 | 574 | 1.0 |
| CONVENTIONAL NO. 2 DIESEL | 13.2 | 394 | 495 | 682 | 4.0 |
| NO. 2 DIESEL/2040 | 11.9 | 395 | 489 | 677 | 3.3 |
| SHALE-DERIVED JP-4 | 14.3 | 276 | 406 | 601 | 1.2 |

TABLE 5

## PRATT AND WHITNEY TEST FUEL PROPERTIES, ESTIMATED

| TEST FUEL TYPE | $\%H_2$ | IBP | DISTILLATION, K 20% RECOVERY | EP | VISCOSITY cSt 300K |
|---|---|---|---|---|---|
| CONVENTIONAL JP-4 | 14.5 | 293 | 363 | 589 | 0.9 |
| SHALE-DERIVED JP-4 | 14.4 | 273 | 407 | 583 | 1.2 |
| IGNITION FUEL BLENDS | | | | | |
| 1 | 14.2 | 325 | 394 | 586 | 1.7 |
| 2 | 13.4 | 315 | 428 | 586 | 1.2 |
| 3 | 14.0 | 368 | 451 | 550 | 1.7 |
| 4 | 12.3 | 270 | 367 | 567 | 0.7 |
| DURABILITY FUEL BLENDS | | | | | |
| 5 | 13.4 | 385 | 457 | 638 | 1.8 |
| 6 | 12.9 | 283 | 393 | 649 | 1.4 |
| 7 | 11.6 | 405 | 432 | 826 | 2.8 |
| 8 | 11.5 | 418 | 479 | 852 | 2.8 |

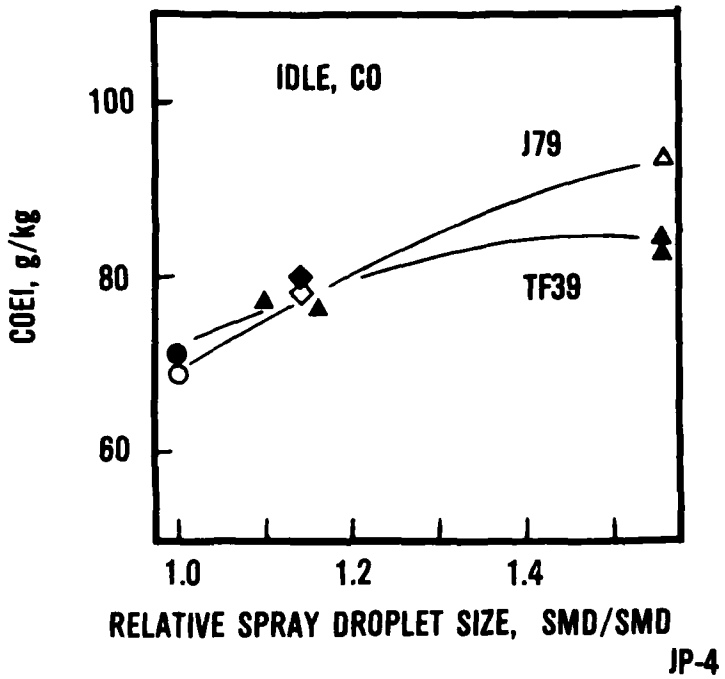


Figure 1. Effect of Fuel Atomization on Idle CO Emissions Levels for the J79 and TF39 Engines

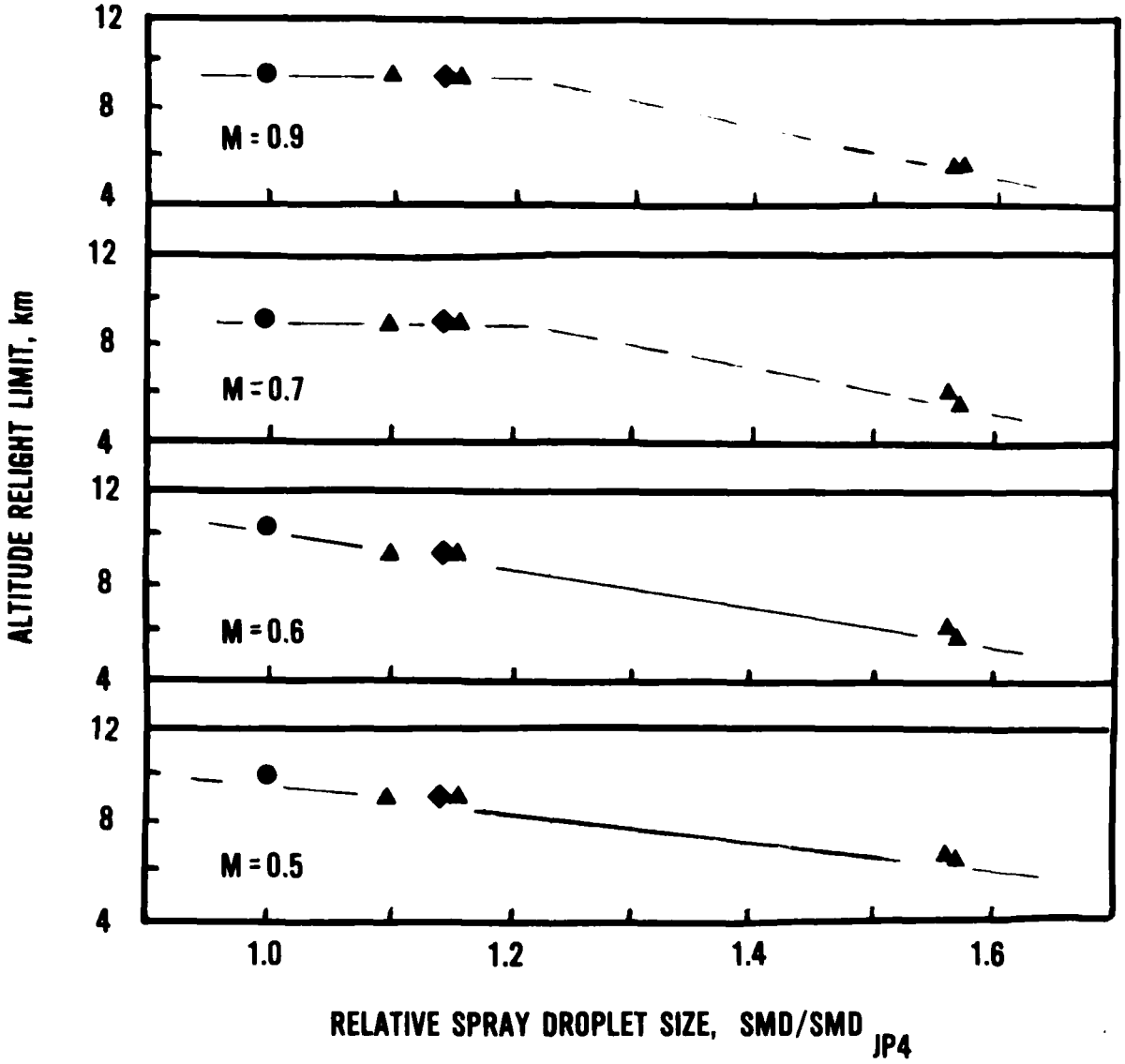


Figure 2. Effect of Fuel Atomization on Altitude Relight Limits, TF39 Engine (Four Different Values of Simulated Mach Number)

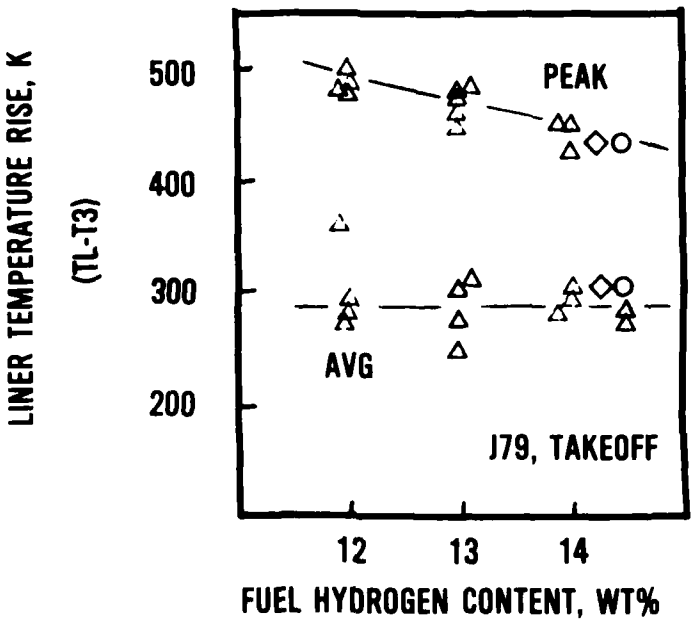


Figure 3. Effect of Fuel Hydrogen Content on the Inner Liner Temperature Rise, J79 Engine

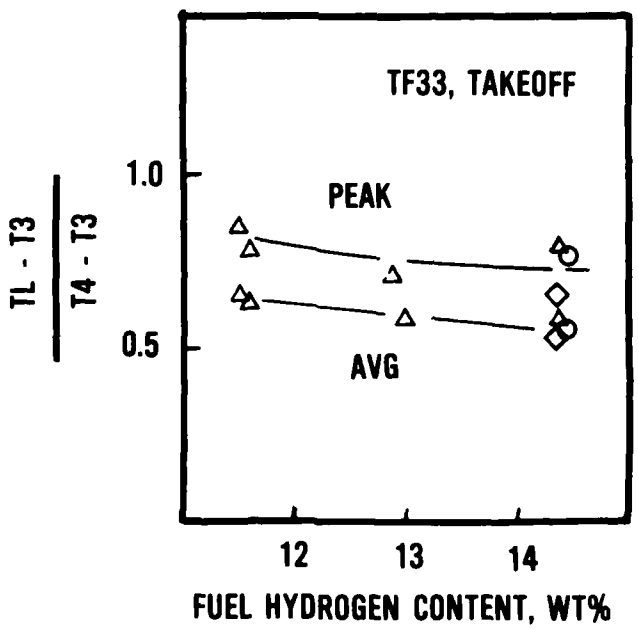


Figure 4. Effect of Fuel Hydrogen Content on the Normalized Liner Temperature Rise, TF33 Engine

VII

# CATALYST DEVELOPMENT FOR JET FUEL FROM SHALE OIL

By

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Amoco Oil Company

# CATALYST DEVELOPMENT FOR JET FUEL FROM SHALE OIL

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## ABSTRACT

New experimental catalysts have been developed for the direct hydrocracking on shale oil to produce JP-4 jet fuel boiling range material. The catalysts contain cobalt oxide, molybdenum oxide, and a third metal oxide as stabilizer. Alumina, silica alumina, and sieve alumina supports have been tested with an Occidental shale oil feed. Denitrogenation activity increases with support acidity while incorporation of molecular sieves into the support increases cracking activity. The catalysts effectively remove contaminants such as nitrogen. The most active catalyst tested, a 1.5% CoO, 15% $MoO_3$ and 10% stabilizer on 50% Ultrastable molecular sieve/50% alumina produced a product containing <5 ppm nitrogen and ~80% JP-4 boiling range material at 780°F, 1800 psi, and 0.5 Vo/Vc/hr on a once-through basis.

## INTRODUCTION

Amoco Oil has been active in catalyst development for many years. For the past 10 to 15 years much of the work has been directed toward upgrading heavy petroleum residues, tar sands oil, and shale oils. In the course of this work a number of catalysts with superior properties for upgrading such feeds have been developed. This report describes work within Amoco Oil to optimize one of these previously developed catalysts for production of jet fuel from an Occidental whole shale oil. The catalyst contains cobalt, molybdenum and a third metal component which acts as a stabilizer. The stabilized catalyst can operate at high temperatures and moderate hydrogen pressure with a relatively low activity decline rate. For this report the catalyst will be referred to as "stabilized cobalt/moly." All of the work was carried out at our Research Center in Naperville, Illinois using small-scale automatic pilot plants which operate continuously.

The program, which began late last year, is sponsored by the U.S. Air Force and Wright-Patterson Air Force Base via a 19-month contract. Although other companies--UOP, Ashland, and Sun--are conducting more extensive process and design work, our objective is limited to catalyst development for increased jet fuel production. The Air Force's interest in shale oil as a source of jet fuel is understandable since available domestic reserves are not subject to foreign political instability. To maximize jet fuel, a catalyst must be capable of sustained high cracking activity in the presence of large quantities of ammonia as well as high denitrogenation and desulfurization activity. Cracking and nitrogen removal imply high saturation activity, and as well, we need high selectivity toward jet fuel boiling range material.

The contract calls for four major tasks:

(I) A process variable study on existing catalysts.

(II) A catalyst composition study, i.e., metal concentrations and support composition.

(III) Catalyst physical properties study, i.e., pore size, surface area, and pore volume.

(IV) An activity maintenance test of at least two months.

Results will be presented for Tasks I and II.

Table I shows selected analytical data for three different shale oils. The Tosco and Paraho oils were produced by above-ground retorting, whereas the Occidental oil was obtained by in situ retorting. The API gravities of just over 20° are in the range for heavy petroleum crudes. All have high pour points dictating the use of wax modifiers or heated pipe lines for off-site processing or alternatively on-site processing. The H/C atomic ratios are on the low end of the scale for petroleum crudes and consequently hydrogen consumption, even without the amount required for oxygen and nitrogen removal, will be high for producing jet fuel. Sulfur content is low but the nitrogen content of up to 2.5 wt% is an order of magnitude higher than that found in most petroleum crudes.

Of the three shale oils shown, the Occidental oil has the best overall quality. It contains more hydrogen and less nitrogen; consequently, the amount of hydrogen required for upgrading will be significantly less than that required for either the Tosco or Paraho oils.

The key to successful shale oil upgrading is an effective initial hydrotreating step to remove contaminants, particularly nitrogen. Aromatic nitrogen compounds must be fully saturated prior to nitrogen removal and subsequent cracking reactions. Nitrogen species are severe poisons in downstream cat cracking and reforming processes and also cause color instability and gum precipitation in distillate and in gasolines.

## RESULTS AND DISCUSSION

The initial catalyst selection was based on two types of catalysts--the stabilized cobalt/moly and a nickel/moly/phosphorous--both developed by Amoco. The stabilized cobalt/moly was known to have high cracking and desulfurization activity, good high-temperature stability but untested denitrogenation activity. The Ni/Mo/P system was known to have high activity for nitrogen and sulfur removal from shale oil but low cracking activity and poor stability at high temperature.

For Task I, two process variable studies were made. In one the stabilized cobalt/moly catalyst was used alone, while in the other an equal amount of the Ni/Mo/P and the stabilized cobalt/moly catalyst was used in a two-reactor system. Processing conditions were varied over the ranges of 1400 to 2400 psi, 760° to 810°F, and 0.25 to 1.0 Vo/Vc/hr, one variable at a time. After each process period, an activity check was made at the base conditions of 1800 psi, 0.5 LHSV, and 790°F.

Figure 1 shows plots of relative denitrogenation activities at base conditions for the two systems over the test period of ~50 days with the single-catalyst system assigned an activity of 100 for days 2 through 5. For clarity, results for other conditions are not shown but are represented by the smoothed curves.

The results indicate that under all conditions of P, T and SV the use of the stabilized cobalt/moly catalyst by itself was preferred. This was due to the fact that for the two-catalyst system the Ni/Mo/P part of the bed was always held at 735°F to avoid known deactivation. As the graphs show, activities for the base conditions decline rapidly perhaps due to changing process conditions and the extreme combination of conditions used.

In Table II, comparison of the product qualities with feed properties at the base conditions of 1800 psi, 0.5 LHSV indicates that both systems initially achieve more than 98% denitrogenation. However, the single catalyst, stabilized cobalt/moly on alumina, is better for saturation as judged by the API gravity, better for nitrogen removal and has higher cracking activity as judged by the increased yields of JP-4 jet fuel boiling range material.

Because of the high temperature advantage of the stabilized cobalt/moly catalyst, further development was confined to this system.

Figures 2 and 3 show kinetic results for the stabilized cobalt/moly system from the process variable study. Nitrogen removal is shown to be first order in nitrogen concentration down to ~.01% or 99% removal. Some deviation at very low product nitrogen was observed and may be due to catalyst bypassing or analytical error. It should be noted that this catalyst gives 2 ppm product nitrogen at ~.27 LHSV, 1800 psi and 790°F. Denitrogenation was found to be first order with hydrogen pressure up to 2400 psi.

Figure 4 shows the relationship between product nitrogen and hydrogen consumption for the single-catalyst system. The three points represent ~1, .5 and .27 space velocities at 790°F and 1800 psi. The results show that ~1100 SCFB hydrogen is consumed for a product nitrogen of ~.1% and that only an additional 200 SCFB hydrogen is required for almost complete removal.

As indicated previously, the catalyst of choice was the stabilized cobalt/moly system. In Task II, the system was optimized both with respect to metals concentration and support type.

First the optimum metal loadings on alumina were determined. This was done by systematically varying the concentration of each metal oxide component within a range shown in Table III while holding the other two components constant. For example, catalysts containing 1.5, 3, and 5 wt% CoO were prepared on the same alumina support containing 10% $MoO_3$ and 10% of the metal oxide used as stabilizer. Each catalyst was then tested under the standard conditions of 1800 psi, 0.5 LHSV and 780°F.

An example of the effect of molybdenum oxide concentration is shown in Figure 5. At constant CoO and stabilizer concentrations of 1.5 and 10 wt% respectively, the effect of increasing $MoO_3$ concentration from 5% to 15% was to decrease product nitrogen from ~500 ppm to <100 ppm. The curve suggests that $MoO_3$ loading greater than about 15% would not result in a significant increase in initial activity.

Relative activities for three catalysts with different $MoO_3$ loadings are shown in Figure 6. For this and other activity curves, the 1/10/10 system was considered the base case catalyst with an activity of 100. The catalyst containing 5% $MoO_3$ is decidely less active whereas the highest loading shows increased activity and good activity maintenance for the test period.

Similar activity plots for various CoO and stabilizer loadings are shown in Figures 7 and 8 respectively. For cobalt, the 3.6 wt% loading results in lowered activity whereas the catalyst containing 5 wt% loses some activity over the six-day run. For the stabilizer, best overall performance is observed at a loading of 10 wt%.

Based on the initial activities and activity maintenance for the seven catalysts tested, all further development was based on optimum oxide loadings of ~1.5% CoO, 15% $MoO_3$ and 10% stabilizer.

With the metals optimized, the next step in Task II was to determine the best support composition. Catalysts with the same metals loadings were prepared on alumina, phosphated alumina, silica, silica/alumina and an Ultrastable (US) molecular sieve/alumina. These represent both neutral and acidic supports.

Results for the various supports are shown in Figure 9 in a plot of relative activity for denitrogenation versus days on oil. With the alumina system designated as the base case with an assigned denitrogenation activity of 100 on day 2, activities for the catalyst on the other supports range from about 30 for silica to over 150 for the silica/alumina or sieve/alumina. The phosphated alumina system had an activity similar to that of alumina but appeared to deactivate more rapidly. The results indicate that relative activities increase with increasing support acidity.

Table IV illustrates how increased activity affects total product nitrogen levels and other product properties for three of these systems. Compared to the base case alumina system, the 20% $SiO_2$/alumina and the 30% US sieve/alumina systems give almost complete nitrogen removal down from 13,000 ppm nitrogen. As well, the sieve/alumina system has better cracking activity resulting in a lower pour point and in a significant increase in jet fuel production from 38% to 54%.

At this point in the work, all results were presented to contract personnel and the contract was subsequently expanded to include a more thorough investigation of the effect of silica concentration and molecular sieve type and concentration on both cracking and denitrogenation activity.

A series of silica/alumina catalysts containing 10 to 70 wt% silica were prepared. Generally, increasing silica concentration above 50% resulted in product qualities tending toward those obtained with the pure silica-based catalysts. Thus, the product nitrogen increased and JP-4 fraction decreased. Little reduction in pour point was observed for any of these catalysts due to lack of long-chain paraffin cracking.

Figure 10 shows product nitrogen on a log scale versus weight percent silica. The 0% silica corresponds to the 100% alumina base case. The data show an optimum activity or lowest nitrogen at the 20 wt% silica level with good performance also observed at the 30 and 50 wt% levels.

This optimum silica content of ~20% appears to represent a compromise between maximum hydrogenation activity on alumina and maximum acidity at the 70% silica level.

Results for the effect of sieve type with the same metals loadings and process conditions are summarized in Table V. Compared to the alumina base case, the US-sieve-containing catalyst gives almost total nitrogen removal, 54% jet fuel boiling range material and good pour point reduction. The ZSM-5-containing system is slightly less active for nitrogen removal and jet fuel production but selectively reduces pour point. The Zeolon-molecular-sieve-containing catalyst appears equivalent to alumina alone and perhaps because of its very small pores is acting as a diluent. The catalyst containing a rare-earth-exchanged Y sieve gives mixed results with excellent nitrogen removal but comparatively poor jet fuel production or pour point reduction. Gas yields and hydrogen consumptions generally increase with denitrogenation and cracking, as would be expected.

Based on these results, the US-sieve-containing system appeared promising and consequently catalysts containing 20 to 50 wt% sieve were prepared and tested. Results are shown in Table VI along with the alumina base case and the best silica/alumina system. All three catalysts produce very low product nitrogens. The JP-4 fraction increases from ~40 to 77 wt% with increasing sieve content accompanied by an increase in hydrogen consumption. Gas make is higher also for the 50% sieve case.

The effect of sieve concentration on product fractions is shown in Figure 11. Over the range of 20 to 50 wt% sieve, the JP-4 fraction almost doubles from 40 to 77 wt% whereas the diesel and gas oil fractions decrease in a parallel manner. At the 50% sieve level, ~92% of the product boils below 650°F. It should be noted also that the product fraction levels for the 20% US sieve system are not much different than those for the pure alumina-based catalyst.

The correlation between cracking activity to produce JP-4 boiling range material and hydrogen consumption is shown in Figure 12. The points represent the alumina base case catalyst on the left and the 20, 30 and 50 wt% sieve-containing catalysts. The results show a smooth and rapid increase in hydrogen consumption with increasing JP-4 yields. Selected product qualities for a JP-4 boiling fraction are shown in Table VII. All measured qualities are well within product specifications for JP-4 jet fuel from this single-pass, deep hydrocracking system.

The remaining contract tasks will focus on optimizing the support physical properties, surface area, pore volume, and average pore diameter for the best US sieve/alumina catalyst and on a final activity test.

SUMMARY

We have developed high-temperature stable catalysts capable of effecting significant improvements in shale oil upgrading. Although the alumina-based catalyst can be considered an excellent hydrotreating catalyst, addition of silica or molecular sieve increases denitrogenation significantly. As well, molecular sieve-containing catalysts are capable of increased hydrocracking activity for shale oil in a single-stage process, despite the very high nitrogen content of the feed used.

## Table I

## Selected Shale Oil Properties

| | Tosco | Paraho | Occidental |
|---|---|---|---|
| API° | 21.0 | 20.2 | 23.8 |
| Pour point, °F | 75 | 90 | 60 |
| H/C | 1.56 | 1.61 | 1.67 |
| N, Wt% | 1.88 | 2.18 | 1.32 |
| S, Wt% | 0.75 | 0.66 | 0.64 |
| 0, Wt% | 1.39 | 1.16 | 1.33 |

## Table II

## Initial Product Qualities for One- and Two-Catalyst Systems

(1800 psi, 0.5 LHSV)

| | NiMoP + Stabl. CoMo | Stabl. CoMo | Feed |
|---|---|---|---|
| Temperature, °F | 735/790 | 790 | -- |
| API° | 37 | 39 | 24 |
| Pour point, °F | 75 | 75 | 60 |
| Nitrogen, ppm | 250 | 116 | 13,000 |
| JP-4, Wt% | 22 | 34 | 14 |
| 650°F-, Wt% | 66 | 74 | 44 |

## Table III
## Metals Optimization on Alumina

| CoO Wt% | $MoO_3$ Wt% | Stabilizer, Wt% |
|---|---|---|
| 1.5-5.0 | 10 | 10 |
| 1.5 | 10 | 5-15 |
| 1.5 | 5-15 | 10 |

## Table IV
## Effect of Support Composition on Selected Product Qualities

| | $AL_2O_3$ | 20% $SiO_2$ /$Al_2O_3$ | 30% US Sieve/$Al_2O_3$ |
|---|---|---|---|
| Nitrogen, ppm | 83 | 8 | 5 |
| Pour point, °F | 80 | 65 | 30 |
| JP-4, Wt% | 38 | 35 | 54 |

## Table V

## Effect of Molecular Sieve Type on Selected Product Qualities and Hydrogen Consumption

| Support | Nitrogen, ppm | JP-4 WT% | Pour Point, °F | $C_1$-$C_4$, Wt% | SCFBH |
|---|---|---|---|---|---|
| $Al_2O_3$ | 83 | 38 | 80 | 2.9 | 1280 |
| 30% US Sieve/$AL_2O_3$ | <5 | 54 | 30 | 3.6 | 1520 |
| 20% ZSM-5 | 35 | 42 | -10 | 3.5 | 1370 |
| 20% Zeolon | 80 | 34 | 65 | 2.7 | 1320 |
| 20% REY | <10 | 31 | 75 | 2.6 | 1340 |

## Table VI

## Effect of Sieve Concentration on Product Qualities and Hydrogen Consumption

| Catalyst | JP-4, Wt% | Nitrogen, ppm | $C_1$-$C_4$, Wt% | SCFBH |
|---|---|---|---|---|
| -- | 14 | 13,000 | -- | -- |
| $AL_2O_3$ | 38 | 83 | 2.9 | 1280 |
| 20% $SiO_2$ | 35 | 8 | 3.0 | 1280 |
| 20% US Sieve | 41 | 3 | 3.7 | 1360 |
| 30% US Sieve | 54 | 5 | 3.6 | 1520 |
| 50% US Sieve | 77 | 3 | 5.6 | 1700 |

## Table VII

## JP-4 Jet Fuel Properties

50% US Sieve/Alumina
780°F, 1800 psi, 0.5 LHSV

| | |
|---|---|
| API | 51.4° |
| Nitrogen | 2 ppm |
| Pour point | ‹ -70°F |
| Viscosity, 40°C | 1.07 cst |
| Aromatics | 14.3% |
| Olefins | ‹ 0.1% |
| Acid number | ‹ 0.002 mg/g |

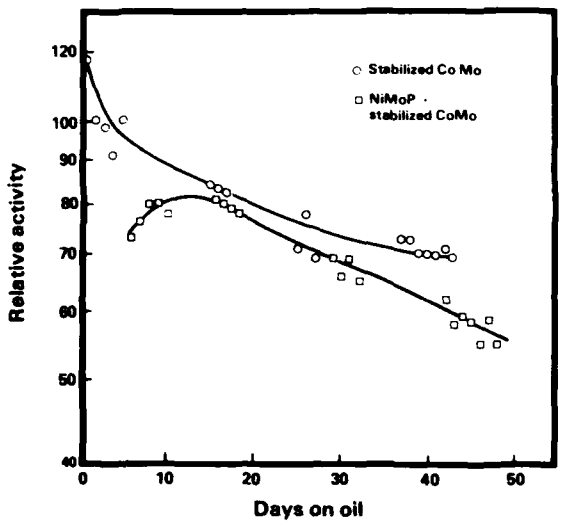


Figure 1

**Catalyst relative activities during process variable study**

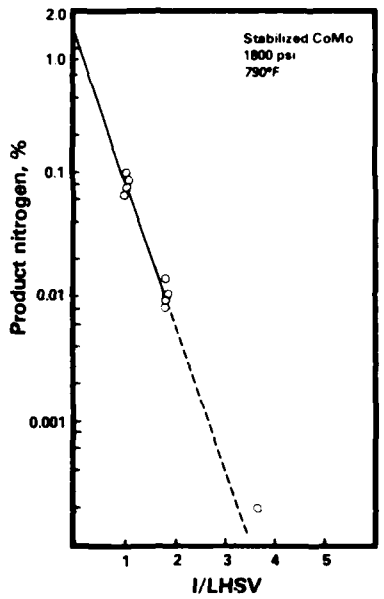


Figure 2

**Effect of space velocity on nitrogen removal**

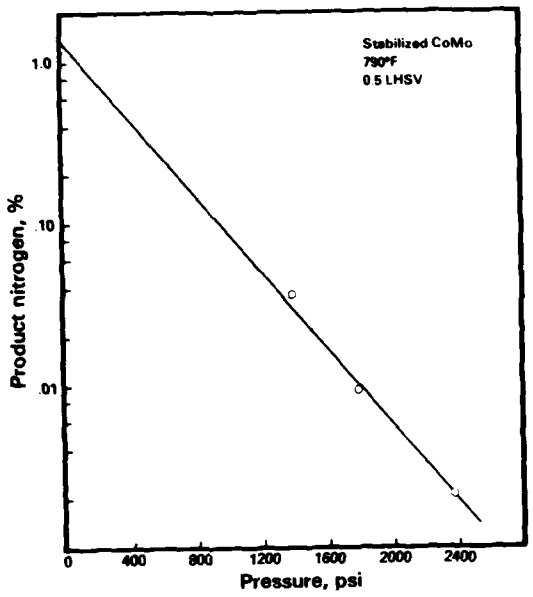


Figure 3

**Effect of pressure on nitrogen removal**

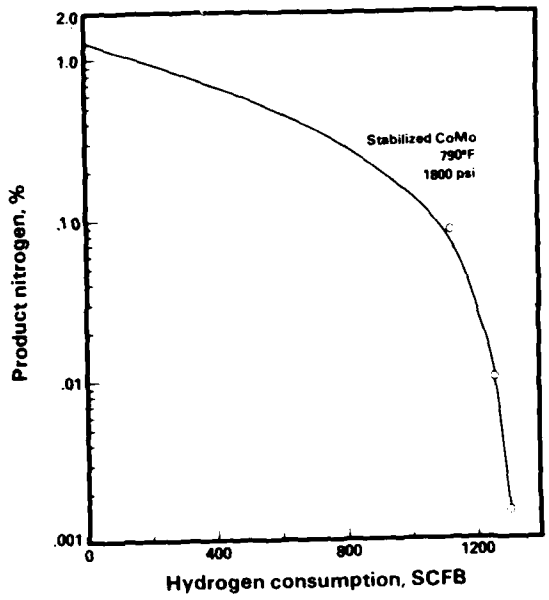


Figure 4

**Chemical hydrogen consumption for shale oil denitrogenation**

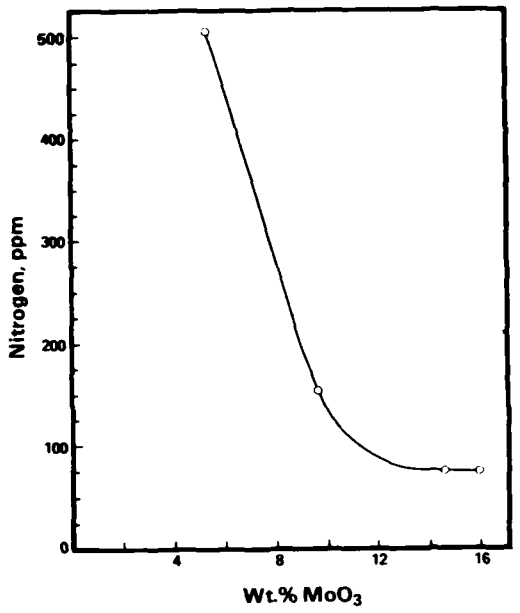


Figure 5

**Effect of $MoO_3$ concentration on nitrogen removal**

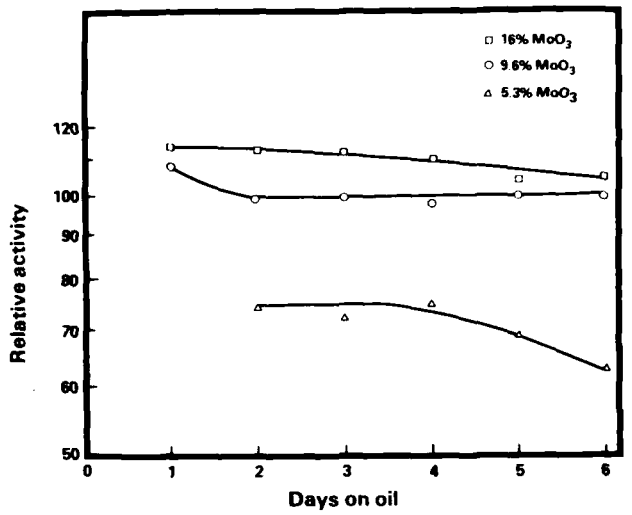


Figure 6

**Effect of $MoO_3$ concentration on denitrogenation activity**

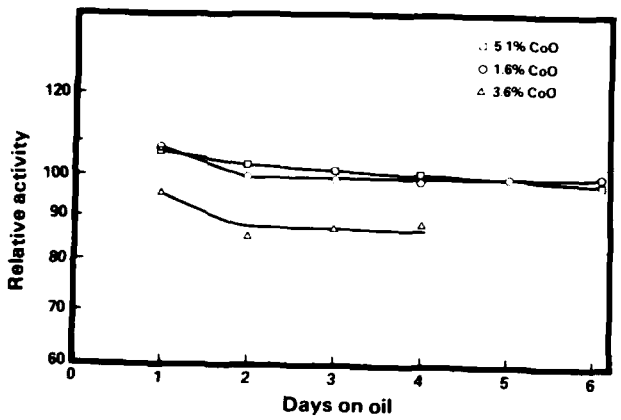


Figure 7

**Effect of CoO concentration on denitrogenation activity**

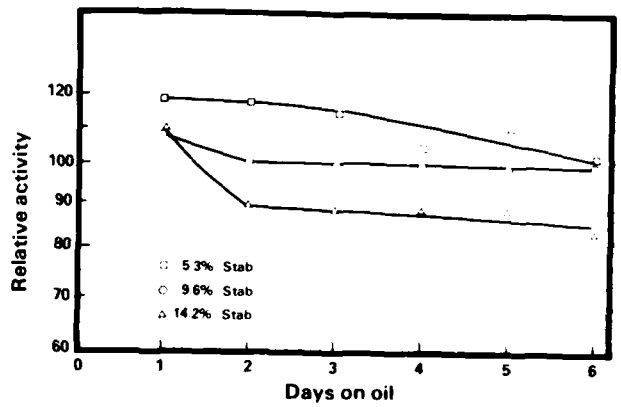


Figure 8

**Effect of stabilizer concentration on denitrogenation activity**

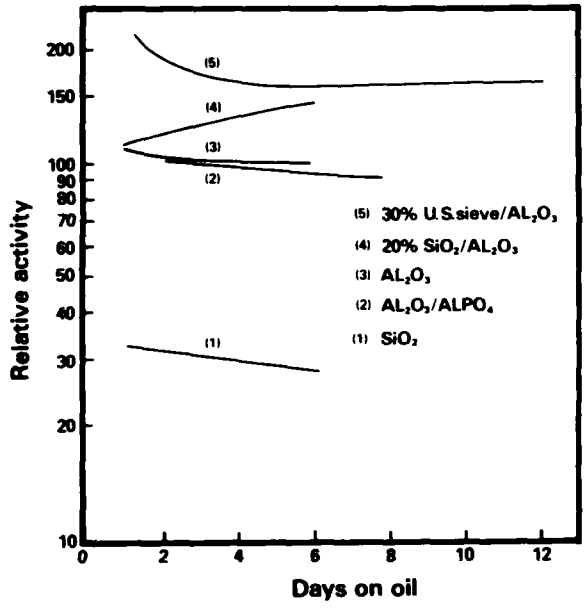


Figure 9

**Effect of support composition on denitrogenation activity**

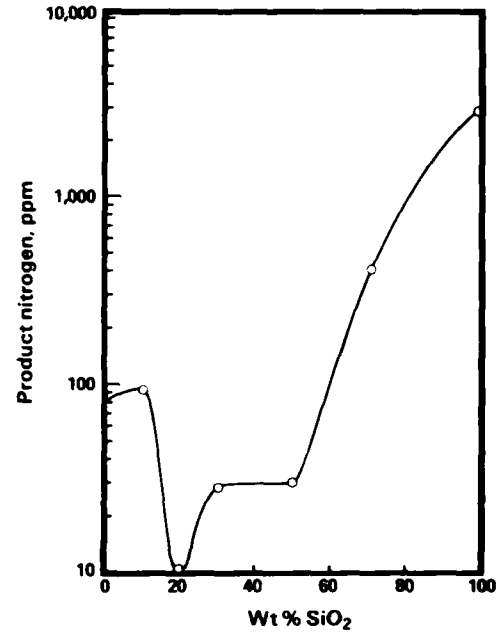


Figure 10

**Effect of silica concentration on nitrogen removal**

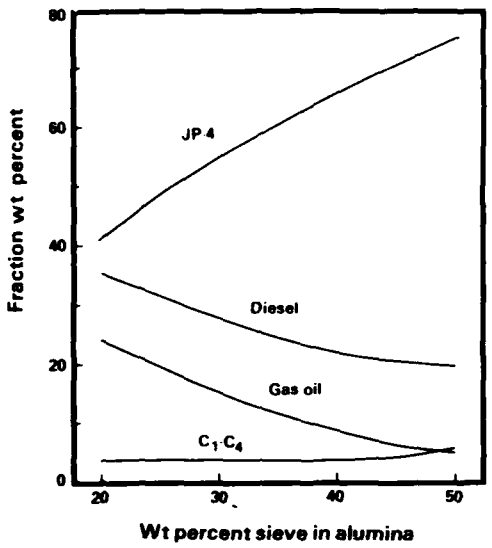


Figure 11

**Effect of sieve concentration on product boiling range**

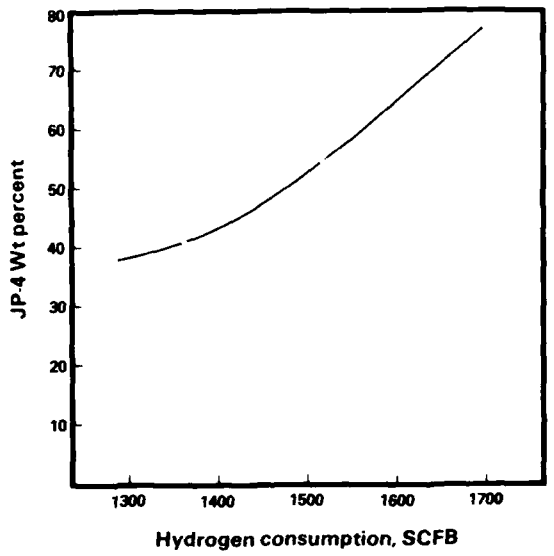


Figure 12

**Correlation of JP-4 yeild and hydrogen consumption**



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