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# JET FUEL FROM SHALE OIL — 1981 TECHNOLOGY REVIEW

*DR. HERBERT R. LANDER, JR.*

*FUELS BRANCH*
*FUELS AND LUBRICATION DIVISION*

DECEMBER 1981

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AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
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WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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ERRATA - January 1982

The following typographical corrections are applicable to AFWAL-TR-81-2135, "Jet Fuel From Shale Oil - 1981 Technology Review", Unclassified Report, December 1981:

Page 210

Change data of SOHIO 62P sample for

| | |
|---|---|
| Total Paraffins MS(Wt) to read | 76.90 |
| Total Aromatics MS(Wt) to read | 23.00 |

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The "Jet Fuel From Shale Oil - 1981 Technology Review" culminated three years of Air Force Shale Oil related programs. Final economic optimized results of three processing studies evaluating the yield, cost and quality of JP-4 and JP-8 jet fuel produced from whole crude shale oil are discussed. Reported also are technologies associated with a newly developed nitrogen tolerant catalyst and conclusions of combustion studies performed on shale derived JP-4 jet fuel samples and Nuclear Magnetic Resonance (NMR) analyses of the composition of shale derived jet fuel samples.

## FOREWORD

This report contains the proceedings of a symposium sponsored by the Fuels Branch (POSF), Fuels and Lubrication Division (POS), Aero Propulsion Laboratory (PO), Air Force Wright Aeronautical Laboratories (AFWAL). The Air Force contracts reviewed are sponsored under Projects 2480 and 3048. Contractors, AFWAL/POSF, contract numbers, and work units are listed below:

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| Amoco Oil Company | F33615-79-C-2095 | 30480507 |
| General Electric Company | F33615-79-C-2009 | 24800101 |
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The Conference Chairman, Dr Herbert R. Lander; Symposium Moderator, Mr Arthur V. Churchill; Symposium Manager, Ms Eva M. Conley and Symposium Vice Manager, Ms Charlotte R. Eigel, Fuels Branch, Aero Propulsion Laboratory, would like to thank Dr Edmund J. Rolinski, Symposium Contract Manager, Chemical Engineering Department, University of Dayton, Dayton, Ohio, and all others for their support and assistance in bringing this "Jet Fuel From Shale Oil - 1981 Technology Review" to a successful end.

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# JET FUEL FROM SHALE OIL OVERVIEW

By

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# JET FUEL FROM SHALE OIL OVERVIEW

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In order to accomplish its basic mission - aircraft operations - the Air Force must maintain large numbers, as well as a wide variety, of aircraft. The Air Force currently has over 9,300 aircraft in its inventory. The largest number of these are fighters which are high-technology, high-performance aircraft necessary for combat support and air-to-air missions. To operate its aircraft, the Air Force requires large amounts of jet fuel. During fiscal year (FY) 1980, the Air Force consumed 87 million barrels (3.7 billion gallons) of jet fuel. The total petroleum usage by the Air Force for FY 1980 was 89 million barrels which was 61 percent of the Defense Department's (DOD) requirement which is 2.8 percent of the petroleum requirement of the United States.

The Air Force has complied with various presidential and DOD directives and has managed to accomplish its energy-intensive mission at reasonable costs. In spite of drastic efforts to reduce jet fuel consumption, the Air Force's energy costs have risen more than 125 percent since FY 1973, even though its energy usage decreased by about 38 percent, from 143 million barrels in 1973 to 87 million barrels in 1980. The energy savings in aircraft operations since 1973 have resulted from avoidance of flying hours which were reduced from 4.9 million hours in FY 1973 to 3.2 million hours in FY 1979. This reduction in flying hours was to some extent the result of a decrease in the total number of active aircraft, from 10,800 in FY 1973 to the current figure of about 9,300, and the use of aircraft simulators for training. In addition, procedural changes - including improved mission planning, training activities, and ground, departure, enroute and arrival operations - and equipment modifications to improve aerodynamics and the efficiency of aircraft propulsion systems also contributed to the reduction of aviation fuel consumption. (1)

Since the OPEC Oil Embargo of 1973 when the United States, as well as the rest of the world, was alerted to the end of an era of inexpensive and plentiful energy, conservation has become a way of life. The Air Force has directed research and development efforts at alleviating the magnitude of the problem and its impact on national security by evaluating the potential of domestic alternative sources of jet fuel.

The United States Air Force Aviation Turbine Fuel Technology Program's primary goal is to improve the availability of jet fuel and this includes the evaluation of alternative sources. The routes toward accomplishing this goal are by relaxing military jet fuel specifications, thus permitting reduction in processing severity of conventional petroleum based crudes, and by determining the feasiblity of producing aviation turbine fuels from alternate sources such as oil shale, and possibly, coal liquids.

From an early study with Exxon Research and Engineering, domestic oil shale was determined to be the most viable near term alternative source of syncrude available for processing into military aviation jet fuels (2). The key to converting shale oil into any transportation fuel is an upgrading step whereby the nitrogen level is reduced. Once this is accomplished, the syncrude can be processed in conventional refineries without nitrogen destroying the processing catalyst. Resulting from this study and as a part of the Air Force Aviation Turbine Fuel Technology Program, a program entitled, "A Program Leading to Specifications for Aviation Turbine Fuels Produced from Whole Shale Oil" was initiated.

In 1979, the Aero Propulsion Laboratory's Fuels Branch embarked upon a program to define and develop processing technology to economically produce high yields of specification military jet fuels from whole crude shale oil. The program began with contractual awards to Ashland Petroleum Company, UOP Process Division and the Suntech Group. Each company proposed a different approach and processing scheme for progressing through the phases. The final and ultimate goal being a high yield, economic refining process with the ultimate potential for commercialization. These four phases were:

PHASE I - Preliminary Process Analysis

PHASE II - Bench Scale Process Evaluation

PHASE III - Pilot Plant Process Evaluation

PHASE IV - Overall Optimized Economic Evaluation

Each contractor has provided quantities of shale derived jet fuel samples for tests and evaluations to ascertain fuel characteristics which will be related to fuel performance in other phases of the total Air Force effort. Each contractor has also evaluated the economics of his processing scheme. The processing schemes used met the following goals:

a. Be novel yet show demonstrated potential for scale-up

b. Maximize the yield of jet fuel while limiting the yield of residual fuel to no more than ten percent of the products

c. Have an overall thermal efficiency of at least 70 percent

d. 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 noteworthy Chevron Research Company effort under a Department of Energy contract (3).

Another Air Force shale oil related program recently completed with Amoco Oil Company investigated catalyst properties and developed a hydrotreating catalyst with the potential for having a higher nitrogen tolerance than existing hydrotreating catalysts. Catalyst compositions and substrates were varied in order to determine the best possible combinations.

This 1981 Shale Oil Technology Review culminates the Air Force's shale oil related programs and efforts over the past three years. Results of these processing and combustion studies will enable the Air Force to embark on an operational use of oil shale derived jet fuel. This part of the original program will be coordinated with the recent amendment to the Defense Production Act in the Energy Security Act of 1980. The Air Force has identified various bases for the first commercial shale oil production and this could materialize as early as 1983.

Thus, in many ways, we are today in the midst of an exciting era, and for many -- a dream come true. It is the fantasy of the "rock that burns", oil shale, and an emerging synthetic fuels technology industry which has sputtered for many years. Industry has taken the lead to establish a new technology base for a bridge between fossil fuels and renewable fuels, a bridge which may last for a long period of time.

Such projects as the Union Oil Company project which is scheduled to have the first commercial production of oil from Colorado shale in 1983, the Colony project design plans and construction by Exxon, the projects of Rio Blanco, Occidental, White River and others, form the basis of new and renewed technology and social commitments for the recovery of over 600 billion barrels of shale oil in the United States. Announced early this year, United States shale oil projects are projected to yield a total of 480,000 barrels of shale oil per day by 1992.

The "liquid that burns", JP-4, and its continued supply has made the Department of Defense a concerned consumer of fossil fuels. Projected needs for continued supplies of turbine fuels cause the Air Force to be a concerned consumer of synthetic fuels -- therefore, the Air Force has been instrumental in the development of the "rock that burns". It has been a shared partner in the technological advances of the oil shale industry when it awarded contracts on the preliminary process designs and bench scale evaluations of shale oil products in 1979.

Therefore, we can simply state the objectives of this technology review by the transformation of the "rock that burns" to the "liquid that burns" and the important technological steps which are needed to make this transformation a reality.

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## II

# USAF SHALE OIL FUELS PROGRAM

## PHASES III AND IV

By

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J. G. Gatsis, E. J. Latos,
T. G. Board, J. G. Sikonia,
and J. R. Wilcox

UOP, Inc.

# USAF SHALE OIL TO FUELS PROGRAM
# PHASES III AND IV

by

L. Hilfman, W. C. Laughlin, J. G. Gatsis, E. J. Latos,
T. G. Board, J. G. Sikonia, and J. R. Wilcox

UOP Inc.
Des Plaines, Illinois

## INTRODUCTION

The overall objective of the program developed by UOP Inc. was to demonstrate innovative technology to reduce the cost of converting shale oil to high yields of aviation turbine fuels. The purpose of this presentation is to highlight the results of the work completed under Phases III and IV of DOD contract F33615-78-C-2079.

The UOP approach to shale oil conversion to high quality fuels involved three distinct processing steps: two stages of specifically designed hydrotreating, followed by hydrocracking using an advanced process flow scheme. Previous work completed in this program has been presented in reports of Phases I and II submitted to the USAF and at the 1980 Technology Review sponsored by the Air Force Wright Aeronautical Laboratories Fuels Branch of the Aero Propulsion Laboratory, Wright-Patterson Air Force Base.

The scope of this presentation is necessarily limited and is not intended to serve as the final report of this project. Topics to be reviewed include pilot plant processing, spent catalyst treating, shale oil fouling, shale oil compatability and stability, and shale oil upgrading economics.

## PILOT PLANT PROCESSING RESULTS

The pilot plant work to be reported includes both first-stage hydrotreating and hydrocracking studies. In the hydrotreating operation, catalyst stability was to be demonstrated. The hydrocracking operation was conducted to produce fuel samples required by the USAF and also to get a preliminary indication of catalyst stability.

### First-Stage Hydrotreating

A six-month first-stage hydrotreating run was made to provide additional processing and catalyst stability data required to support the equipment design of the plant. The specific data needed for this design work were the effect of metals deposition, particularly arsenic and iron on catalyst activity and stability.

A schematic diagram of the plant used for this run is shown in Figure 1. Fresh feed and hydrogen are combined and flow concurrently downflow over the catalyst. The effluent passes to a series of separators where the gas (mainly hydrogen) is separated, water scrubbed, and recycled back to the reactor together with makeup hydrogen. The liquid is sent to a stripper to remove hydrogen sulfide and ammonia and is then collected under nitrogen in a glass receiver.

The processing objective was to stabilize the material and reduce the arsenic content to less than 1 ppm. Process conditions used are comparable to those commercially employed for hydrotreating a coke oven light oil. The catalyst was one of UOP's proprietary catalysts for processing feeds with high metals content.

The feedstock was an Occidental shale oil produced from a modified in-situ retort. The "as-received" shale oil was dewatered and desalted in a two-stage electric desalter. Inspections of the treated shale oil are shown in Table 1. This 22.9 °API gravity material contained 1.51 wt-% nitrogen, 27.5 ppm arsenic, and 45 ppm iron.

The catalyst maintained its activity for both metals removal and hydrotreating over the entire 170-day run. As shown on Figure 2, the product arsenic content was maintained at less than 0.2 ppm and the iron at less than 1 ppm. About 32% of the nitrogen and 90% of the sulfur were removed from the feed.

The product inspections in Table 1 show that the hydrogen content was increased from 12.3 to 12.6% and the Conradson carbon content was reduced by about 70%. The overall yields shown in Table 2 include a $C_6$ plus product in the range of 99 wt-%. At the end of the run, the catalyst was unloaded in five sections. It was free flowing and showed no signs of fouling. In general, it showed the pattern of higher to lower concentration of metal deposition from catalyst inlet to outlet.

Fouling did occur three times during the course of the run. Each time, a deposit was formed at the top of the quartz chip preheater zone which caused a high pressure drop across the reactor, resulting in a "forced" shutdown. The reactor was opened and the fouled material removed and replaced. No loss in catalyst activity was observed as a result of these shutdowns. The composition of the fouled material was quite similar. The data in Table 3 show the analyses of preheater material after 3073 hours on stream. The major constituents found on the quartz chips were carbon, hydrogen, arsenic, iron and sulfur, the remainder being trace metals.

Based on the results of the six-month first-stage hydrotreating operation, it is concluded that:

1. The UOP catalyst maintained its activity and stability for arsenic and iron removal over the entire 170-day run.

2. A total of 30 wt-% metals was accumulated on the catalyst during the course of the run.

3. Product arsenic was consistently below 1 ppm and iron at 1 ppm or less.

4. The fouling which occurred in the pilot plant preheater zone must be considered in the design of a commercial unit.

## Hydrocracking

### Production of Fuel Samples

One of the objectives of the Phase III hydrocracking program was to produce five-gallon samples of JP-4, JP-8, diesel fuel marine (DFM) and motor diesel (DF-2) for the USAF for further laboratory testing.

In the hydrocracking flow scheme, fresh feed, recycle liquid, recycle gas, and makeup hydrogen are charged to the reactor section. Gas is recycled from the high pressure separator. The reactor liquid effluent is charged to a series of separators that produce liquid product and a recycle liquid stream. In the pilot plant operations, reactor temperatures were adjusted to achieve 100% conversion of the feed to products. During these operations, no bottoms product was withdrawn as net product.

The hydrocracker feedstock is a second-stage hydrotreated Occidental shale oil, whose properties are shown in Table 4. This stock was produced by hydrotreating the first-stage product at relatively severe condition to reduce the high levels of impurities such as nitrogen and oxygen that are still present. The measured nitrogen content of the material was 780 ppm. The sulfur content was 139 ppm, the oxygen content 545 ppm, and the bromine number 1.1.

The shale oil hydrocracking process conditions used in the production run are comparable to those for hydrocracking a petroleum vacuum gas oil. The product distribution obtained when hydrocracking the hydrotreated Occidental shale oil to make JP-4 and JP-8 are shown in Table 5. The JP-4 yield was better than 84 wt-%, and the chemical hydrogen consumed was 1029 SCFB. The JP-8 yield was 75 wt-% and required 921 SCFB of hydrogen.

The inspections of the JP-4 jet fuel sample are shown in Table 6 along with the USAF specifications. With the exception of the slightly high 50 and 90% points of the distillation and the conductivity, this product meets all U.S. military specifications and should be environmentally acceptable in view of the low nitrogen and sulfur contents. The combustion value is some 300 Btu/lb higher than required and is a reflection of the high hydrogen content obtained in the parallel flow hydrocracking operation.

Inspections of the JP-8 jet fuel produced are shown in Table 7, along with the USAF specifications. These inspections meet all of the U.S. military specifications except for freeze point (-54°F vs. -58°F) and conductivity. These can be easily met by slightly lowering the end point and including an additive, respectively. The combustion value is 200 Btu/lb higher than required and again shows the high hydrogenation capability of the parallel flow hydrocracking operation.

The product distributions for hydrocracking the hydrotreated Occidental shale oil to DF-2 and DFM are shown in Table 8. The yields of 98.6 wt-% and 96.2 wt-% were achieved for DF-2 and DFM, respectively. To produce the same product end point, the chemical hydrogen consumption was 800 SCFB for both the DF-2 and DFM cases.

Inspections of the DF-2 and DFM, together with the U.S. military specfications, are shown in Tables 9 and 10, respectively. These inspections show that the diesel fuels met all specifications.

Both diesel fuels show excellent stability and, with their low nitrogen and sulfur content, they should be environmentally acceptable. In addition, their low acid numbers, copper strip corrosions, sediments, particulates, excellent stabilities, and high cetane numbers should pose no problems for storage and use in engines.

## Catalyst Stability Demonstration

A second objective in the Phase III hydrocracking program was to make an extended catalyst stability study to provide information regarding longer term effects of processing shale oil in the proposed UOP turbine fuels refinery and to assess the advantage of parallel flow over single-stage hydrocracking in terms of catalyst stability.

The stability run was made in the same hydrocracking operation used for the sample production. After the diesel samples were made, the plant was switched to the JP-8 mode, and the operation continued for a period of 1200 hours.

The deactivation was measured by the degrees of reactor temperature increased per unit of operating time required to maintain constant conversion to a specified product end point. In this case, the end point was that required to make JP-8 jet fuel. Results of the run are shown in Figure 3. The rate of deactivation is slightly lower than was reported for a similar operation over a shorter period of time in the Phase II program and as shown in the Phase II report, much improved over the expected result for the single-stage operation.

## Overall Conclusions

Based on the results of these hydrocracking operations, it was concluded that:

1. The parallel flow hydrocracker can produce military turbine fuels and diesel fuel in excellent yields.

2. These fuels not only meet, but exceed military specifications, particularly in combustion value and nitrogen and sulfur content.

3. The parallel flow hydrocracker offers improved catalyst stability when compared with single-stage hydrocracking.

## ARSENIC MANAGEMENT STUDIES

Shale oils produced by current retorting operations contain arsenic in such concentrations that it deserves special attention. Two approaches to the shale oil arsenic management problem have been investigated in this program:

1. Crude shale oil arsenic solubilization

2. Deposited arsenic passivation or extraction.

### Shale Oil Arsenic Solubilization

The first technique investigated involved converting the arsenic in the raw shale oil to a water soluble compound. This might be accomplished by injecting a reagent downstream of the retort into the oil-water mixture. With intimate mixing of the reagent, oil and water may convert the arsenic into water soluble compounds. After the two phases are allowed to coalesce, the water phase is drained off leaving a shale oil with reduced arsenic content. The water containing arsenic could then be further treated, if necessary, to render it environmentally safe.

Desalted Occidental shale oil with 19 ppm arsenic was utilized as the hydrocarbon source for a series of experiments attempting to convert arsenic into water soluble compounds. For these experiments, the water, reagent and shale oil were intimately contacted utilizing a shear-type mixer. Each test was performed by mixing the oil and water for 15 minutes at about 95°C. The type of emulsion formed while adding various reagents was observed, and the arsenic level left in the oil was measured after each test.

A summary of results is shown in Table 11. Arsenic solubilization ranged from 13 to 52%. The removal of arsenic was probably accomplished by the formation of an insoluble material that is associated with the emulsion. The use of a wide range of reagents along with shear mixing to effect water solubilization of arsenic from shale oil does not appear to be very promising.

### Arsenic Passivation and Extraction

The high concentration of arsenic in the raw shale oil and its removal and containment on the first-stage hydrotreater catalyst poses some special handling problems. Before arsenic-laden catalysts can be disposed of as non-hazardous wastes, the aqueous solubility of arsenic as measured by the EPA Toxicity test must be reduced to less than 5 ppm. In an effort to meet this requirement for safe disposal, the following objectives were considered:

1. Ascertain the composition of arsenic-containing species on used catalyst.
2. Determine the arsenic solubility of aqueous extracts of used catalysts.
3. Evaluate methods of passivating soluble arsenic.
4. Determine the effect of various gases on arsenic volatility.
5. Evaluate the extraction behavior of arsenic from untreated and thermally treated used catalysts using various solvents.
6. Determine the conditions for complete dissolution of used catalysts.

## Experimental Procedure

Samples of used catalysts were thermally treated in a 1-inch silica tube under controlled atmospheres. Five gram samples of thermally treated and as-received catalyst were extracted in 200 ml of various solvents on a wrist shaker for 3 hours.

## Elemental Analysis

The elemental analyses of spent catalyst beds removed from two first-stage hydrotreating pilot plant reactors show that the arsenic concentration declines rapidly downward through the bed. As shown in Table 12, iron exhibits a similar profile while the remaining elements are fairly evenly distributed. The major difference between the two catalysts is the much higher arsenic level on the used catalyst designated as Number 2. The relative concentrations of the arsenic and iron throughout the catalyst bed are not significantly different.

An identification of the arsenic compounds present on the catalyst was considered necessary in order to determine the best methods to either fix the leachable arsenic by further chemical reaction or convert the arsenic into a highly soluble form. X-ray diffraction patterns obtained for the two samples were analyzed and the results are summarized in Table 13. The peak positions were calculated, and a manual search was made of the powder diffraction files in order to determine which compounds were present.

The $\alpha$-$Al_2O_3$ of the catalyst base is a major component in both samples. Trace levels of -quartz and boehmite were also detected. The rest of the standard patterns listed fit the sample patterns well, but the actual components present may have slightly different compositions.

Both samples contain a major phase similar to pyrrhotite [$Fe_{(1-x)}S$, where $x \leq 0.1$]. A slight increase in sulfur content would lead to a mixture of pyrrhotite and pyrite ($FeS_2$). There is evidence of pyrite in the sample designated "Catalyst 1".

$Co_{0.84}Ni_{0.16}As_{1.04}$ is the cobalt analog of niccolite $(NiAs)_1$. Their patterns are similar. The peaks in the pattern more closely match the former ($Co_{0.84}Ni_{0.16}As_{1.04}$); however, the actual compound present may have a formula somewhere between the two arsenides.

Although some of the peaks for the two used catalysts match the pattern of $Cu_{24}As_{12}S_{31}$, there was no copper detected in the elemental analysis. It is possible a similar compound was present with other metals substituted for the copper.

The chloroform-washed samples were subjected to a modified EPA Toxicity test for arsenic. The modification in procedure was the use of 10 grams in place of 100 gram samples. As shown in Figure 4, the As solubility of the chloroform-washed catalyst appears to be a linear function of the As content of the catalyst. In order to meet the EPA limit, the catalyst would have to contain less than 0.2 wt-% As.

Metal salts were blended with the used catalyst, then heated in an inert atmosphere in an attempt to fix the arsenic as metal arsenides or metal arsenous sulfides. It was anticipated that conversion to these compounds would cause the arsenic to be less soluble; however, as shown in Figure 4, this proved not to be the case.

The EPA test was performed on several used catalysts that had been previously extracted with sulfuric and nitric acid solutions. The arsenic solubility was decreased; however, the arsenic level remaining on the catalyst was still too great for direct disposal. As shown in Figure 4, in order to meet the EPA limit, it will be necessary to reduce the As content on the catalyst to about 0.5 wt-%.

If essentially all of the arsenic could be volatilized in a roasting process, arsenic collection would be feasible. Considering the relatively high vapor pressures of arsenic, arsenic sulfide and arsenic oxide, it appears that arsenic would be removed at elevated temperatures in either oxidizing, reducing, or neutral atmospheres.

As shown in Figure 5, the volatility of arsenic from spent catalyst was dependent upon temperature, residence time and atmosphere. It appears that a temperature of about 500°C is required to break down the original arsenic minerals and to ensure adequate vapor pressure of volatile species. If the rate of arsenic volatilization can be increased, arsenic might be recovered by such a process.

Extractants were chosen to discern the state of arsenic present on the catalyst following thermal pretreatment. $H_2SO_4/FeCl_3$ and $HNO_3$ are strong oxidizing agents capable of oxidizing sulfide minerals. Sulfuric acid is a non-oxidizing acid which can solubilize sulfates and arsenates. Sodium sulfide forms complex anionic arsenous sulfides which are highly soluble.

Arsenic extraction results from catalysts that were thermally oxidized at the severe conditions of 500°C in 5% $O_2$ were very similar. The data shown in Figure 6 indicate that the arsenic has probably been converted to an arsenate.

The data plotted in Figure 7 indicate that catalysts pretreated under rather neutral conditions, 25% $H_2O$/75% $N_2$, were more effectively extracted with oxidizing acids than with the other leachants. The arsenous sulfide minerals are only beginning to be broken down at the highest temperature, 600°C.

As shown in Figure 8, using $SO_2$ in the thermal treatment step produces a different response to the extractants. At temperatures below 500°C, the $SO_2$ atmosphere produced little change in arsenic chemistry. At 500°C, $SO_2$ reacted slowly with carbon to form sulfur and $CO_2$ and converted the metal arsenous sulfides to more leachable forms. All of the extractants remove approximately the same level of arsenic.

None of the thermal pretreatments produced a material that allowed high levels of arsenic extraction. In the best case, about 80% of the arsenic was removed by a combination of thermal treatment and leach extraction. Increasing the leachant concentration to increase the arsenic extraction would result in considerable alumina dissolution.

An alternate approach to arsenic recovery utilized solution oxidation. Acid digestion of as-received used catalyst was performed in a stoichiometric quantity of sulfuric acid assuming the catalyst weight to be entirely $Al_2O_3$ with the following reaction:

$$Al_2O_3 + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\ H_2O$$

The digestion was carried out under reflux for 8 hours. In order to obtain high recoveries of the elements, the reaction had to be carried out at a positive solution potential. This was accomplished by adding 3 wt-% $HNO_3$ to the sulfuric acid. As shown in Table 14, 90% recovery of arsenic was achieved with both the 10 and 20 sulfuric acid solutions. Only molybdenum was poorly recovered in this solvent; however, molybdenum can be recovered from the residue using other techniques. Digestion of thermally treated catalysts was not as effective in recovering arsenic as solution oxidation of the as-received used catalyst.

## Conclusions

1. Used catalysts from processing shale oil will contain higher levels of soluble arsenic than allowed by the EPA for non-hazardous disposal.

2. Much of the arsenic is present on the catalyst as thermally stable metal arsenides and metal arsenous sulfides.

3. It was not possible to fix or passivate the arsenic on the catalyst in an insoluble form by thermally treating the catalyst with or without additives.

4. Leachants, which do not dissolve excessive quantities of alumina, extract only about 20% of the arsenic from non-thermally treated catalysts.

5. Of the thermal treatments investigated, only dilute oxidizing atmospheres, 5% $O_2$ or less, at elevated temperatures, $\geq$ 500°C, for extended time result in appreciable arsenic volatilization. This indicates that arsenic is not present on the catalyst as a simple sulfide, oxide or metallic compound.

6. Increasingly severe thermal pretreatments allow up to 75% of the arsenic to be extracted by dilute leachants.

7. Both temperature and gas composition are important variables in converting the arsenic to a leachable form.

8. Results of toxicity tests on previously treated catalysts indicate that high extraction levels are necessary before the residue is acceptable.

9. Digestion of as-received spent catalyst requires a high solution potential in order to achieve good extractions.

10. Digestion of thermally oxidized catalysts yields poorer arsenic extractions than from solution oxidation of as-received catalysts.

11. Topics worthy of further investigation include the evaluation of different ratios of As, Fe, C and S on arsenic volatility and solubility; the recovery of arsenic by thermal means; the development of methods to recover arsenic from acidic solutions; and the determination of the minimum acid necessary to achieve good extractions of arsenic without excessive dissolution.

## SHALE OIL FOULING STUDY

The objective of the fouling study was to evaluate the relative thermal fouling characteristics of shale and petroleum base stocks. This was accomplished using the Monirex® Fouling Monitor which quantitatively determines the fouling rate of a heated wire probe in a circulating oil stream.

It was previously reported (Phase II) that a desalted Arabian Light Berri crude oil is a relatively low fouling base stock. A kerosine derived from this oil fouled at a still lower rate. A desalted crude Occidental shale oil fouled at a lower rate than the raw shale oil, and at approximately the same rate as the desalted Arabian Light Berri oil. Fouling data obtained with a desalted Paraho oil indicated a relatively low fouling material although these data were suspect due to the unknown history of the sample.

During Phase III of this program, it was shown that sample aging had a significant effect on the rate of fouling of both the petroleum and shale oils. As shown in Figure 9, aging for approximately 9 months at 4.4°C decreased the 300°C fouling rate of the desalted Arabian Light Berri petroleum oil by 39% and the desalted Occidental shale oil by 59%. These data emphasize the need for fresh samples to obtain meaningful fouling data.

Fouling tendency interactions between shale oil and petroleum were also investigated. The data on Figure 10 show that blending 10 to 30%, by weight, of the desalted Occidental shale oil had no significant effect on the fouling properties of the desalted Arabian Light Berri oil.

A comparison of the fouling tendencies of various materials derived from Occidental shale oil is shown on Figure 11. A severely hydrotreated desalted shale oil had a very low fouling rate. A JP-8 fuel derived from the hydrotreated Occidental shale oil had a fouling rate somewhat higher than the hydrotreated oil. As a point of comparison with the $4 \times 10^{-5}$ fouling rate observed with the shale-derived JP-8 at 400°C, the kerosine from the Arabian Light Berri oil fouled at a rate of $11 \times 10^{-5}$.

A relatively fresh sample of a desalted Paraho shale oil (3 months) was found to be a high fouling material with a rate of $35 \times 10^{-5}$ at 225°C. As shown in Figure 12, the addition of 40 ppm of a proprietary antifoulant reduced the fouling rate at 225°C to $12 \times 10^{-5}$.

Although fouling resistance data under specific field processing conditions were not available, it has been reported that the Paraho shale oil was high fouling and the Arabian Light Berri and a derived kerosine were relatively low fouling materials.

Because sample aging had a significant effect on fouling characteristics, it is recommended that future fouling studies be done with fresh samples. Kinetic studies are feasible with the Monirex Fouling Monitor and the foulant remaining on the wire probe can be characterized with various analytical techniques. It is recommended that detailed studies be made to analyze these deposits to permit the development of a fouling mechanism.

## SHALE OIL/CRUDE OIL COMPATIBILITY AND STABILITY STUDY

The objective of this study was to determine the compatibility/stability of primary shale oils and treated products with petroleum crude oil. The compatibility of shale oils with petroleum crude oil is an important consideration in their blending, particularly with respect to co-processing shale oil/petroleum crude oil blends in existing refineries. The resulting blends should form a homogeneous mixture that neither separates nor is altered by chemical interaction. The physical and chemical properties of the blend should not be adversely affected. The stability in storage is also of concern. Whereas many studies have been made on the stability of petroleum liquids, stability studies of shale oils have been limited by unavailability of shale oils. Their resistance to chemical change and to physical disintegration on storage is not well known.

## Methodology

Compatability studies were conducted on a shale oil/crude oil blend consisting of 30 vol-% shale oil. The compatibility of the blend was determined by comparing the experimental values of viscosity, heptane insolubles and toluene insolubles of the blend to calculated values. The calculated value of viscosity was determined from a viscosity blending chart. The calculated value of heptane insolubles and toluene insolubles was determined from the amount of insolubles present in each of the original samples.

Stability studies were conducted on deoxygenated samples of the petroleum crude oil, shale oil, treated shale oil products and a 30/70 shale oil/crude oil blend. The stability tests selected for study were three months 110°F Dark Storage Fuel Oil Stability Test; E. I. DuPont de Nemours and Co., 300°F Accelerated Fuel Oil Stability Test; and ASTM 2274-74, Oxidation Stability of Distillate Fuel Oil. These tests are applicable to distillate fuels and were modified to permit stability testing of petroleum crude oils, shale oils and blends. To assess the stability, formation of adherent insolubles and changes in heptane insolubles, toluene insolubles and viscosity were measured.

## Description of Samples

The crude oil selected was a heavy Arabian crude. The primary shale oils selected were a raw Paraho shale oil and raw Occidental shale oil. Treated shale oils selected for study had been subjected to single-stage and two-stage hydrotreatment. A complete analytical description of all samples is given in Tables 15 and 16. The compatibility and stability results of the blended samples are given in Table 17.

## Discussion of Results

The raw shale oils and hydrotreated products were found to be compatible with the heavy Arabian crude oil. As shown in Table 18, good agreement is obtained between calculated and analyzed values for viscosity, heptane insolubles, and toluene insolubles.

The heavy Arabian crude oil, raw shale oils and the low pressure hydrotreated shale oils indicated some degree of instability. As illustrated on Figure 13, the raw Paraho shale oil, particularly with respect to viscosity, was more stable than the heavy Arabian crude oil. Both the crude oil and Paraho shale oil show some instability with respect to heptane insolubles content as a result of the three-month 110°C Dark Storage Test. As shown on Figure 14, the crude oil heptane insolubles content increased from 4.6 to 6 wt-%; the raw Paraho shale oil insolubles went from 0.2 to 0.9 wt-%. Similar results were found with the blends containing the Occidental shale oil materials.

Stability of the shale oil increased with hydrotreatment. The two-stage hydrotreated Paraho and Occidental shale oils were stable. Instability reflected in the shale oil/petroleum crude oil blend is accounted for to a great extent by the instability of the petroleum crude oil. Blending of the shale oil/petroleum crude oils should have no adverse effects in co-processing.

## SHALE OIL UPGRADING ECONOMICS

In addition to selecting a novel conversion processing scheme for high jet fuel yield, the proposed flow scheme should help provide a realistic and economical solution to the problem of shale oil conversion. The UOP processing scheme, as shown in Figure 15, provides for the removal of arsenic and stabilization of the raw shale oil in a relatively moderate, first-stage pretreatment step. Denitrification is accomplished in a more severe, second-stage hydrotreatment. Finally, the upgraded shale oil is converted to transportation fuels in the hydrocracker. Hydrocracker jet and diesel fuel products do not require further treatment, thus providing an overall cost benefit for this processing scheme.

The basis for establishing the processing scheme and developing reliable estimates of external requirements and investment costs for the key processing units includes the following:

A. The refinery design and flow schemes are based on processing 100,000 BPSD of desalted Occidental shale oil.

B. Two primary products -- JP-4 and JP-8 aviation turbine fuels -- are required. Coproducts such as various grades of diesel fuel, fuel oil, motor gasoline, aviation gasoline, or other grades of turbine fuel may be produced.

C. Only commercially proven processes are to be considered in the refinery processing schemes.

D. There are no outside feed streams to be processed with the raw shale oil. Fuels for heating are to be internally generated.

E. The refinery is assumed to be a grassroots facility located at a Rocky Mountain site.

F. Capital Investment

1. Western U.S. location
2. 100,000 BPSD crude shale oil capacity
3. First quarter 1981 cost base
4. 100% equity financing
5. Investment timing over a three year construction period
    a. 25% first year
    b. 50% second year
    c. 25% third year
6. 10% investment tax credit
7. 45% of plant onsites (not including feed and product storage) will be used to generate plant offsite cost.

G. Working Capital

1. 21 days crude storage capacity with 14 days crude inventory
2. 14 days product storage capacity with 7 day product inventory
3. Crude shale oil valued at $40.00 per barrel
4. Product valued at determined cost
5. Debt financed at 15%

H. Capital Return

1. 15% DCF rate of return on capital
2. 13 years sum of years digits depreciation
3. Zero salvage value

I. Operating Basis

1. 16 year plant operating life
2. 50% operating capacity first year, 100% thereafter
3. 90% on-stream factor
4. 100,000 BPSD capacity
5. All process fuel/heat requirements shall be generated internally from the original shale oil feed.

J. Operating Cost Basis

1. Crude Shale Oil -- $40.00 per barrel
2. Cooling Water -- $0.03 per 1000 gals.
3. Electricity -- $0.045 per kWh
4. Operators -- $12.00 per hour
5. Helpers -- $10.50 per hour
6. Labor Supervision -- 25% of direct labor
7. Overhead -- 100% of direct labor
8. Federal and State Taxes -- 50%
9. Maintenance, Local Taxes and Insurance -- 4.5% of fixed investment
10. Product Values -- all liquid fuel products are of equal value
11. By-product Values
    a. Ammonia at $155/short ton
    b. Sulfur at $105/long ton

K. Miscellaneous

1. Use English units
2. Mass flow rates
    a. Barrels per stream day (BPSD)
    b. Short tons per day (ST/D)
    c. Standard cubic feet per day (SCFD)

The processing schemes for the production of JP-4 and JP-8 jet fuels, shown in Figures 16 and 17, respectively, are nearly identical except for the size of the units. A naphtha hydrotreating and Platforming® unit are added to the flow scheme when producing JP-8. Various combinations of jet fuel and diesel fuel are produced by utilizing the same flow schemes by varying the hydrocracking severity to produce the desired product slate. Overall material balances for the maximum JP-4 and JP-8 jet fuel cases are shown in Table 19.

## Operating Cost

The overall refinery operating costs for the JP-4 and JP-8 cases are shown in Table 20. Operating costs are divided into direct and indirect operating costs which are as follows:

### Direct Operating Cost

Refinery Labor -- Refinery labor includes all the personnel for the process units hired at $12.00 per hour for operators and $10.50 per hour for helpers. To arrive at a total labor cost, a 100% overhead allowance is added to these base rates. A 25% allowance for supervision is also made.

Maintenance Allowance -- The maintenance allowance covers normal operating maintenance and turnaround contract maintenance for all refinery equipment including process units, offsites and depreciable assets. An amount equal to 3% of erected plant investment is allocated for maintenance.

Utilities -- Refinery fuel is generated internally for both JP-4 and JP-8 cases. Power is purchased at $0.045 per kWh and cooling water is priced at $0.03 per 1000 gallons. Boiler feed water is estimated at $0.50 per 1000 pounds. Steam (600 psig) is generated at $0.68 per 1000 pounds (fuel provided from internal sources). All utilities are consumed at normal average operating rates.

Catalyst, Solvents and Chemicals -- Catalyst consumption is based on the expected catalyst life for normal operating conditions. Similarly, solvents and chemicals are based on normal average operating usage.

### Indirect Operating Cost

Local Taxes -- An allowance of 1% of erected plant investment, catalyst and working capital is allocated toward local taxes.

Insurance -- An allowance of 1/2% of erected plant investment, catalyst and working capital is allocated toward insurance.

## Process Design and Capital Cost

Process designs were prepared for the first- and second-stage hydrotreaters and for the primary conversion section, the hydrocracker. These designs were based on the yields and operating conditions developed from the specific laboratory and pilot plant data generated during the earlier phases of this project. Each process design includes a heat and material balance, characteristics of principal equipment, and a detailed process flow diagram. The heat and material balance includes stream quantities (mass and volume) and compositions ($H_2$, $H_2S$, $NH_3$, $H_2O$, light hydrocarbons), molecular weights, flowing densities and enthalpies entering and leaving each major equipment item, in addition to pressures and temperatures.

In order to provide more definitive cost data for these primary units, the process design was used as a basis for generating EFCEST (Engineering for Cost Estimating) data. EFCEST data provide a sufficient level of detailed project engineering work to appropriately describe the equipment required. The EFCEST data were then used to prepare a detailed cost estimate with an estimated precision of ± 25% for first quarter, 1981.

Material balances prepared for the naphtha hydrotreating and Platforming units, amine treating and sulfur recovery, sour water stripping, raw feed desalting, ammonia plant and hydrogen production units include stream quantities and compositions. Considering the extent of UOP experience with these types of units, reliable cost and utility estimates were provided without preparing EFCEST data and detailed cost estimates. The material and labor estimates provided for the above units were derived by scaling detailed estimates prepared for similar units.

The use of UOP's linear programming (LP) capabilities permitted the evaluation of numerous processing and product blending alternatives required in this shale oil upgrading study. The linear programming technique, using a multitude of mathematical calculations, allowed various alternatives to be quickly examined to determine the best or optimal processing scheme. Once developed, LP models were used to perform sensitivity analysis, wherein the effect of varying feedstock value, product prices, quantities and specification can be considered.

The UOP LP system was developed over the years to apply this powerful mathematical method to the analysis of refinery "grassroots" and expansion projects. LP techniques are effectively used in: feedstock evaluation and selections, operations planning, financial planning for new facilities or expansion of existing ones, and development of planned turnaround maintenance. Combining the market data of product prices and demands with data describing technology and economics factors, the LP model can be used to evalaute many alternatives quickly and efficiently. Although the results are a linear representation of reality, they can give the planner a logical basis for a systematic approach to solving these problems.

To illustrate the mathematical relationships and the extent to which the refinery interactions are considered, a matrix representation of the linear equations are used to describe the refinery. In this arrangement, data relationships cascade from one activity to the next, much the same way material flows through the refinery. The model can consider the following general components of refinery profitability:

- Availability of raw materials
- Component blending relationships and recycle streams

- Process unit material balances
- Addition requirements for product quality improvements
- Utility consumptions and conversions (purchase vs. internal generation)
- Market demands for finished products

The constraints or limitations on the model are contained in the rows of the matrix. The constraints considered in the refinery optimization are:

- Raw material purchase limits
- Unpooled utility limits to sale or purchase
- Product quality specifications
- Material balances on all streams in the refinery
- Capacity limits in process units
- Additive blending
- Utility balances (choice between purchase and internal generation)
- Product demands at market centers
- Physical and social requirements (e.g., emission limits)

Investment in onsite process equipment and related offsite facilities is handled in a manner that considers the non-linear relationship between capital cost and plant capacity. UOP's linear programming system has the ability to recurse on the capital cost to ensure that the capital charges used by the model are consistent with the calculated process unit capacity. The effect of physical and social policy requirements can be evaluted by placing additional constraints on the model and evaluating the results.

The output of the LP program is in the form of reports that allow management to evaluate the results in familiar terms including such items as:

- Material balances including plant yields and product blends
- Processing schemes
- Utility balances
- Investing requirements
- Operating requirements
- Production costs

In addition, the LP allows the investigation of the sensitivity of the solution through a technique called post optimal analysis. This feature permits the quantified measurement of varying key parameters such as:

- Sales of selected products on various markets
- Capacity of particular process units
- Finished product qualities
- Prices of products and feedstocks.

Utility requirements are estimated from the process design data and the information provided for the auxiliary units. Utilities estimated include: electric power, fuel, steam at recommended pressure levels, boiler feedwater, condensate, and cooling water.

In Table 21, the capacity and estimated erected cost (EEC) for individual process units are shown. The costs for the JP-4 and JP-8 cases are similar with the exception that a naphtha hydrotreater and Platformer unit combination is included in the JP-8 case. The common facilities cost includes such items as buildings, (process control house and substations), electrical power distribution and area lighting, and site development in the process area.

Offsite costs are influenced more by the characteristics of the site, local regulations, and policies of the refiner than by minor differences in process scheme. Allowances for offsite costs are included, with recognition of special requirements such as for waste treatment, where applicable. The offsite facility cost estimates were based on 45% of the plant onsite investment minus the cost of specified tankage capacity for storing crude and products. This basis was used to estimate offsite facility costs as no other design information was available. As such, the offsite cost is an order-of-magnitude cost estimate and has no meaningful accuracy range.

The capital investment summary for the JP-4 and JP-8 cases are presented in Table 22. The total capital investment is estimated to be $\$913 \times 10^6$ for the maximum JP-4 case and $\$948 \times 10^6$ for the maximum JP-8 case.

## Production Costs

The total costs of producing JP-4 and JP-8 are tabulated in Table 23. Incorporating the feedstock cost, operating costs, capital charges, taxes, and a 15% DCF rate, and assuming that all liquid products have equal value, the cost of the total liquid fuel production from the maximum JP-4 refinery is $52.26 per barrel of shale oil feed, and from the maximum JP-8 refinery is $52.74 per barrel of feed. The difference in cost 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. This is calculated by dividing production costs by the volume fraction yield of liquid fuel. This calculation results in total liquid fuel costs of $56.48 and $58.41 per barrel for the maximum JP-4 and maximum JP-8 cases, respectively.

## SUMMARY

UOP Inc. has demonstrated innovative technology to produce high yields of aviation turbine fuels from shale oil. First-stage hydrotreating catalyst stability was demonstrated during a six-month run. High quality jet and diesel fuel samples were produced using a novel hydrocracking process scheme which also allows improved catalyst stability.

Fundamental development work was done to quantify other aspects of shale oil upgrading. The fouling tendencies of shale oil derived materials were determined and found to be highly dependent on sample history. No unusual stability/compatibility problems were detected with shale oil/petroleum blends. Various techniques were investigated to render non-toxic, the arsenic-contaminated used catalyst.

It was determined that on the basis of 100,000 BPSD of raw shale oil, 92,530 BPSD of JP-4 or 81,370 BPSD of JP-8 could be produced. Shale oil refining costs were determined after completing engineering designs of the key process units. With a total capital investment requirement for the JP-4 and JP-8 cases of \$913 x $10^6$ and \$948 x $10^6$, respectively, and allowing for a 15% DCF rate of return on investment, the production costs, stated on a "per barrel of total liquid product" basis, were \$56.48 and \$58.41.

This study has demonstrated that state-of-the-art, commercially practical refining processes are available to produce high quality fuels from shale oil at a cost which should make this resource an important part of our energy supply.

## TABLE 1

## FIRST-STAGE HYDROTREATING
## OCCIDENTAL SHALE OIL
## FEED AND PRODUCT COMPARISON

| | Feed | Product |
|---|---|---|
| API Gravity at 60°F | 22.9 | 26.7 |
| Specific Gravity at 60°F | 0.9165 | 0.8944 |
| Distillation (D-1160), °F | | |
| IBP | 376 | 370 |
| 5% | 467 | 472 |
| 10% | 570 | 508 |
| 30% | 670 | 600 |
| 50% | 712 | 698 |
| 70% | 820 | 799 |
| 90% | 953 | 940 |
| 95% | - | 984 |
| EP | - | - |
| % Over | 87 | 92 |
| Pour Point, °F | +65 | +75 |
| Viscosities | | |
| Kinematic at 122°F, cSt | 21.94 | 11.54 |
| Kinematic at 210°F, cSt | 5.268 | 3.473 |
| Carbon, wt-% | 84.85 | 84.85 |
| Hydrogen, wt-% | 12.27 | 12.63 |
| Total Nitrogen, wt-% | 1.51 | 1.17 |
| Sulfur, wt-% (ppm) | 0.64 | (479) |
| Chloride, wt-ppm | < 1.0 | - |
| BS and W, vol-% | 0.2 | - |
| Conradson Carbon, wt-% | 1.36 | 0.45 |
| Ash, wt-% | 0.014 | 0.001 |
| Heptane Insolubles, wt-% | 0.34 | 0.01 |
| Pentane Insolubles, wt-% | 1.65 | 0.07 |
| Metals by Emission (AAS), ppm | | |
| Fe | 45 | (0.2) |
| Ni | 6.7 | (2.2) |
| V | 0.42 | (< 0.1) |
| Pb | < 0.1 | |
| Cu | < 0.1 | |
| Na | 11 | |
| Mo | 1.6 | |
| Arsenic, wt-ppm | 27.5 | < 0.1 |
| Bromine No. | 23.6 | 7.5 |
| Oxygen, wt-% | 0.65 | 0.34 |
| Water, wt-% | 0.05 | |

## TABLE 2

## SINGLE-STAGE HYDROTREATER
## OCCIDENTAL SHALE OIL
## PRODUCT YIELDS

| | Yields, Wt-% of Feed |
|---|---|
| $H_2O$ | 0.50 |
| $NH_3$ | 0.50 |
| $H_2S$ | 0.65 |
| $C_1$ | 0.03 |
| $C_2$ | 0.06 |
| $C_3$ | 0.09 |
| $C_4$ | 0.12 |
| $C_5$ | 0.15 |
| $C_6+$ | 98.86 |
| Total | 100.96 |

Chemical Hydrogen Consumption = 581 SCFB

## TABLE 3

## FIRST-STAGE HYDROTREATING ANALYSIS OF PREHEATER MATERIAL

| | |
|---|---|
| Time on Stream, hours | 3072 |
| Dry Ash, wt-% | 89.7 |
| Carbon, wt-% | 8.15 |
| Hydrogen, wt-% | 1.18 |
| Arsenic, wt-% (AAS) | 0.56 |
| Sulfur, wt-% | 1.52 |
| Emission Wt-% Metal | |
| Fe | 2.4 |
| Ni | 0.12 |
| Ca | < 0.3 |
| Mg | < 0.01 |
| Mn | 0.015 |
| Cr | 0.025 |
| Sn | < 0.03 |
| Cu | 0.017 |
| Zn | < 0.4 |
| Pb | < 0.04 |
| Na | < 0.45 |
| Mo | 0.11 |
| Si | Major |

## TABLE 4

## HYDROCRACKING FEEDSTOCK

### Occidental Shale Oil

| | |
|---|---|
| API Gravity at 60°F | 32.0 |
| Sp. Gr. 60/60°F | 0.8654 |
| Distillation (D-1160), °F | |
| IBP | 390 |
| 5% | 469 |
| 10% | 495 |
| 30% | 581 |
| 50% | 663 |
| 70% | 760 |
| 90% | 898 |
| 95% | 958 |
| EP | 988 |
| % Over | 97.0 |
| Carbon, wt-% | 86.99 |
| Hydrogen, wt-% | 13.41 |
| Nitrogen, ppm | 780 |
| Sulfur, ppm | 139 |
| Pentane Insolubles, wt-% | 0.12 |
| Heptane Insolubles, wt-% | 0.05 |
| Conradson Carbon, wt-% | 0.09 |
| Ash, wt-% | 0.001 |
| Bromine Number | 1.1 |
| BS & W, wt-% | 0.4 |
| Toluene Insolubles, wt-% | 0.01 |
| Oxygen, ppm | 545 |
| Molecular Weight | 305 |

## TABLE 5

## HYDROCRACKER PRODUCT DISTRIBUTIONS
## HYDROTREATED OCCIDENTAL SHALE OIL FEED

| Product Desired | JP-8 | JP-4 |
|---|---|---|
| Wt-% | | |
| Fresh Feed | 100.00 | 100.00 |
| $H_2$ Consumption, wt-% | 1.61 | 1.80 |
| $H_2$ Consumption, SCFB | 921 | 1029 |
| $NH_3$ | 0.08 | 0.08 |
| $H_2S$ | 0.01 | 0.01 |
| $C_1$-$C_3$ | 1.50 | 1.88 |
| $C_4$ | 3.73 | 4.80 |
| $C_5$-$C_6$ | 9.29 | 11.03 |
| $C_7$-250 | 11.75 | 12.18 |
| 250-EP | JP-8 75.25* | JP-4 71.82** |
| Total | 101.61 | 101.80 |
| Vol-% | | |
| Fresh Feed | 100.00 | 100.00 |
| $C_4$ | 5.78 | 7.43 |
| $C_5$-$C_6$ | 12.62 | 14.75 |
| $C_7$-250 | 13.76 | 14.31 |
| 250-EP | 80.40* | 78.68** |
| Total | 112.56 | 115.17 |

* Product EP ∿ 550°F

** Product EP ∿ 520°F

## TABLE 6

## JP-4 JET FUEL
## PRODUCTION SAMPLE

| | USAF Specs. | |
|---|---|---|
| API Gravity at 60°F | 0.751-0.802 | 49.6 |
| Sp. Gr. 60/60°F | | 0.7813 |
| D 86-Engler, vol-% | | |
| IBP, °F | report | 202 |
| 5% | | 236 |
| 10% | report | 255 |
| 20% | 293 | 288 |
| 30% | | 321 |
| 40% | | 354 |
| 50% | 374 | 386 |
| 60% | | 414 |
| 70% | | 437 |
| 80% | | 456 |
| 90% | 473 max. | 478 |
| 95% | | 495 |
| EP, °F | 518 max. | 517 |
| Freeze Point, °F | -72 max. | Below -70°F |
| Smoke Point | 20 min. | 28.5 |
| Vapor Pressure, 38°C | 14-21 max. | 0.8 lb. |
| Viscosity -20°C, cSt | | 3.207 |
| Acid No., mg KOH/mg | 0.015 max. | 0.012 |
| Copper Strip Corrosion | 1B max. | 1A |
| Coulometric Sulfur, ppm | 0.4 wt-% max. | 737 |
| Mercaptan Sulfur, wt-% | 0.001 max. | 0.0001 |
| Coulometric N | | 0.37 |
| Carbon, wt-% | | 84.23 |
| Hydrogen, wt-% | 13.6 min. | 14.39 |
| FIA, vol-% | | |
| P + N | | 91.3 |
| O | 5.0 max. | - |
| A | 25.0 max. | 8.7 |
| Combustion, Btu/lb | 18,400 min. | 18,700 |
| Existent Gum, Unwashed/Washed, per 100 ml | 7 mg max. | 7.8 mg/4.0 mg |
| Naphthalenes, UV wt-% | | 0.28 |
| Conductivity | 50-300 | 1 $\bar{p}$ S/M |
| Water Separation D 1094 | | |
| Interface Rating | 1B max. | 1B |
| Separation Rating | 1 max. | 1 |
| Demulsification | | No Emulsion<br>Oil Layer Clear<br>No Scum |

**JFTOT**

| Temp., °C | Min. | ΔP mm Hg | TDR Spun | ASTM Code |
|---|---|---|---|---|
| 260 | 150 | 1.5 | 1.5 | 0 |

# TABLE 7

## JP-8 JET FUEL
## PRODUCTION SAMPLE

| | USAF Specs. | |
|---|---|---|
| API Gravity at 60°F | 37-51 | 46.0 |
| Sp. Gr. 60/60°F | 0.775-0.840 | 0.7972 |
| D 86-Engler, vol-% | | |
| IBP, °F | report | 288 |
| 5% | | 308 |
| 10% | 401 max. | 321 |
| 20% | | 352 |
| 30% | | 384 |
| 40% | | 412 |
| 50% | | 434 |
| 60% | | 455 |
| 70% | | 474 |
| 80% | | 492 |
| 90% | | 512 |
| 95% | | 525 |
| EP, °F | 572 max. | 552 |
| % Over | | 99.0 |
| Smoke Point | 25 min. | 27.2 |
| Freeze Point, °F | -58 max. | -54 |
| Flash Point, °F | 100 min. | 100 |
| Viscosity -20°C, cSt | 8.0 max. | 5.670 |
| Acid No., mg KOH/gm | 0.015 max. | 0.01 |
| Coulometric Sulfur, ppm | 0.4 wt-% max. | 499 |
| Mercaptan Sulfur, wt-% | 0.001 max. | 0.00048 |
| Carbon, wt-% | | 84.63 |
| Hydrogen, wt-% | 13.6 min. | 14.14 |
| FIA, vol-% | | |
| P + N | | 90.7 |
| O | 5.0 max. | - |
| A | 25.0 max. | 9.3 |
| Combustion, Btu/lb | 18,400 min. | 18,600 |
| Copper Strip Corrosion | 1B max. | 1A |
| Coulometric N | | 0.7 |
| Existent Gum, Unwashed/Washed, per 100 ml | 7 mg max. | 4.1 mg |
| Naphthalenes, UV wt-% | 3 max. | 0.35 |
| Conductivity | 50-300 | 4 p S/M |
| Water Separation D 1094 | | |
| Interface Rating | 1B max. | 1 |
| Separation Rating | 2 max. | 1 |

JFTOT

| Temp., °C | Min. | ΔP mm Hg | TDR Spun | ASTM Code |
|---|---|---|---|---|
| 260 | 150 | 0 | 1.0 | 0 |

## TABLE 8

## HYDROCRACKING HYDROTREATED OCCIDENTAL SHALE OIL TO DF-2 AND DFM DIESEL FUELS

| | Feed | DF-2 | DFM |
|---|---|---|---|
| Product Distribution, wt-% | | | |
| $H_2S$ | | 0.01 | 0.01 |
| $NH_3$ | | 0.10 | 0.10 |
| $H_2O$ | | 0.06 | 0.06 |
| $C_4$ minus | | 1.68 | 1.68 |
| $C_5$ and/or $C_6$ | | 1.00 | 2.36 |
| Flash Point* to EP Diesel Fuel | 44.0 | 98.55 | 96.19 |
| Total | | 101.40 | 101.40 |
| * Flash Point, °F | | 133 | 140 |
| Hydrogen Consumption, SCF/B | | 800 | |

## TABLE 9

## DIESEL FUEL DF-2
## PRODUCTION SAMPLE

| | USAF Specs. | | |
|---|---|---|---|
| API Gravity at 60°F | 32.9-41 | 38.8 | |
| Sp. Gr. 60/60°F | | 0.8309 | |
| D 86-Engler, vol-% | | | |
| IBP, °F | | 320 | |
| 5% | | 362 | |
| 10% | | 400 | |
| 20% | | 452 | |
| 30% | | 486 | |
| 40% | | 513 | |
| 50% | report | 542 | |
| 60% | | 568 | |
| 70% | | 593 | |
| 80% | | 618 | |
| 90% | 675 max. | 646 | |
| 95% | | 664 | |
| EP, °F | 700 max. | 678 | |
| % Over | | 98.5 | |
| Flash Point, °F | 133 min. | 134 | |
| Cloud Point, °F | 20 min. | 32 | |
| Pour Point, °F | | 5 | |
| Aniline Point, °F | | 173.1 | |
| Viscosity 100°C, cSt | 1.8-9.5 | 3.367 | |
| D 1500 Color | report | < 2 | |
| Acid No., mg KOH/gm | 0.10 max. | 0.018 | |
| Copper Strip Corrosion, 100°C | 1 max. | 1A | |
| Coulometric Sulfur, ppm | 0.70 wt-% max. | 1.2 | |
| Cetane No. | 45 min. | 55.1 | |
| Water and Sediment D 2709, wt-% | 0.01 max. | < 0.005 | |
| Demulsification, 25°C | | No Emulsion<br>Oil Layer Clear | |
| Particulate Cont., D 2276, mg/l | 8 max. | 8 | |
| Carbon Residue on 10% Botts., D 524, wt-% | 0.2 max. | 0.11 | |
| Ash, wt-% | 0.02 max. | < 0.001 | |
| Stability, D 2274 | | | |
| Adherent gum, mg/100 ml | 1.5 max. | 0.45 | Total 0.8 |
| Sediment, mg/100 ml | | 0.35 | |

## TABLE 10

## DIESEL FUEL MARINE DFM
## PRODUCTION SAMPLE

| | USAF Specs. | | |
|---|---|---|---|
| API Gravity at 60°F | report | 38.7 | |
| Sp. Gr. 60/60°F | | 0.8314 | |
| D 86-Engler, vol-% | | | |
| IBP, °F | | 348 | |
| 5% | | 376 | |
| 10% | | 420 | |
| 20% | | 465 | |
| 30% | | 498 | |
| 40% | | 525 | |
| 50% | report | 550 | |
| 60% | | 575 | |
| 70% | | 598 | |
| 80% | | 624 | |
| 90% | 675 max. | 650 | |
| 95% | | 672 | |
| EP, °F | 725 max. | 680 | |
| % Over | | 99.0 | |
| Flash Point, °F | 140 min. | 144 | |
| Cloud Point, °F | 30 min. | 28 | |
| Pour Point, °F | 20 max. | 5 | |
| Aniline Point, °F | report | 173.1 | |
| Viscosity 100°C, cSt | 1.7-4.3 | 3.444 | |
| D 1500 Color | 3 max. | < 3 | |
| Acid No., kg KOH/gm | 0.30 max. | 0.021 | |
| Copper Strip Corrosion, 100°C | 1 max. | 1A | |
| Coulometric Sulfur, ppm | 1.0 wt-% max. | 1.9 | |
| Cetane No. | 45 min. | 55.3 | |
| Water and Sediment D 2709, wt-% | | < 0.005 | |
| Demulsification, 25°C, minutes | 10 max. | No Emulsion<br>Oil Layer Clear | |
| Particulate Cont., D 2276, mg/l | | 5 | |
| Carbon Residue on 10% Botts., D 524, wt-% | 0.2 max. | 0.11 | |
| Ash, wt-% | 0.005 max. | < 0.001 | |
| Stability, D 2274 | | | |
| Adherent gum, mg/100 ml | 2.0 max. | 0.3 | Total 0.7 |
| Sediment, mg/100ml | | 0.3 | |

## TABLE 11

## SHALE OIL ARSENIC SOLUBILIZATION STUDY

Arsenic in Feed = 19 ppm

| Reagent | Observation | Arsenic, ppm In Oil |
|---|---|---|
| 10% KOH | Emulsion stable, broken by addition of isooctane/methanol. | 10.8 |
| 10% $H_2SO_4$ | No emulsion formed. | 16.6 |
| 50% acetic acid | Formed emulsion which slowly broke. | 14.7 |
| 10% $Na_2S$ | Formed emulsion which did not break with isooctane/methanol treatment. | |
| | 1) One hour at 220°C under 100 ATM of $N_2$-broke. | 11.7 |
| | 2) Centrifuged at 7000 rpm, part of the emulsion broke. | 9.1 |

## TABLE 12

## FIRST-STAGE HYDROTREATER SPENT CATALYST ANALYSIS

| Sample Location | Element, wt-% | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Catalyst 1 | Fe | C | N | S | H | As | Mo | Co |
| Upper Section | 6.3 | 10.4 | .47 | 9.3 | 1.6 | 2.4 | + | + |
| Upper Middle | 4.5 | 10.5 | .34 | 8.6 | 1.4 | 1.2 | + | + |
| Middle Section | 1.0 | 13.4 | .57 | 8.2 | 1.6 | 0.32 | + | + |
| Lower Middle | 0.4 | 13.3 | .59 | 7.8 | 1.4 | 0.12 | + | + |
| Lower Section | 0.4 | 14.1 | .67 | 7.5 | 1.3 | 0.07 | + | + |
| Catalyst 2 | | | | | | | | |
| Top | 6.0 | 9.11 | 3.9 | 6.2 | | 8.4 | + | + |
| Top Middle | 3.7 | 10.2 | .43 | 6.4 | | 5.6 | + | + |
| Middle | 1.9 | 10.1 | .43 | 5.7 | | 3.4 | + | + |
| Bottom Middle | 1.0 | 10.2 | .85 | 5.8 | | 1.6 | + | + |
| Bottom | 0.9 | 10.3 | .22 | 5.5 | | 1.3 | + | + |

+ = Present.

## TABLE 13

## X-RAY DIFFRACTION DATA ON USED CATALYSTS

| Compound Identification | Catalyst 1 Upper Section | Catalyst 2 Upper Section |
|---|---|---|
| $\gamma\ Al_2O_3$ | m | m |
| $\alpha\ SiO_2$ | t | t |
| AlO(OH) boehmite | t | |
| $Fe_{(1-x)}S$ pyrrhotite | m | m |
| $FeS_2$ pyrite | | t |
| $Co_{0.84}Ni_{0.16}As_{1.04}$ | t | m |
| $Cu_{24}As_{13}S_{31}$ | t | m |

m = major

t = trace

## TABLE 14

## DIGESTION OF USED CATALYST

Used Catalyst Analysis: Arsenic, wt-% 1.16

| Digestion Solution | | |
|---|---|---|
| $H_2SO_4$, wt-% | $HNO_3$, wt-% | As Extraction, % |
| 10 | - | 24 |
| 10 | 3 | 90 |
| 20 | - | 23 |
| 20 | 3 | 90 |
| 40 | - | 24 |
| 40 | 3 | 72 |

Thermally Treated Catalyst
Extracted in 40 wt-% $H_2SO_4$

| Thermal Treatment | | | % As Removed | | |
|---|---|---|---|---|---|
| Temp, °C | Gas | Time, Hr | Volatilization | Extraction | Total Removal |
| 550 | 5% $O_2$ | 6 | 69 | 50 | 74 |
| 650 | 5% $O_2$ | 2 | 58 | 53 | 80 |
| 250 | 5% $O_2$ | 6 | 9 | 74 | 76 |

## TABLE 15

## SHALE OIL-PETROLEUM OIL COMPATIBILITY-STABILITY STUDY

| Name | Heavy Arabian Crude | Paraho Shale Oil | | | Occidental Shale Oil | | |
|---|---|---|---|---|---|---|---|
| | | Raw | First-Stage Hydrotreated | Second-Stage Hydrotreated | Raw | First-Stage Hydrotreated | Second-Stage Hydrotreated |
| API at 60°F | 26.4 | 25.2 | 30.3 | 33.5 | 22.5 | 26.2 | 32.2 |
| Specific Gravity at 60°F | 0.8961 | 0.9303 | 0.9111 | 0.8576 | 0.9188 | 0.8973 | 0.8644 |
| Distillation, D-1160, °F | | | | | | | |
| IBP | 138 | 372 | 390 | 344 | 399 | 422 | 356 |
| 5% | 189 | 450 | 471 | 438 | 479 | 508 | 450 |
| 10% | 290 | 500 | 517 | 471 | 512 | 538 | 488 |
| 20% | 420 | 585 | 590 | 521 | 572 | 589 | 532 |
| 30% | 518 | 665 | 651 | 574 | 623 | 631 | 570 |
| 40% | 626 | 728 | 710 | 620 | 677 | 672 | 615 |
| 50% | 735 | 784 | 760 | 670 | 729 | 718 | 660 |
| 60% | 851 | 840 | 810 | 721 | 775 | 767 | 710 |
| 70% | 971 | 888 | 861 | 765 | 822 | 812 | 760 |
| 80% | (76) 1039 | 950 | 919 | 821 | 878 | 872 | 810 |
| 90% | | 1025 | (95) 1043 | (EP) 1009 | 960 | (94) 1010 | (EP) 979 |
| % Over | 76.0 | 90.0 | 95.0 | 99.0 | 90.0 | 94.0 | 97.0 |
| % Bottoms | 24 | 10.0 | 5.0 | 1.0 | 10.0 | 6.0 | 3.0 |
| Carbon, wt-% | 80.88 | 84.6 | 85.28 | 85.93 | 84.59 | 85.02 | 85.73 |
| Hydrogen, wt-% | 11.22 | 11.4 | 12.05 | 12.40 | 12.42 | 12.60 | 13.01 |
| Oxygen, wt-% | 0.93 | 1.76 | 0.60 | 0.26 | 1.55 | 0.52 | 0.28 |
| Sulfur, wt-% | 2.97 | 0.71 | 0.0746 | 0.00323 | 0.68 | 0.0261 | < 0.03 |
| Nitrogen, wt-% | 0.17 | 2.19 | 1.90 | 0.06 | 1.42 | 1.09 | 0.09 |
| $C_7$ Insolubles, wt-% | 4.67 | 0.44 | 0.14 | 0.01 | 0.26 | 0.01 | 0.01 |
| Toluene Insolubles, wt-% | < 0.01 | 0.01 | < 0.01 | 0.01 | < 0.01 | 0.01 | < 0.01 |
| Viscosity at 100°F, SUS | 118.5 | 213 | 156.0 | 54.2 | 186.7 | 124.6 | 60.1 |
| Viscosity at 100°F, cSt | 24.80 | 45.72 | 33.23 | 8.633 | 39.98 | 26.20 | 10.35 |
| Steam Jet Gum, mg/100 ml | 35,875.0 | 26,463.0 | 22,129.0 | 5,668.1 | 21,314.8 | 16,940.5 | 7,823.5 |
| Bromine Number | 2.4 | 30.2 | 15.8 | 0.8 | 19.4 | 7.8 | 1.9 |
| Nickel, ppm | 13 | 3.5 | 3.0 | < 0.1 | 8.8 | 3.2 | < 0.1 |
| Vanadium, ppm | 47 | 0.5 | 0.5 | < 0.1 | 0.5 | < 0.2 | < 0.2 |
| Iron, ppm | 2.8 | 108 | 13 | < 0.3 | 53 | 14 | < 0.1 |
| Arsenic, ppm | < 1 | 30 | < 1 | < 1 | 28 | < 1 | < 1 |
| Conradson Carbon, wt-% | 7.98 | 2.35 | 1.57 | 0.01 | 1.05 | 0.44 | 0.03 |

## TABLE 16

## SHALE OIL-PETROLEUM OIL COMPATIBILITY-STABILITY STUDY

| Name | Heavy Arabian Crude | Paraho Shale Oil |  |  | Occidental Shale Oil |  |  |
|---|---|---|---|---|---|---|---|
|  |  | Raw | First-Stage Hydrotreated | Second-Stage Hydrotreated | Raw | First-Stage Hydrotreated | Second-Stage Hydrotreated |
| Initial Analysis |  |  |  |  |  |  |  |
| $C_7$ Insolubles, wt-% | 4.67 | 0.44 | 0.14 | 0.01 | 0.26 | 0.01 | 0.01 |
| Toluene Insolubles, wt-% | < 0.01 | 0.01 | < 0.01 | 0.01 | < 0.01 | 0.01 | < 0.01 |
| Viscosity at 100°F, SUS | 118.5 | 213 | 156 | 54.2 | 186.7 | 124.6 | 60.1 |
| cSt | 24.8 | 45.72 | 33.23 | 8.63 | 39.98 | 26.20 | 10.35 |
| Steam Jet Gum, g/100 ml | 35.875 | 26.463 | 22.129 | 5.6681 | 21.3148 | 1.69405 | 7.8235 |
| Du Pont F-21-61 |  |  |  |  |  |  |  |
| $C_7$ Insolubles, wt-% | 5.92 | 0.40 | 0.2 | < 0.01 | 0.50 | 0.40 | 0.01 |
| Toluene Insolubles, wt-% | 0.07 | < 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Viscosity at 100°F, SUS | 190.9 | 268 | 183.7 | 56.3 | 210 | 135 | 63.6 |
| cSt | 40.88 | 57.73 | 39.3 | 9.268 | 44.99 | 28.56 | 11.34 |
| D-2274 16-hr Heat Treatment |  |  |  |  |  |  |  |
| $C_7$ Insolubles, wt-% | 6.23 | 1.70 | 0.79 | 0.02 | 3.18 | 0.11 | < 0.01 |
| Toluene Insolubles, wt-% | < 0.01 | < 0.01 | 0.01 | < 0.01 | 0.01 | < 0.01 | < 0.01 |
| Viscosity at 100°F, SUS | 214 | 325 | 205 | 55.4 | 260 | 140.1 | 62.2 |
| cSt | 45.93 | 70.13 | 43.96 | 9.008 | 56.03 | 29.68 | 10.94 |
| Adherent Gum, g/100 ml | 1.2 |  |  |  |  | 0.9 | 1.1 |
| 3-months Dark Storage, 110°F |  |  |  |  |  |  |  |
| $C_7$ Insolubles, wt-% | 6.07 | 0.97 | 0.29 | 0.01 | 0.88 | 0.03 | < 0.01 |
| Toluene Insolubles, wt-% | 0.01 | < 0.01 | 0.01 | < 0.01 | < 0.11 | < 0.01 | < 0.01 |
| Viscosity at 100°F, SUS | 381 | 311 | 171 | 55.5 | 221 | 131.6 | 59.7 |
| cSt | 82.21 | 67.01 | 36.56 | 9.027 | 47.50 | 27.77 | 10.27 |
| Adherent Gum, g/100 ml | 0.5 | 0.5 | 0.8 | 0.8 | 0.7 | 0.1 | 0.2 |

## TABLE 17

## SHALE OIL-PETROLEUM OIL COMPATIBILITY-STABILITY STUDY

| Name | 30% Paraho Shale Oil | | | 30% Occidental Shale Oil | | |
|---|---|---|---|---|---|---|
| | Raw | First-Stage Hydrotreated | Second-Stage Hydrotreated | Raw | First-Stage Hydrotreated | Second-Stage Hydrotreated |
| | 70% Arabian Crude | | | 70% Arabian Crude | | |
| Initial Analysis | | | | | | |
| $C_7$ Insolubles, wt-% | 3.23 | 3.24 | 3.30 | 3.21 | 3.00 | 3.28 |
| Toluene Insolubles, wt-% | < 0.01 | 0.01 | < 0.01 | < 0.01 | 0.02 | < 0.01 |
| Viscosity at 100°F, cSt | 27.54 | 25.17 | 17.381 | 27.97 | 24.15 | 18.06 |
| SUS | 130.6 | 124.5 | 86.9 | 132.5 | 115.6 | 89.7 |
| Steam Jet Gum, g/100 ml | 34.7780 | 37.2820 | 28.3094 | 32,515 | 30.343 | 29.3746 |
| Du Pont F-21-61 | | | | | | |
| $C_7$ Insolubles, wt-% | 3.38 | 3.28 | 3.60 | 3.38 | 3.39 | 3.51 |
| Toluene Insolubles, wt-% | 0.01 | 0.01 | < 0.01 | < 0.01 | 0.01 | < 0.01 |
| Viscosity at 100°F, cSt | 38.28 | 34.58 | 23.21 | 36.26 | 31.15 | 22.38 |
| SUS | 178.9 | 162.1 | 111.5 | 169.7 | 146.7 | 107.9 |
| D-2274 16-hr. Heat Treated | | | | | | |
| $C_7$ Insolubles, wt-% | 5.17 | 4.23 | 4.19 | 4.95 | 3.94 | 4.17 |
| Toluene Insolubles, wt-% | 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| Viscosity at 100°F, cSt | 52.86 | 41.66 | 24.20 | 44.94 | 36.21 | 25.0 |
| SUS | 246 | 194.3 | 115.9 | 209 | 169.5 | 119.4 |
| Adherent Gum, g/100 ml | 70.6 | 2.2 | 0.9 | 2.4 | 0.4 | 1.7 |
| 3-months Dark Storage, 110°F | | | | | | |
| $C_7$ Insolubles, wt-% | 4.48 | 4.12 | 4.14 | 4.68 | 3.97 | 4.17 |
| Toluene Insolubles, wt-% | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| Viscosity at 100°F, cSt | 77.16 | 61.52 | 33.11 | 71.0 | 52.46 | 34.88 |
| SUS | 358 | 286 | 155.4 | 329 | 244 | 163.5 |
| Adherent Gum, g/100 ml | 2.1 | 0.3 | 0.2 | 0.9 | 0.3 | 0.3 |

## TABLE 18

## SHALE OIL COMPATIBILITY/STABILITY STUDY COMPARISON OF ANALYZED AND CALCULATED VALUES

| | Analytical cSt Viscosity | Calculated cSt Viscosity | |
|---|---|---|---|
| 30 Vol-% Raw Paraho Shale Oil | 27.54 | 29.2 | 29.66 |
| 30 Vol-% Paraho Shale Oil First-Stage Hydrotreated | 25.17 | 26.9 | 27.03 |
| Vol-% Paraho Shale Oil Second-Stage Hydrotreated | 17.38 | 17.5 | 17.59 |
| 30 Vol-% Raw Occidental Shale Oil | 27.97 | 28.0 | 28.55 |
| 30 Vol-% Occidental Shale Oil First-Stage Hydrotreated | 24.15 | 25.2 | 25.2 |
| 30 Vol-% Occidental Shale Oil Second-Stage Hydrotreated | 18.06 | 18.8 | 18.73 |

| | Analytical | | Calculated | |
|---|---|---|---|---|
| | % $C_7$ Insol. | % Toluene Insol. | % $C_7$ Insol. | % Toluene Insol. |
| 30 Vol-% Raw Paraho Shale Oil | 3.23 | < 0.01 | 3.36 | < 0.01 |
| 30 Vol-% Paraho Shale Oil First-Stage Hydrotreated | 3.24 | 0.01 | 3.29 | < 0.01 |
| 30 Vol-% Paraho Shale Oil Second-Stage Hydrotreated | 3.30 | < 0.01 | 3.31 | < 0.01 |
| 30 Vol-% Raw Occidental Shale Oil | 3.21 | < 0.01 | 3.32 | < 0.01 |
| 30 Vol-% Occidental Shale Oil First-Stage Hydrotreated | 3.00 | 0.02 | 3.27 | < 0.01 |
| 30 Vol-% Occidental Shale Oil Second-Stage Hydrotreated | 3.28 | < 0.01 | 3.31 | < 0.01 |

## TABLE 19

## OVERALL MATERIAL BALANCE
## MAXIMUM JET FUEL CASES

| | Max. JP-4 | | Max. JP-8 | |
|---|---|---|---|---|
| Feed | Wt-% | Vol-% | Wt-% | Vol-% |
| Shale Oil | 100.00 | 100.00 | 100.00 | 100.00 |
| Liquid Products | | | | |
| Gasoline | - | - | 7.27 | 8.92 |
| Jet Fuel JP-4 | 78.83 | 92.53 | - | - |
| Jet Fuel JP-8 | - | - | 71.47 | 81.37 |
| TOTAL LIQUID PRODUCTS | 78.83 | 92.53 | 78.74 | 90.29 |
| By-Products | | | | |
| Sulfur (S Tons/CD) | 0.61 | - | 0.61 | - |
| Ammonia (S Tons/CD) | 1.91 | - | 1.92 | - |
| Water (Net Make) | 0.72 | 0.66 | 0.72 | 0.66 |
| TOTAL BY-PRODUCTS | 3.24 | - | 3.25 | |
| Streams Utilized as Fuel | | | | |
| Fuel Oil | 13.48 | 14.30 | 7.73 | 8.20 |
| Naphtha | - | - | 5.96 | 8.22 |
| TOTAL FUELS | 13.48 | 14.30 | 13.69 | 16.42 |
| Material Lost in Production | | | | |
| TOTAL LOSSES | 4.45 | - | 4.32 | - |

## TABLE 20

## ESTIMATED OPERATING COST

(Millions of Dollars per Year)

| | Max. JP-4 | Max. JP-8 |
|---|---|---|
| **Direct Operating Cost** | | |
| Refinery Labor | 9.01 | 10.38 |
| Maintenance | 22.11 | 23.13 |
| Utilities | 20.09 | 20.75 |
| Catalyst and Chemicals | 8.75 | 8.96 |
| TOTAL DIRECT OPERATING COST | 59.96 | 63.22 |
| **Indirect Operating Cost** | | |
| Local Taxes | 3.68 | 3.86 |
| Insurance | 7.37 | 7.71 |
| TOTAL INDIRECT OPERATING COST | 11.05 | 11.57 |
| TOTAL OPERATING COST | 71.01 | 74.79 |

## TABLE 21

## PROCESS UNITS CAPACITIES AND CAPITAL INVESTMENTS

| | Max. JP-4 | | Max. JP-8 | |
|---|---|---|---|---|
| | (S Ton/SD) BPSD | MM Dollars | (S Ton/SD) BPSD | MM Dollars |
| Feed Preparation | 100,000 | 9 | 100,000 | 9 |
| LP Hydrotreating (RCD Unibon) | 100,000 | 59 | 100,000 | 59 |
| HP Hydrotreating | 102,920 | 97 | 102,920 | 97 |
| Hydrocracking (HC Unibon) | 94,340 | 169 | 100,745 | 177 |
| Fractionation | - | 7 | - | 8 |
| Fuel Gas Treating | - | 4 | - | 4 |
| Sulfur Plant | (97.5) | 6 | (97.5) | 6 |
| Hydrogen Plant (Steam Ref.) | (796.4) | 122 | (813.9) | 124 |
| Naphtha Hydrotreating | - | - | 6,535 | 4 |
| Platforming | - | - | 6,535 | 11 |
| Sour Water Treating | 19,495 | 10 | 19,955 | 10 |
| Fuel Oil Stabilizer | 15,025 | 3 | 8,615 | 2 |
| Common Facilities | - | 11 | - | 11 |
| TOTAL PROCESS INVESTMENT | | 497 | | 522 |

Note: Capital Investment as of 1st Quarter 1981.

## TABLE 22

## CAPITAL INVESTMENT SUMMARY
(Millions of Dollars)

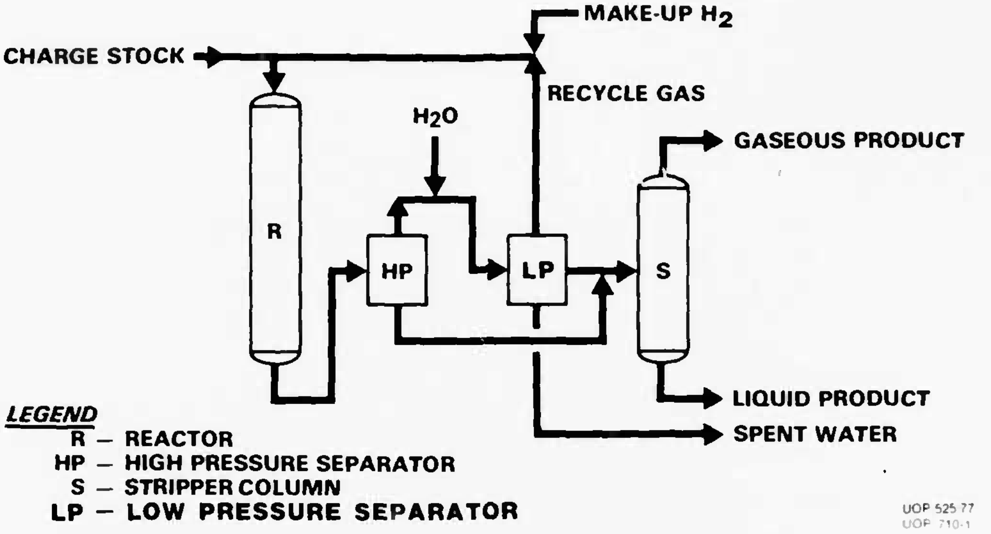
| 100,000 BPSD Refinery | Max. JP-4 | Max. JP-8 |
|---|---|---|
| Process Units Erected Cost | 497 | 522 |
| Allowance for Offsites, including Royalties and Know-How Fees | 296 | 308 |
| TOTAL DEPRECIABLE INVESTMENT | 793 | 830 |
| Initial Catalyst Inventory | 27 | 25 |
| Working Capital Allowance | 93 | 93 |
| TOTAL CAPITAL INVESTMENT | 913 | 948 |

## TABLE 23

## COST OF PRODUCTION BREAKDOWN

### 100,000 BPSD Charge Rate

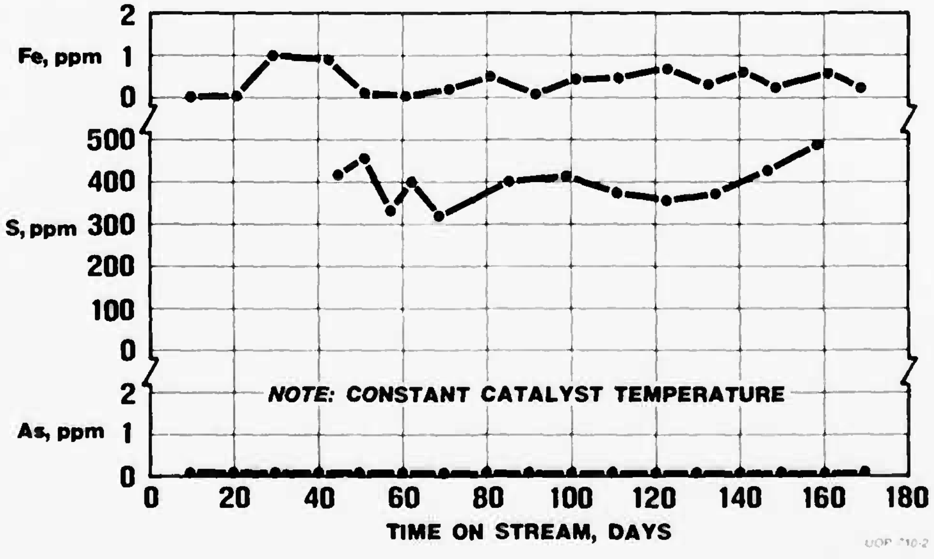
| | Max. JP-4 | Max. JP-8 |
|---|---|---|
| Operating Cost, $/Bbl of Feed | 2.26 | 2.38 |
| Cost of Feed, $/Bbl | 40.00 | 40.00 |
| Capital Charges for 15% DCF Return, $/Bbl of Feed | 10.00 | 10.36 |
| Total Cost of Production, $/Bbl of Feed | 52.26 | 52.74 |
| Total Cost of Liquid Products, $/Bbl | 56.48 | 58.41 |



FIRST STAGE HYDROTREATING PILOT PLANT

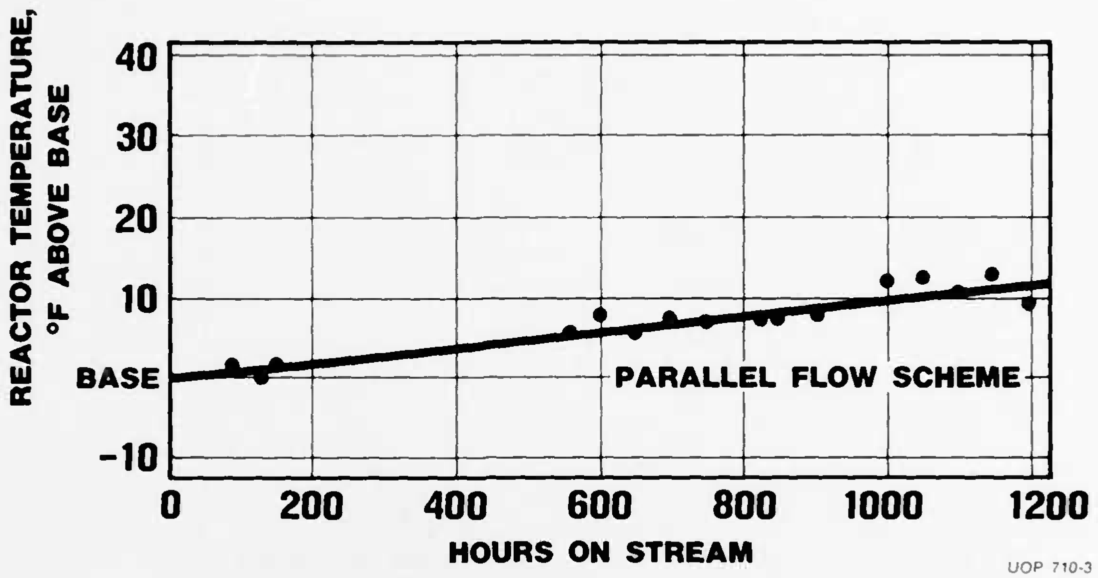
SCHEMATIC FLOW DIAGRAM

FIGURE 1



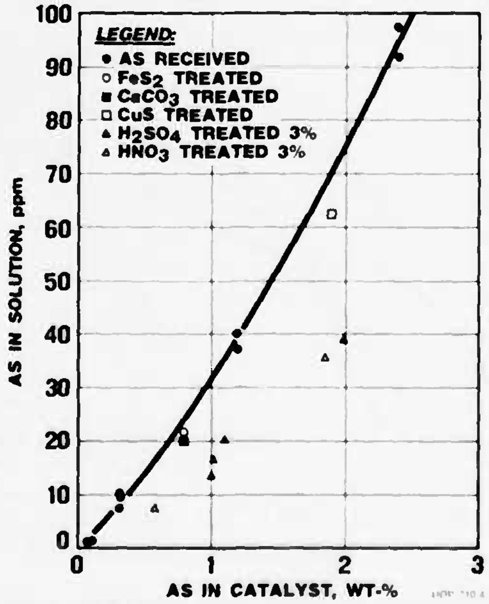
FIRST STAGE HYDROTREATING CATALYST STABILITY DEMONSTRATION

FIGURE 2



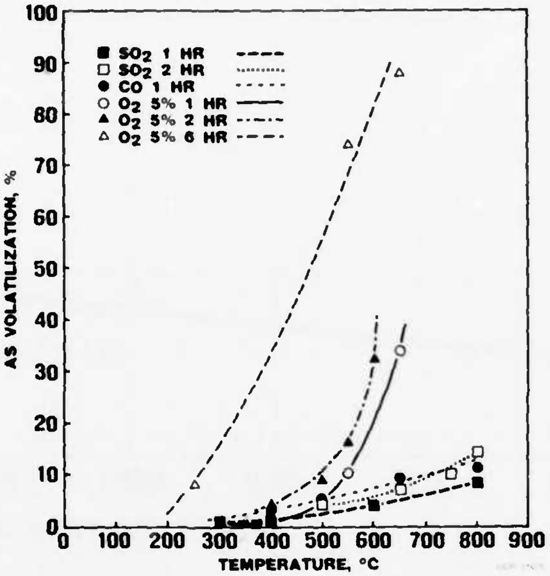
**HYDROCRACKING CATALYST STABILITY DEMONSTRATION**

**FIGURE 3**



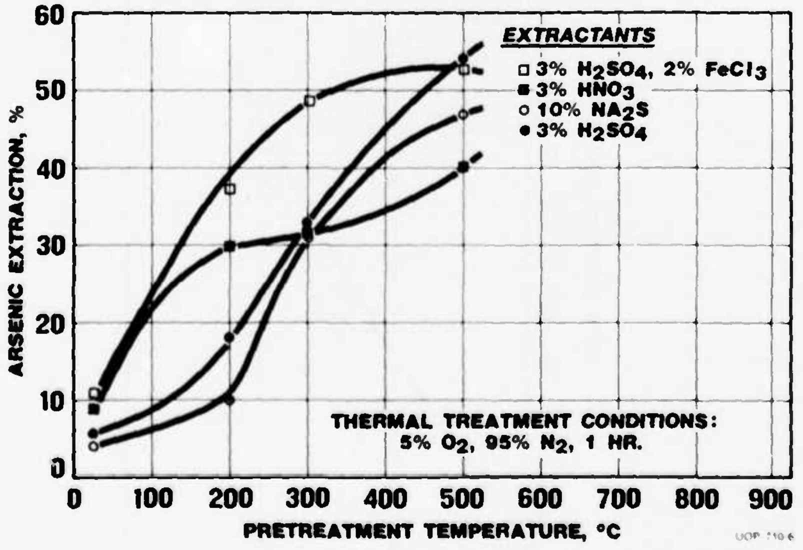
**SIMULATED EPA TOXICITY TEST ON USED CATALYST**

**FIGURE 4**



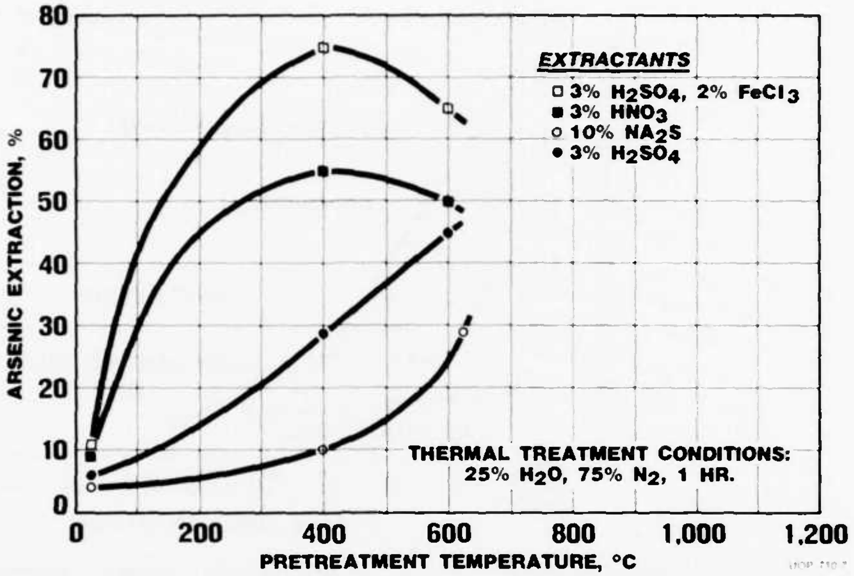
**EFFECT OF THERMAL TREATMENT ON ARSENIC VOLATILIZATION**

**FIGURE 5**



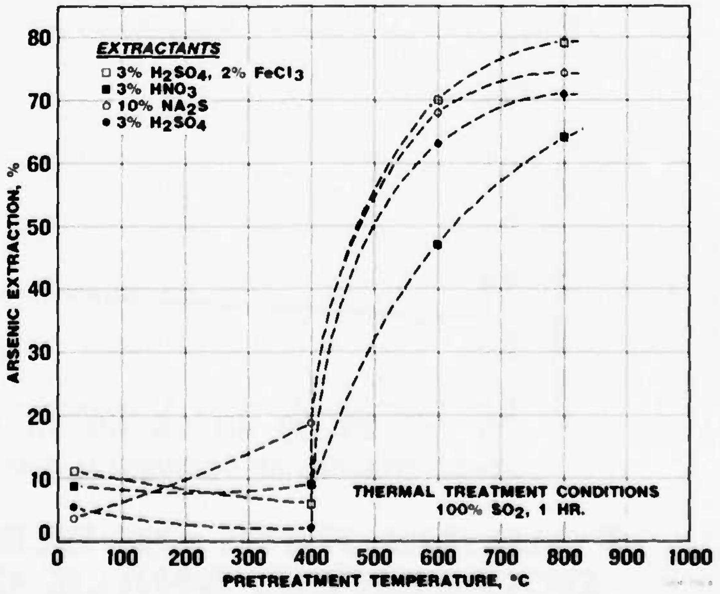
**EFFECT OF SEVERE OXIDATION ON ARSENIC EXTRACTION FROM USED CATALYST**

**FIGURE 6**



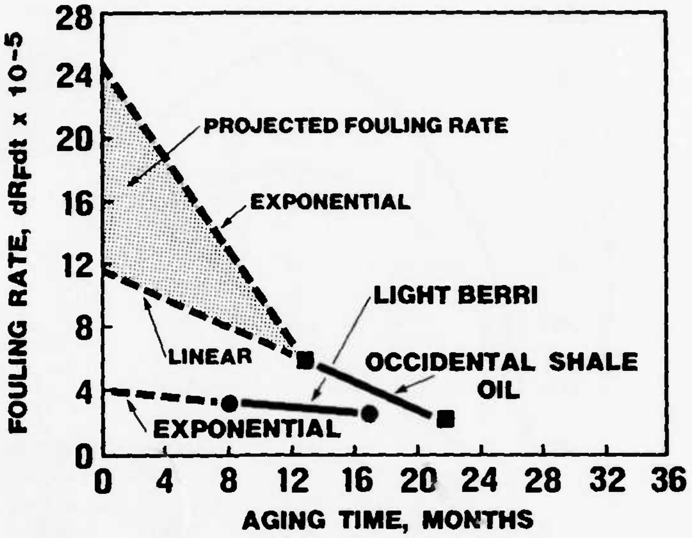
EFFECT OF MILD OXIDATION ON ARSENIC EXTRACTION FROM USED CATALYST

FIGURE 7



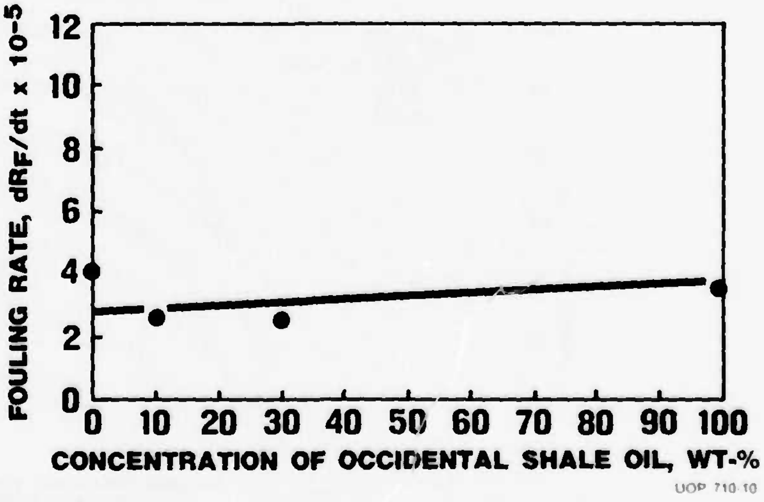
EFFECT OF SULFUR TREATMENT ON ARSENIC EXTRACTION FROM USED CATALYST

FIGURE 8



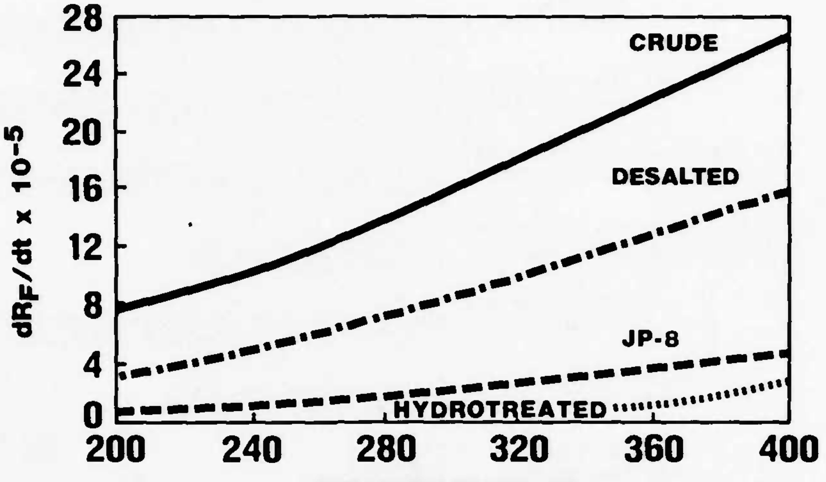
**EFFECT OF AGING ON FOULING RATE**

**FIGURE 9**



**FOULING RATE OF BLENDS OF OCCIDENTAL SHALE OIL AND ARABIAN LIGHT BERRI CRUDE**

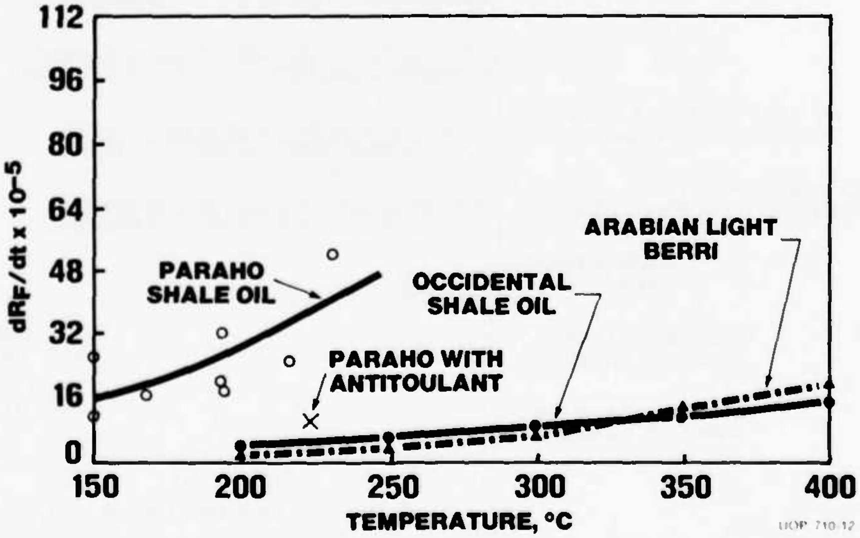
**FIGURE 10**



UOP 688-5
UOP 710-11

**EFFECT OF TEMPERATURE ON THE FOULING RATE OF OCCIDENTAL SHALE OIL DERIVED FEEDS**

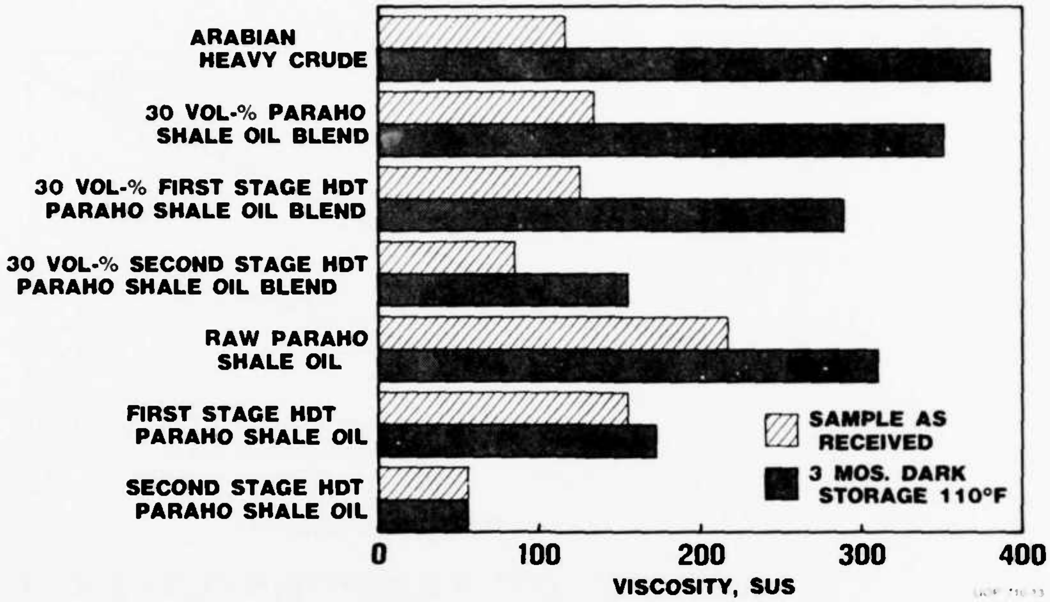
**FIGURE 11**



UOP 710-12

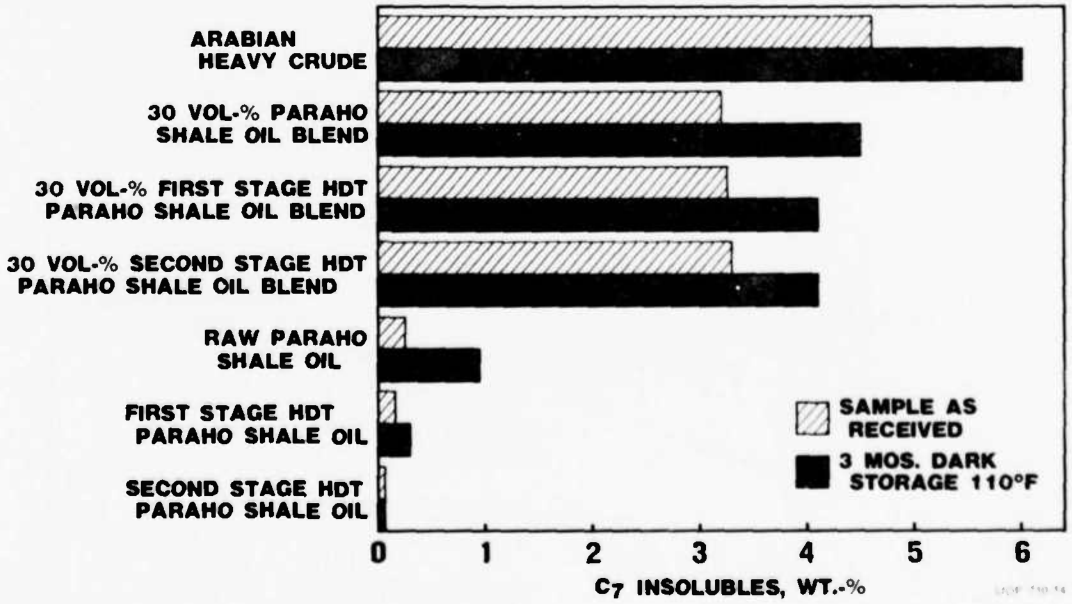
**EFFECT OF TEMPERATURE ON FOULING RATE OF SHALE AND PETROLEUM OILS**

**FIGURE 12**



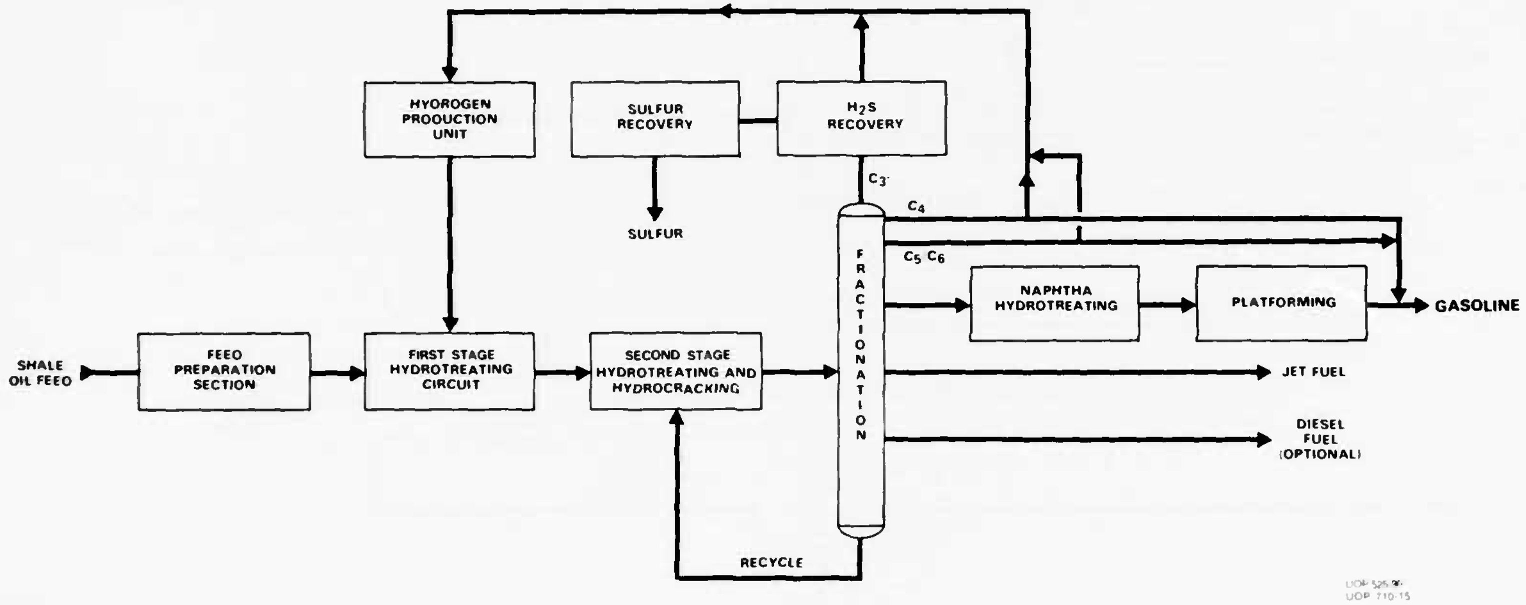
EFFECT OF STORAGE ON VISCOSITY

FIGURE 13



EFFECT OF STORAGE ON HEPTANE INSOLUBLE CONTENT

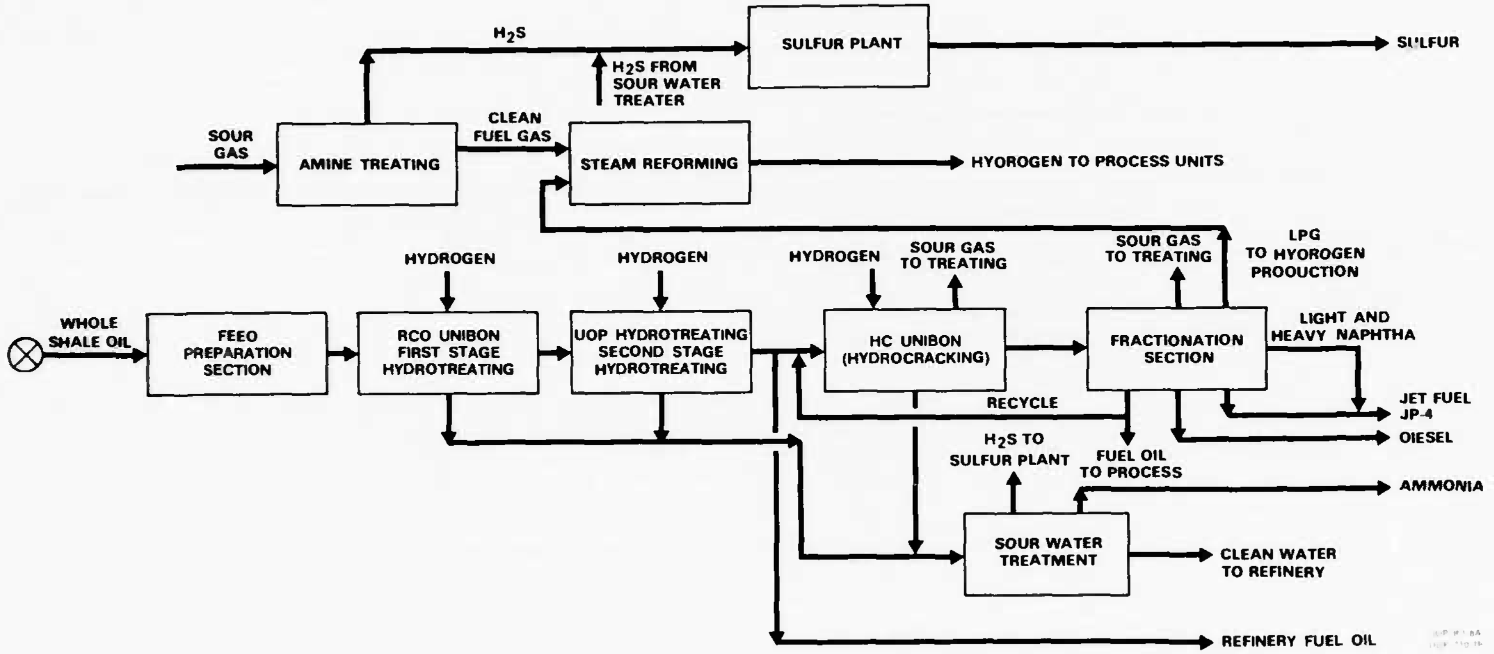
FIGURE 14



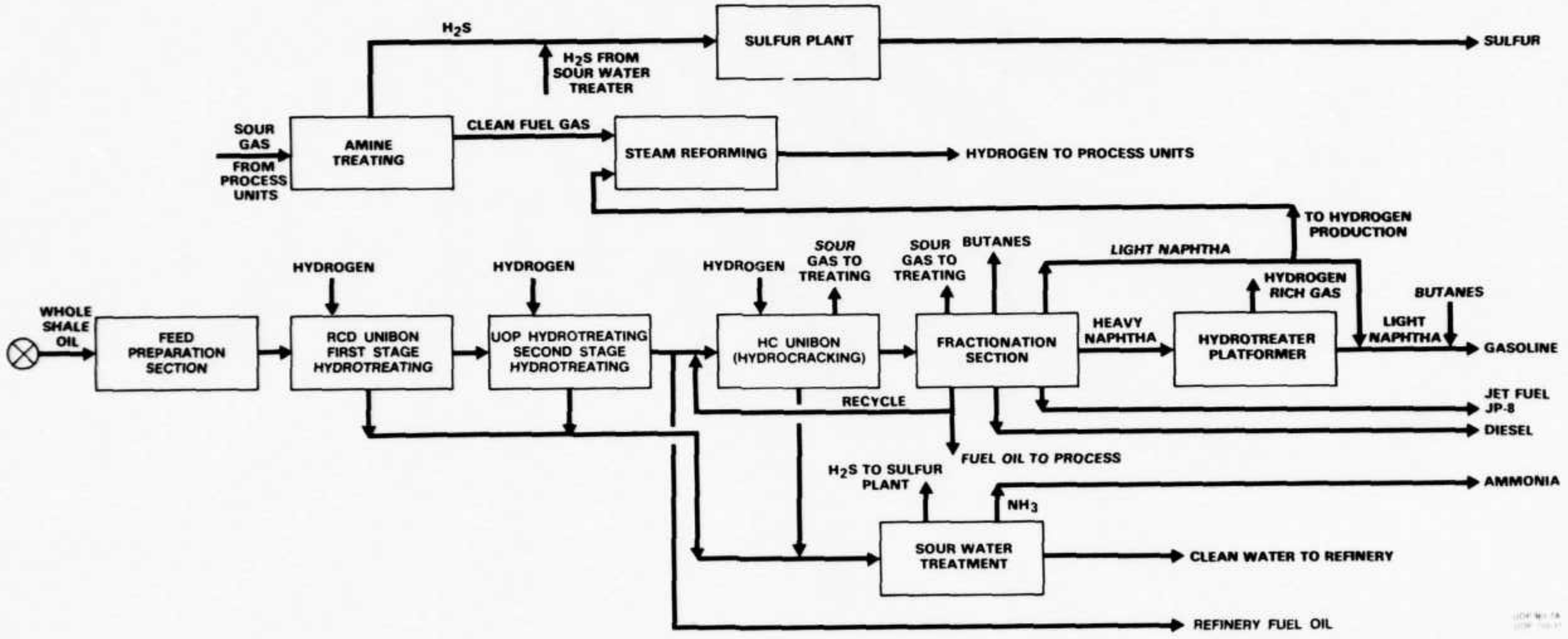
UOP SHALE OIL TO FUELS

OVERALL BLOCK FLOW DIAGRAM

FIGURE 15



**PRODUCTION OF JP-4 JET FUEL**
**BLOCK FLOW DIAGRAM**
**FIGURE 16**



**PRODUCTION OF JP-8 JET FUEL**
**BLOCK FLOW DIAGRAM**

**FIGURE 17**

## III

# MILITARY JET FUELS FROM SHALE OIL

By

R. P. Long, H. F. Moore
W. A. Sutton, and F. H. Turrill

Ashland Petroleum Company

## SUMMARY

Ashland Petroleum Company began the work under Contract F33615-78-C-2080 on February 15, 1979 to characterize two whole crude shale oils in terms of processability via the EXTRACTACRACKING process for the production of aviation turbine fuels. Data and results have been presented at previous symposia on Phase I and Phase II of the program. From the Phase II work nine (9) potential turbine fuel samples were provided to the Air Force for evaluation.

This presentation provides data on Ashland's Phase III and Phase IV efforts in the program. Work performed in Phase III was aimed at confirming final process design estimates proposed in Phase I and producing sample lots of aviation turbine fuels and other military type fuels. Our Phase IV program provides an overall economic optimization study involving computer modeling.

This presentation is composed of three parts: (1) background to the contract, (2) data from the Phase III pilot plant operating units and product quality, and (3) data from the Phase IV economic evaluation.

## BACKGROUND

The traditional source of aviation turbine fuels has been the refining of petroleum crude oil. The lessening world supply of crude oil, the increased cost of crude, and dependence on foreign crude oil sources have emphasized the need for a secure and reliable source of alternate synthetic crude to provide the required military fuels essential to our national defense. Research and Development efforts have shown that fuels derived from crude shale oil present one of the best potentials as an alternate source of military aviation turbine fuels. As a result of this recognized need for alternate sources of aviation turbine fuel, the Air Force awarded Research and Development contracts for the design and operation of proposed processes on a laboratory and pilot plant scale.

The objectives and goals as defined in the original contract document are shown in Slide 1 and the four-phased components of the contract program are shown in Slide 2.

The major problems expected to be encountered in the processing of crude shale oil are shown in Slide 3. The foremost problem to be considered was the high nitrogen content and the approaches for removal of nitrogen compounds via the EXTRACTACRACKING process. In Slide 4 we show the EXTRACTACRACKING process configuration in this overall flow diagram.

Ashland's EXTRACTACRACKING process and the answers to the problems to be encountered by each of the six process modules is indicated in Slide 5.

## PHASE III

The major objectives of Ashland's Phase III EXTRACTACRACKING work are shown on Slide 6, and the steps used in our processing sequence are outlined on Slide 7.

### Crude Shale Hydrotreating (CSHT)

The crude shale hydrotreater provides desulfurization, demetallization, olefin saturation, deoxygenation, and denitrogenation. The low severity operating conditions are intended to minimize hydrogen consumption and denitrogenation while increasing the relative proportion of basic nitrogen.

The average conditions used, and the product yield structure are given on Slide 8, and the average feed and product properties are shown on Slide 9. Aging trends for heteroatom removal are shown on Slide 10.

### Modified Reduced Crude Conversion (MRCC)

Fluid catalytic cracking (actually a modified version of our Reduced Crude Conversion Process) cascades gas oil and heavier components into the jet fuel and gasoline boiling range, and accomplishes a degree of heteroatom removal without external hydrogen addition.

The MRCC feedstocks to be discussed in this presentation are shown on Slide 11, and the yield structure and the feed and product properties for the 100% CSHT >600°F base case are given on Slide 12 and Slide 13.

Lumped product distributions which were obtained for the various feedstocks are shown in Slide 14. This slide points out the effects of high basic nitrogen levels on conversion and distillate yields.

### Recycle Oil Hydrotreating (COHT)

Hydrotreating of MRCC bottoms can be used to produce a low sulfur, reduced nitrogen fuel oil, or to provide an upgraded recycle oil stream for further fluid catalytic cracking.

The results of our recycle oil hydrotreating work are given on Slide 15 and Slide 16.

### Acid Extraction

Acid extraction removes a large portion of the basic nitrogen compounds without the use of hydrogen.

The feedstocks investigated are listed on Slide 17, and the operating conditions, feed, and product properties are shown on Slides 18, 19, and 20.

A correlation developed from experimental data which illustrates the importance of several extraction variables is shown on Slide 21.

## Guardcase Hydrotreating (GCHT)

Guardcase hydrotreating removes the final traces of nitrogen and sulfur, and prepares the feedstock for further catalytic processing.

The results of processing this operation on the extraction raffinates forming the JP-8 pool are shown on Slides 22 and 23. Similar results for JP-4 pool processing are given on Slides 24 and 25.

## Reforming

In the EXTRACTACRACKING process, freeze point modification by a novel and innovative reforming process is a major objective of the process. A secondary objective is the production of a reformate fraction for use in gasoline blending.

Some results of our reforming work with the JP-8 pool are given on Slides 26 and 27; similar data on JP-4 pool reforming is shown on Slides 28 and 29.

## Aromatic Saturation

Aromatic saturation reduces the aromatic content of the reformate to levels acceptable for aviation turbine fuels.

Conditions, yield structures, and the properties of the feeds and products are listed on Slides 30 through 33.

## Final Products

The properties of the final turbine fuels produced are given on Slide 34. These fuels met all established or proposed specifications.

The properties of the diesel fuels are shown on Slide 35, and the properties of the gasoline blending component and a residual fuel are shown on Slides 36 and 37.

## PHASE IV

The Phase IV effort was provided in order to evaluate, via computer modeling, optimum economic regions of operation for this process. The modeling was accomplished on a specially modified version of a commercially available linear programming system.

Slide 39 delineates the analysis bases utilized for this portion of the program. Of particular importance, up-dated capital costs from Phase I, variable response data from Phase II, and scale-up and aging data from Phase III were utilized to define model input matrices. The process configuration described in previous meetings of this type, as well as in the foregoing portions of this presentation, were used with two exceptions. First, due to time constraints and some experimental problems in Phase III, we were unable to prove operability of the cycle oil hydrotreater and, therefore, have deleted this unit from the flowsheet for this evaluation. Second, we have provided the option to use the nitrogen extract as feed to a partial oxidation unit for hydrogen production.

Slides 40 through 44 present other bases and assumptions used during the evaluation. For the most part, these factors were defined by the contract monitors to be consistent between contractors. Optional values for fuel gas, propylene, isobutane and n-butane have been added at the fuel oil equivalent of $40/barrel. LPG is also included at a May 1981 posting.

Economic optimization was performed for both Occidental and Paraho shale oil. These evaluations were accomplished by using a complete data matrix spanning the region of operating interest, from minimum to maximum severity. The optimization goal was to determine the product price required to return a 15% DCF.

Slide 46 shows product cost versus hydrogen plant size (expressed as SCFB of crude shale oil) for the data matrix used for Occidental Oil. The points represent minimum cost at each extremum examined, while the line represents an optimum trace between options. Since the region between 800-1100 SCFB was not represented by a search point, additional cases were added to the program leading to definition of the base case optimum shown.

Slides 47 and 48 compare results determined from these optimizations. Very similar prime product yields were obtained, although a relatively large quantity of by-products were obtained for the Occidental Oil. For both oils, the crude shale hydrotreater was the primary element of capital cost. Final product prices defined in Slides 49 and 50 show a constant advantage of $2-3/barrel for the Occidental Oil. This is primarily due to higher operating and capital costs with lower by-product recovery for the Paraho material.

One of our early interests in this program was maximization of turbine fuel production and definition of the incremental cost involved. As shown in Slide 51, the incremental cost is relatively low. Turbine fuel costs of $1.18/gallon (Occidental) and $1.24/gallon (Paraho) would be increased by up to 10¢/gallon at roughly 50M BPD of incremental production.

Further sensitivities were also evaluated for several items for the Occidental Oil. Slide 52 shows the impact of allowing gas sales, for a reduction in product price of $1.40. Potential changes in turbine fuel aromatic specifications were evaluated in Slide 53. Reduction of the specification to 15 percent resulted in no turbine fuel being produced (at no net product cost change) while an increase to 35 percent resulted in a similar volume, but slightly lower cost (by 10¢/bbl).

A further evaluation was performed by adding the option of building alkylation and/or polymerization capacity. As shown in Slides 54 and 55, the model chose to build both with a savings of 50¢/barrel.

Finally, a set of present product values was input to the models to determine a representative value of the shale oil feedstock in terms of today's market. As shown in Slides 56 and 57, the resulting value was $31/barrel at 15 percent DCF. Interestingly enough, neither this product value change nor the previous addition of alkylation and polymerization capacity significantly changed the location of the optimum in terms of process severity. In each case, only dollar magnitudes changed.

Each of these major items are shown in conclusion in Slides 58 through 61. Overall, major questions remaining at the end of this program are shown in the last slide. All major program objectives and requirements have been met under this program.

## 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

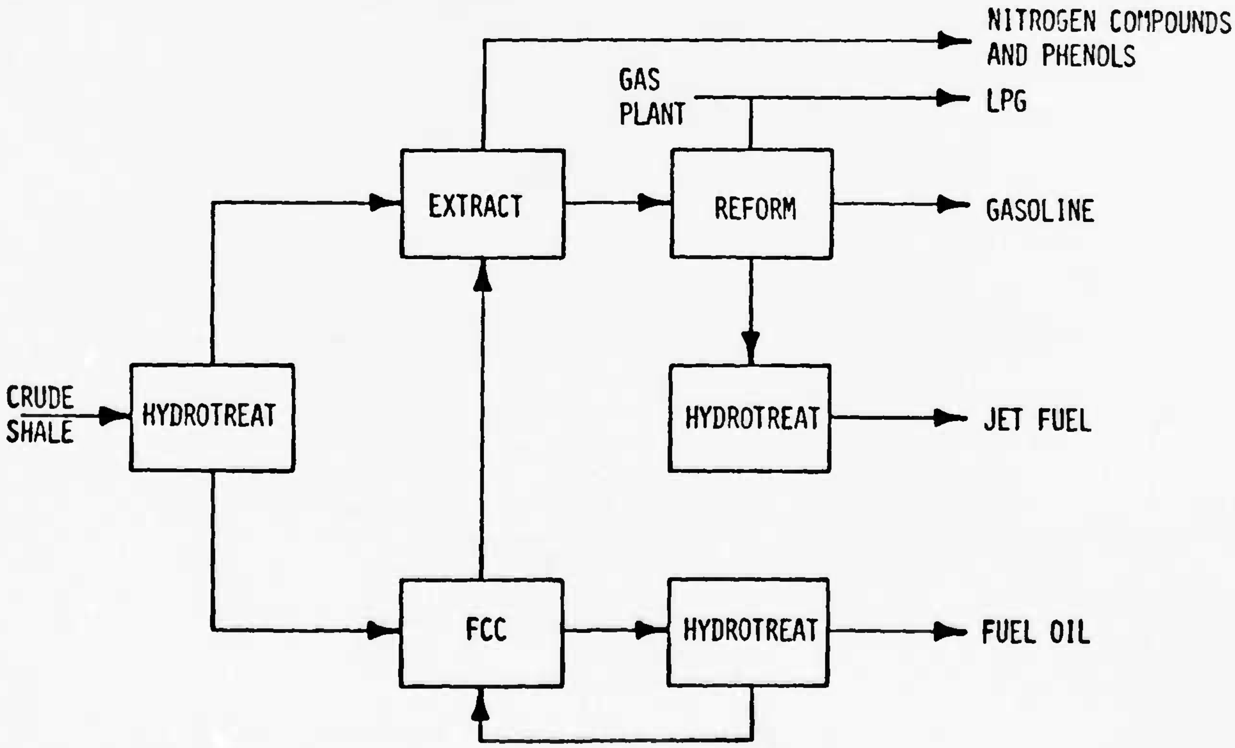
| | |
|---|---|
| PHASE 1. | PRELIMINARY PROCESS ANALYSIS |
| PHASE II. | LABORATORY SAMPLES |
| PHASE III. | COMPONENT TEST SAMPLES |
| PHASE IV. | OVERALL ECONOMIC OPTIMIZATION |

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


CRUDE SHALE
HYDROTREAT
EXTRACT
FCC
REFORM
GAS PLANT
HYDROTREAT
HYDROTREAT
NITROGEN COMPOUNDS AND PHENOLS
LPG
GASOLINE
JET FUEL
FUEL OIL

THE EXTRACTACRACKING 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

## PHASE III OBJECTIVES

- ■ PRODUCE DATA RELATING TO SCALE UP AND CATALYST LIFE FOR USE IN PHASE IV ANALYSIS.
- ■ PRODUCE FUEL SAMPLES FOR LARGER SCALE EVALUATION.

Slide 6

Crude Shale Hydrotreating

Modified Reduced Crude Conversion

(Recycle Oil Hydrotreating)

Acid Extraction

Guardcase Hydrotreating

Reforming

Aromatic Saturation

## PROCESSING SEQUENCE

Slide 7

### AVERAGE CONDITIONS

| | |
|---|---|
| TEMPERATURE, °F | 682 |
| PRESSURE, PSIG | 1240 |
| LHSV ($HR^{-1}$) | 1.47 |
| GAS CHARGE, SCFB | 3910 |
| % VOL $H_2$ | 72 |
| CATALYST | COMMERCIAL Co/Mo |

### YIELD STRUCTURE

(wt% Charge Normalized to 100%)

| | | | |
|---|---|---|---|
| $H_2O$ | 0.72 | $C_5$ | 0.12 |
| $H_2S$ | 0.59 | $>C_5$ | .75 |
| $NH_3$ | 0.35 | Stripper Overhead | 10.62 |
| $H_2$ | -1.08 | Fractionater Overhead | 21.10 |
| $C_1$ | 0 | Fractionater Bottoms | 63.89 |
| $C_2$ | 0.82 | Total Liquid | 95.61 |
| $C_3$ | 1.68 | Closure | 102.9 |
| $C_4$ | 0.45 | Hydrogen Consumption | 646 SCFB |

## CSHT

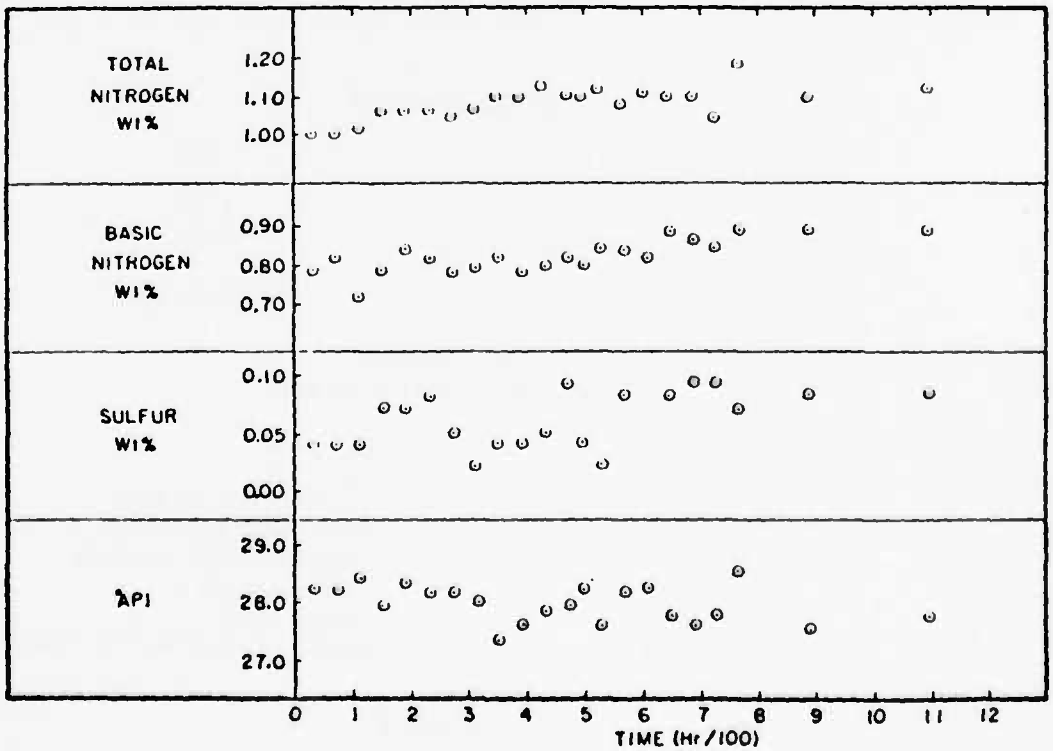
Slide 8

CSHT FEED AND PRODUCT PROPERTIES

| ITEM | FEED | STRIPPER OVERHEAD | FRACTIONATER OVHD | FRACTIONATER BTMS |
|---|---|---|---|---|
| API GRAVITY | 23.8 | 41.0 | 34.1 | 23.6 |
| NITROGEN, WT% | 1.4 | 1.04 | 1.31 | 1.42 |
| BASIC NITROGEN, WT% | 0.83 | 0.81 | 0.74 | 0.77 |
| SULFUR, WT% | 0.63 | 0.02 | 0.04 | 0.10 |
| ARSENIC, PPM | 24 | <1 | <1 | 1 |
| DISTILLATION, D2887. °F | | | | |
| IBP | 330 | 180 | 329 | 583 |
| 10 | 464 | 331 | 431 | 619 |
| 50 | 667 | 444 | 521 | 754 |
| 90 | 872 | 562 | 581 | 913 |
| EP | 952 | 871 | 620 | 976 |

CSHT

Slide 9



CSHT AGING TRENDS

Slide 10

## FEEDSTOCKS
## (ALL FEEDS>600°F)

A. 100% CSHT (BASE CASE)
B. 60% CSHT, 40% HYDROTREATED MRCC RECYCLE
C. 60% CSHT, 40% MRCC RECYCLE
D. 100% HYDROTREATED MRCC RECYCLE
E. 100% MRCC RECYCLE

**MRCC**

## BASE CASE YIELD STRUCTURE
## (WT% FEED NORMALIZED TO 100%)

| | |
|---|---|
| $H_2$ | 0.17 |
| $C_1$ | 0.71 |
| $C_2 + C_2 =$ | 1.40 |
| $C_3$ | 0.50 |
| $C_3 =$ | 1.66 |
| $iC_4$ | 0.27 |
| $nC_4$ | 0.21 |
| $C_4 =$ | 2.14 |
| $C_5$-600°F | 28.83 |
| $600°F^+$ | 56.08 |
| COKE | 8.02 |
| CONVERSION | 43.4 |

**MRCC**

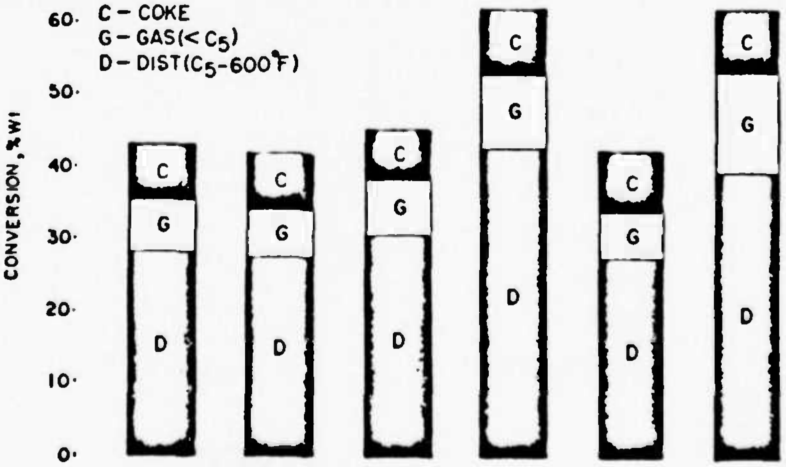
## BASE CASE FEED & PRODUCT PROPERTIES

| ITEM | FEED | <600°F | >600°F |
|---|---|---|---|
| API GRAVITY | 24.2 | 37.9 | 23.5 |
| NITROGEN, WT% | 1.28 | 1.00 | 1.02 |
| BASIC NITROGEN, WT% | 0.74 | 0.52 | 0.48 |
| SULFUR, WT% | 0.10 | 0.04 | 0.06 |
| ARSENIC, WT% | 1 | <1 | 1 |
| RAMSBOTTOM CARBON, % | 0.91 | 0.21 | 0.69 |
| DISTILLATION, D2887, °F | | | |
| IBP | 596 | 139 | 554 |
| 5 | 618 | 187 | 603 |
| 10 | 633 | 213 | 619 |
| 50 | 760 | 387 | 732 |
| 90 | 909 | 553 | 887 |
| 95 | 938 | 559 | 928 |
| EP | 959 | 627 | 979 |

**MRCC**

Slide 13

| | | | | | | |
|---|---|---|---|---|---|---|
| FEEDSTOCK | | | | | | |
| %CSHT | 100 | 60 | 60 | – | – | 100 |
| %RECYCLE | – | – | 40 | – | 100 | – |
| %RECYCLE(HDT) | – | 40 | – | 100 | – | – |
| TEMPERATURE, °F | 1020 | 1020 | 1025 | 1040 | 1035 | 1080 |
| CAT/OIL RATIO | 4 | 4 | 4 | 4 | 4 | 6 |
| BASIC NITROGEN, WT% | 0.74 | 0.56 | 0.58 | 0.32 | 0.36 | 0.84 |



MRCC PRODUCT DISTRIBUTION

Slide 14

## AVERAGE CONDITIONS

| | |
|---|---|
| TEMPERATURE, °F | 675 |
| PRESSURE, PSIG | 1430 |
| LHSV ($HR^{-1}$) | 0.99 |
| GAS CHARGE, SCFB | 5515 |
| HYDROGEN, VOL% | 81.2 |
| CATALYST | COMMERCIAL N./MO |

## YIELD STRUCTURE
(WT% FEED NORMALIZED TO 100%)

| | |
|---|---|
| $H_2O$ | 0.04 |
| $H_2S$ | 0.04 |
| $NH_3$ | 1.17 |
| $H_2$ | -1.10 |
| $C_1$ | 0.02 |
| $C_2$ | 1.08 |
| $C_3$ | 0.63 |
| $C_4$ | 0.96 |
| $C_5$ | 0.03 |
| $C_5$ | 0.80 |
| LIQUID | 96.33 |

HYDROGEN CONSUMPTION, SCFB 660

CLOSURE 100.2%

**COHT**

Slide 15

## AVERAGE FEED AND PRODUCT PROPERTIES

| ITEM | FEED | PRODUCT |
|---|---|---|
| API GRAVITY | 23.5 | 26.1 |
| NITROGEN, WT% | 1.02 | 0.61 |
| BASIC NITROGEN, WT% | 0.47 | 0.32 |
| SULFUR, WT% | 0.06 | 0.01 |
| RAMSBOTTOM CARBON, % | 0.69 | 0.64 |
| DISTILLATION, D2887, °F | | |
| IBP | 575 | 393 |
| 5 | 611 | 575 |
| 10 | 625 | 606 |
| 50 | 747 | 715 |
| 90 | 822 | 873 |
| 95 | 934 | 909 |
| EP | 963 | 947 |
| POLYAROMATICS | 28.3 | 19.7 |

**COHT**

Slide 16

FEEDSTOCKS FOR ACID EXTRACTION

1. 100% CSHT DISTILLATE
2. 68% CSHT, 32% MRCC DISTILLATES
3. 100% MRCC DISTILLATES

## ACID EXTRACTION

Slide 17

FEEDSTOCK: 100% CSHT DISTILLATE

AVERAGE EXTRACTION CONDITIONS

| | |
|---|---|
| OIL CHARGE RATE (LB/HR/FT$^2$) | 526.7 |
| ACID CHARGE RATE (LB/HR/FT$^2$) | 79.6 |
| TEMPERATURE NEAR INTERFACE, °F | 114 |
| ACID STRENGTH, WT% | 41 |

AVERAGE FEED AND PRODUCT PROPERTIES

| ITEM | FEED | EXTRACTOR PRODUCT | WASHER PRODUCT |
|---|---|---|---|
| API GRAVITY | 35.8 | 37.5 | 37.5 |
| NITROGEN, WT% | 0.92 | 0.33 | 0.32 |
| BASIC NITROGEN, WT% | 0.81 | 0.19 | 0.15 |
| BASIC NITROGEN REMOVAL, % FEED | - | 76.5 | 81.5 |
| % HYDROCARBON RECOVERED, % FEED | - | 90.3 | 89.5 |
| BROMINE NUMBER | 13.9 | 12.2 | 13.4 |

## ACID EXTRACTION

Slide 18

## FEEDSTOCK: 68% CSHT, 32% MRCC Distillates
## AVERAGE EXTRACTION CONDITIONS

| | |
|---|---|
| Oil Charge Rate, lb/hr/ft$^2$ | 403.6 |
| Acid Charge Rate, lb/hr/ft$^2$ | 63.8 |
| Temperature Near Interface, °F | 117 |
| Acid Strength, Wt% | 43.0 |

## AVERAGE FEED AND PRODUCT PROPERTIES

| Item | Feed | Extractor Product | Final Washed Product |
|---|---|---|---|
| API Gravity | 36.2 | 38.1 | 37.5 |
| Nitrogen, Wt% | 0.92 | 0.35 | 0.34 |
| Basic Nitrogen, Wt% | 0.70 | 0.14 | 0.11 |
| Basic Nitrogen Removal % Feed | - | 80.0 | 84.3 |
| Hydrocarbon Recovered, % Feed | - | 90.2 | 88.5 |
| Bromine Number | 34.3 | 33.3 | 36.4 |

## ACID EXTRACTION

Slide 19

## FEEDSTOCK: 100% MRCC Distillates
## AVERAGE EXTRACTION CONDITIONS

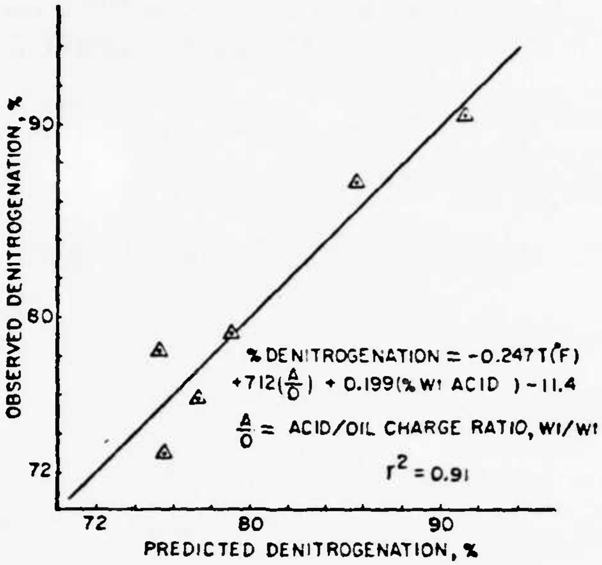
| | |
|---|---|
| Oil Charge Rate, lb/hr/ft$^2$ | 433.6 |
| Acid Charge Rate, lb/hr/ft$^2$ | 76.1 |
| Temperature Near Interface, °F | 120 |
| Acid Strength, Wt% | 37.0 |

## AVERAGE FEED AND PRODUCT PROPERTIES

| Item | Feed | Final Washed Product |
|---|---|---|
| API Gravity | 37.6 | 38.4 |
| Nitrogen, Wt% | 0.79 | 0.34 |
| Basic Nitrogen, Wt% | 0.38 | 0.02 |
| Basic Nitrogen Removed, % Feed | - | 94.7 |
| Hydrocarbon Recovered, % Feed | - | 90.1 |
| Bromine Number | 71.5 | 80.4 |

## ACID EXTRACTION

Slide 20



CORRELATION OF VARIABLES IN ACID EXTRACTION

Slide 21

AVERAGE CONDITIONS

| | |
|---|---|
| TEMPERATURE, °F | 699 |
| PRESSURE, PSIG | 1400 |
| LHSV, $HR^{-1}$ | 0.69 |
| GAS CHARGE, SCFB | 5650 |
| HYDROGEN CONTENT, VOL% | 77.8 |
| CATALYST: COMMERCIAL Ni/Mo | |

YIELD STRUCTURE

(WT% FEED NORMALIZED TO 100%)

| | | | |
|---|---|---|---|
| $H_2O$ | 0.21 | $C_5$ | 0.02 |
| $H_2S$ | 0.04 | | |
| $NH_3$ | 0.41 | $>C_5$ | 3.49 |
| $H_2$ | -1.02 | LIQUID | 94.31 |
| $C_1$ | 0.27 | CLOSURE | 99.2 |
| $C_2$ | 0.95 | HYDROGEN CONSUMPTION, SCFB | 560 |
| $C_3$ | 0.95 | | |
| $C_4$ | 0.36 | | |

GCHT
JP8 POOL

Slide 22

## FEED AND PRODUCT PROPERTIES

| | FEED | PRODUCT |
|---|---|---|
| API GRAVITY | 37.5 | 41.4 |
| NITROGEN, PPM | 3400 | 3 |
| SULFUR, PPM | 340 | 1 |
| BROMINE NO | 36.4 | 0.4 |
| DISTILLATION (D 2887) °F | | |
| IBP | 182 | 194 |
| 5 | 269 | 279 |
| 10 | 316 | 320 |
| 50 | 486 | 464 |
| 90 | 581 | 572 |
| 95 | 593 | 580 |
| EP | 658 | 659 |

## GCHT
## JP8 POOL

Slide 23

## AVERAGE CONDITIONS

| | |
|---|---|
| TEMPERATURE, °F | 729 |
| PRESSURE, PSIG | 1400 |
| LHSV, $HR^{-1}$ | 0.75 |
| GAS CHARGE, SCFB | 6920 |
| HYDROGEN CONTENT, VOL% | 76.4 |

## YIELD STRUCTURE
(WT% CHARGE, NORMALIZED TO 100%)

| | | | |
|---|---|---|---|
| $H_2S$ | 0.04 | $C_5$ | 0.21 |
| $NH_3$ | .41 | $>C_5$ | 6.21 |
| $H_2$ | -2.84 | LIQUID | 90.73 |
| $C_1$ | 0 | CLOSURE | 101.0 |
| $C_2$ | 0.07 | HYDROGEN CONSUMPTION, SCFB | 1553 |
| $C_3$ | 4.21 | | |
| $C_4$ | 0.95 | | |

## GCHT
## JP4 POOL

Slide 24

FEED AND PRODUCT PROPERTIES

| | FEED | PRODUCT | PRODUCT AFTER FRACTIONATION |
|---|---|---|---|
| API GRAVITY | 38.4 | 42.5 | 44.8 |
| NITROGEN, PPM | 3400 | 2 | 1 |
| SULFUR PPM | 400 | 3 | <1 |
| BROMINE NO | 80.4 | 0.5 | 0.4 |
| DISTILLATION (D2887), °F | | | |
| IBP | 132 | 165 | 156 |
| 5 | 167 | 235 | 227 |
| 10 | 229 | 256 | 243 |
| 50 | 380 | 390 | 344 |
| 90 | 356 | 532 | 467 |
| 95 | 589 | 571 | 499 |
| EP | 602 | 637 | 547 |

## GCHT
## JP4 POOL

AVERAGE CONDITIONS

CATALYST: COMMERCIAL REFORMING CAT.

| | |
|---|---|
| TEMPERATURE, °F | 900 |
| PRESSURE, PSIG | 600 |
| LHSV, ($HR^{-1}$) | 4.5 |
| GAS CHARGE, SCFB | 4119 |
| HYDROGEN CONTENT, VOL% | 77.4 |

YIELD STRUCTURE
(WT% FEED NORMALIZED TO 100%)

| | |
|---|---|
| $H_2$ | 1.13 |
| $C_1$ | 2.00 |
| $C_2$ | 0.81 |
| $C_3$ | 1.83 |
| $C_4$ | 0.05 |
| $C_5$ | 0.14 |
| $>C_5$ | 5.24 |

LIQUID 88.81

HYDROGEN PRODUCTION (SCFB) 608

CLOSURE 99.6%

PROPERTIES

| ITEM | FEED | PRODUCT |
|---|---|---|
| F.P. °F | -18.4 | -63.1 |
| FIA | | |
| S | 76.5 | 48.0 |
| O | 1.1 | 1.3 |
| A | 22.4 | 50.7 |

## REFORMING
## JP8 POOL

JP-8 POOL FEEDS & PRODUCTS

| | FEEDS | | PRODUCTS | |
|---|---|---|---|---|
| | GCHT PRODUCT | GCHT OHD REC | REFORMATE | CONDENSATE |
| API Gravity | 41.4 | 47.8 | 39.6 | - |
| Freezing Point °F | -18.4 | -68.8 | -63.4 | -90- |
| FIA Analysis | | | | |
| S | 76.5 | 82.6 | 55.6 | 87.9 |
| O | 1.1 | 2.3 | 1.0 | 2.2 |
| A | 22.4 | 15.1 | 43.4 | 9.9 |
| Distillation °F | D2887 | D2887 | D86 | D2887 |
| IBP | 194 | 185 | 204 | -74 |
| 5 | 279 | 240 | 266 | -6 |
| 10 | 320 | 259 | 302 | 22 |
| 50 | 464 | 337 | 382 | 191 |
| 90 | 572 | 399 | 524 | 290 |
| 95 | 580 | 442 | 558 | 323 |
| EP | 659 | 576 | 582 | 402 |

## REFORMING
## JP8 POOL

Slide 27

AVERAGE CONDITIONS

| | |
|---|---|
| Temperature, °F | 880°F |
| Pressure, PSIG | 495 |
| LHSV, $Hr^{-1}$ | 5.0 |
| Gas Charge, SCFB | 3750 |
| Hydrogen Content, Vol% | 75.9 |

Catalyst: Commercial Reforming Cat

YIELD STRUCTURE
(WT% FEED NORMALIZED TO 100%)

| | |
|---|---|
| $H_2$ | 2.29 |
| $C_1$ | 1.13 |
| $C_2$ | 4.54 |
| $C_3$ | 2.95 |
| $C_4$ | 0.39 |
| $C_5$ | 3.32 |
| $>C_5$ | 0.32 |
| Liquid | 84.55 |
| Hydrogen Production (SCFB) | 1230 |
| Closure | 99.2 |

PROPERTIES

| ITEM | FEED | PRODUCT |
|---|---|---|
| F.P. °F | -73.3 | -90- |
| APIGR | 44.8 | 35.7 |
| FIA Analysis | | |
| S | 73.7 | 35.4 |
| O | 0.9 | 0.3 |
| A | 25.4 | 64.3 |

## REFORMING
## JP4 POOL

Slide 28

JP-4 POOL FEED & PRODUCTS

| | FEED | REFORMATE | CONDENSATE |
|---|---|---|---|
| API GRAVITY | 44.8 | 37.8 | - |
| FREEZING POINT | -73.3 | -90- | -90- |
| FIA ANALYSIS | | | |
| S | 73.7 | 47.0 | 87.9 |
| O | 0.9 | 0.8 | 2.2 |
| A | 25.4 | 52.2 | 9.9 |
| DISTILLATION (D2887), °F | | | |
| IBP | 156 | 113 | -74 |
| 5 | 227 | 223 | -6 |
| 10 | 243 | 244 | 22 |
| 50 | 344 | 362 | 191 |
| 90 | 467 | 493 | 290 |
| 95 | 499 | 524 | 323 |
| EP | 547 | 665 | 402 |

## REFORMING
## JP4 POOL

AVERAGE CONDITIONS

| | JP-8 | BROAD RANGE JP-8 |
|---|---|---|
| TEMPERATURE, °F | 553 | 550 |
| PRESSURE, PSIG | 550 | 500 |
| LHSV, $HR^{-1}$ | 1.93 | 1.92 |
| GAS CHARGE, SCFB | 10,667 | 9,626 |
| HYDROGEN CONTENT, VOL% | 80.2 | 77.5 |
| YIELD STRUCTURE (WT% CG NORMALIZED TO 100%) | | |
| $H_2$ | -1.67 | -1.05 |
| $C_1$ | 0 | 0 |
| $C_2$ | 0 | 0.06 |
| $C_3$ | 0.33 | 0.89 |
| $C_4$ | 1.22 | 0.17 |
| $C_5$ | 0.62 | 0.51 |
| LIQUID | 99.49 | 99.42 |
| HYDROGEN CONSUMPTION, SCFB | 907 | 570 |
| CLOSURE, % | 99.0 | 101.9 |

## AROMATIC SATURATION
## JP8 Pool

FEED AND PRODUCT PROPERTIES

| | FEED | STABILIZED BOTTOMS | | STABILIZATION OVERHEAD |
|---|---|---|---|---|
| | | JP-8 | JP-8(BR) | |
| API Gravity | 39.6 | 41.3 | 39.7 | 61.9 |
| FIA Analysis | | | | |
| S | 55.6 | 79.8 | 65.7 | 87.5 |
| O | 1.0 | 0.9 | 0.5 | 0.5 |
| A | 43.4 | 19.3 | 33.8 | 12.0 |
| Flash Point, TAG, °F | | 114 | 116 | -RT- |
| Distillation, °F | D 86 | D 86 | D 86 | D 2887 |
| IBP | 204 | 319 | 312 | 2 |
| 10 | 302 | 348 | 344 | 134 |
| 20 | 333 | 360 | 362 | 166 |
| 50 | 412 | 409 | 410 | 226 |
| 90 | 524 | 507 | 510 | 262 |
| EP | 582 | 547 | 562 | 294 |

## AROMATIC SATURATION
## JP8 Pool

Slide 31

AVERAGE CONDITIONS

| | |
|---|---|
| Temperature, °F | 556 |
| Pressure, PSIG | 550 |
| LHSV, $HR^{-1}$ | 1.93 |
| Gas Charge, SCFB | 10,912 |
| Hydrogen Content, Vol% | 77.9 |

YIELD STRUCTURE
(WT% FEED NORMALIZED TO 100%)

| | |
|---|---|
| $H_2$ | - 2.35 |
| $C_1$ | 0 |
| $C_2$ | 0 |
| $C_3$ | 0.04 |
| $C_4$ | 0.45 |
| $C_5$ | 0.66 |
| Liquid | 101.2 |
| Hydrogen Consumption, SCFB | 1290 |
| Closure | 99.4 |

## AROMATIC SATURATION
## JP4 Pool

Slide 32

FEED AND PRODUCT PROPERTIES

| | FEED | PRODUCT |
|---|---|---|
| API Gravity | 37.8 | 44.7 |
| FIA Analysis | | |
| S | 47.0 | 88.1 |
| O | 0.8 | 0.7 |
| A | 52.2 | 11.2 |
| Distillation (D2887), °F | | |
| IBP | 113 | 119 |
| 5 | 223 | 217 |
| 10 | 244 | 246 |
| 50 | 362 | 365 |
| 90 | 493 | 473 |
| 95 | 524 | 498 |
| EP | 665 | 548 |

## AROMATIC SATURATION
## JP4 Pool

Slide 33

FINAL TURBINE FUELS

| | JP-4 | JP-8 | BROAD RANGE JP-8 |
|---|---|---|---|
| Mercaptan Sulfur | Neg | 0.0005 | 0.0005 |
| Aromatics, Vol % | 11.0 | 19.3 | 33.8 |
| Distillation, D-86, °F | | | |
| 10 | - | 348 | 344 |
| 20 | 241 | - | - |
| 50 | 304 | - | - |
| 90 | 438 | - | - |
| EP | 496 | 547 | 562 |
| Flash Point, °F | - | 114 | 116 |
| API Gravity | 49.5 | 41.3 | 39.7 |
| Reid Vapor Press. PSI | 2.9 | - | - |
| Freezing Point, °F | -90- | -60.7 | -61.6 |
| Net Heat of Combustion Btu/lb | 18,647 | 18,536 | 18,414 |
| Corrosion, Copper Strip | 1B | 1B | 1B |
| Water Reaction Rating | 1A | 1A | 1A |
| Water Separation Index | - | 92 | 88 |
| Nitrogen | <1 ppm | <1 ppm | <1 ppm |
| Hydrogen, Wt % | 14.14 | 13.83 | 13.27 |

## FINAL PRODUCTS

Slide 34

DIESEL FUELS

| SOURCE | JP-8 GCHT | JP-4 GCHT |
|---|---|---|
| Flash Point °F, PM | 312 | 210 |
| Viscosity @100°F cSt | 2.92 | 3.12 |
| Carbon Residue on 10% Btm | 0.14 | 0.42* |
| Corrosion, Copper Strip | 1b | - |
| Ash, Wt% | 0.01 | - |
| Water & Sediment, Wt% | 0 | - |
| Cetane No | 45 | 57.5 |
| Distillation, D86, °F | | |
| 90 | 557 | 570 |
| EP | 579 | 603 |
| Sulfur, Wt% | 0.005 | 7 ppm |
| Nitrogen, Wt% | 0.036 | 0.002 |
| API Gravity | 37.6 | 38.2 |
| Cloud Point, °F | -6 | +14 |
| Pour Point, °F | -10 | +5 |

## FINAL PRODUCTS

Slide 35

GASOLINE BLENDING COMPONENT

SOURCE: JP-4 REFORMING

| | |
|---|---|
| API Gravity | 44.4 |
| FIA Analysis, LV% | |
| S | 47.7 |
| O | 1.1 |
| A | 51.1 |
| RVP, PSI | 3.9 |
| Existent Gum (mg/100ml) | 39.2 |
| RON, Clear | 84.4 |
| RON, +1cc TEL/gal | 90.0 |
| PON, +4cc TEL/gal | 96.2 |
| MON, Clear | 76.9 |
| MON, +4cc TEL/gal | 86.9 |
| Nitrogen | <1ppm |

| Distillation, D86 | |
|---|---|
| IBP | 128 |
| 10 | 250 |
| 50 | 324 |
| 90 | 380 |
| EP | 431 |

## FINAL PRODUCTS

Slide 36

## RESIDUAL FUEL

SOURCE: MRCC BTMS

| | |
|---|---|
| °API | 12.3 |
| FLASH POINT, °F | 230+ |
| VISCOSITY, 122°F, SUS | 110.8 |
| POUR POINT | +45* |
| CARBON RESIDUE | 3.1 |
| SULFUR, WT% | 0.07 |
| NITROGEN, WT% | 0.64 |

**FINAL PRODUCTS**

Slide 37

# PHASE IV ANALYSIS

## CONTRACT F33615-78-C-2080

1. Assumptions and Bases
2. Occidental Shale Oil
3. Paraho Shale Oil
4. Conclusions

Slide 38

## PHASE IV ANALYSIS BASES

- CAPITAL COSTS:
  - UPDATED, SCALED FROM PHASE I EFFORT. MINOR MODIFICATIONS MADE.
- PROCESS RESPONSE:
  - VARIABLE RESPONSE BASED ON PHASE II DATA.
  - EACH MODULE EVALUATED FOR SCALEUP FROM PHASE III RESPONSE
  - AGING DATA USED FROM PHASE III.
- PROCESS FLOW:
  - AS DEFINED PREVIOUSLY EXCEPT -
  - NO COHT
  - EXTRACT USED FOR HYDROGEN PRODUCTION

## INVESTMENT & RETURN BASES
## PHASE IV

- FIRST QUARTER 1981
- 100% EQUITY FINANCING
- 3-YEAR CONSTRUCTION - INVESTMENT

  25% 1ST YEAR
  50% 2ND YEAR
  25% 3RD YEAR
- OFFSITES AT 45% OF BATTERY LIMITS COSTS

## INVESTMENT & RETURN BASES
## PHASE IV
## CONTINUED

- 10% INVESTMENT TAX CREDIT
- 50% TOTAL INCOME TAX RATE
- 15% DCF RATE
- MID YEAR DISCOUNTING
- 16 YEAR USEABLE LIFE (TOTAL PROJECT 19 YEARS)
- ZERO SALVAGE VALUE
- 13 YEARS SUM OF YEARS DIGITS DEPRECIATION

Slide 41

## PLANT OPERATING BASES
## PHASE IV

---

- 100,000 BPCD RAW SHALE OIL
- 90% ON STREAM FACTOR
- OPERATION @ 50% OF DESIGN - FIRST YEAR
- OPERATION @ 100% OF DESIGN - SECOND THROUGH 16TH YEARS
- WORKING CAPITAL CALCULATED FROM:

  14 DAYS CRUDE SHALE OIL INVENTORY @ $40/BBL
  7 DAYS PRODUCT INVENTORY @ COST

- WORKING CAPITAL FINANCED AT 15% SIMPLE INTEREST

Slide 42

## OPERATING COST BASES
## PHASE IV

| | |
|---|---|
| PROCESS HEAT | INTERNALLY GENERATED |
| COOLING WATER | 3¢/1000 GALLONS |
| POWER | 4.5¢/KWHR |
| BOILER FEED WATER | 5¢/1000 # |
| OPERATOR | $12.00/MAN HOUR |
| HELPER | $10.50/MAN HOUR |
| SUPERVISION | 25% OF DIRECT LABOR |
| OVERHEAD | 100% OF DIRECT LABOR |
| MAINTENANCE, TAXES, AND INSURANCE | 4.5% OF FIXED INVESTMENT |
| SHALE OIL FEEDSTOCK | $40.00/BBL |

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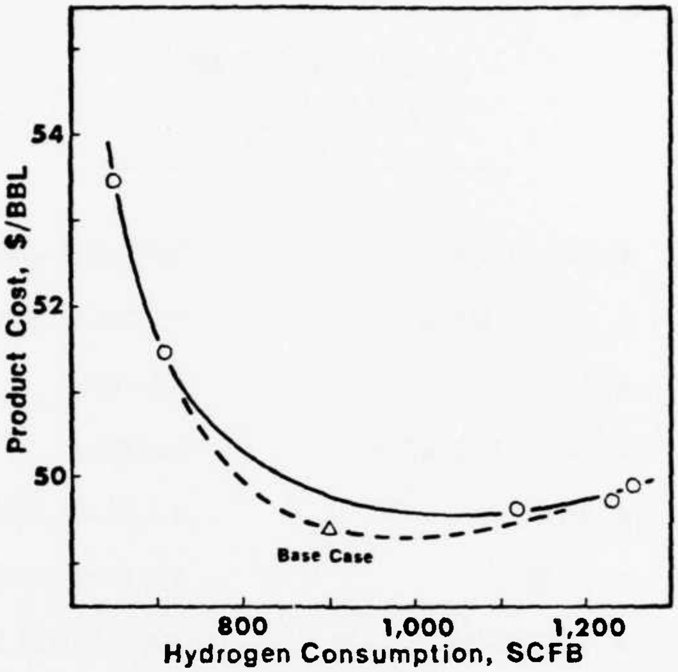
## PRODUCT VALUE BASES
## PHASE IV

| | |
|---|---|
| AMMONIA | $155/SHORT TON |
| SULFUR | $105/LONG TON |
| FUEL GAS | $16.28/BBL |
| LPG | $19.74/BBL |
| PROPYLENE | $23.80/BBL |
| ISOBUTANE | $25.52/BBL |
| N-BUTANE | $26.56/BBL |
| GASOLINE, TURBINE FUELS DIESEL FUEL, AND RESID | AS NECESSARY FOR 15% DCF |

Slide 44



# FINAL
# OPTIMIZATION TRACE
# BASED ON HYDROGEN CONSUMPTION

Slide 45

## BASE PRODUCT SLATE

| PRODUCT | OXY | PARAHO |
|---|---|---|
| LPG | 1,794 | ------ |
| PROPYLENE | 3,844 | ------ |
| N-BUTANE | 1,656 | ------ |
| I-BUTANE | 2,548 | ------ |
| REGULAR GASOLINE | 41,285 | 49,254 |
| JP-4 TURBINE FUEL | 3,594 | 3,409 |
| JP-8 TURBINE FUEL | 18,897 | 28,552 |
| DIESEL FUEL | 19,321 | 2,839 |
| RESIDUAL FUEL | 9,224 | 9,330 |
|  | 102,163 | 93,384 |

Slide 46

## OVERALL MILITARY FUEL YIELDS

| | OXY | PARAHO |
|---|---|---|
| GASOLINE | 41,285 | 49,245 |
| JP-4 | 3,594 | 3,409 |
| JP-8/JP-5 | 18,897 | 28,552 |
| DIESEL FUEL | 19,321 | 2,839 |
| BURNER FUEL | 9,224 | 9,330 |
| TOTAL | 92,321 | 93,384 |

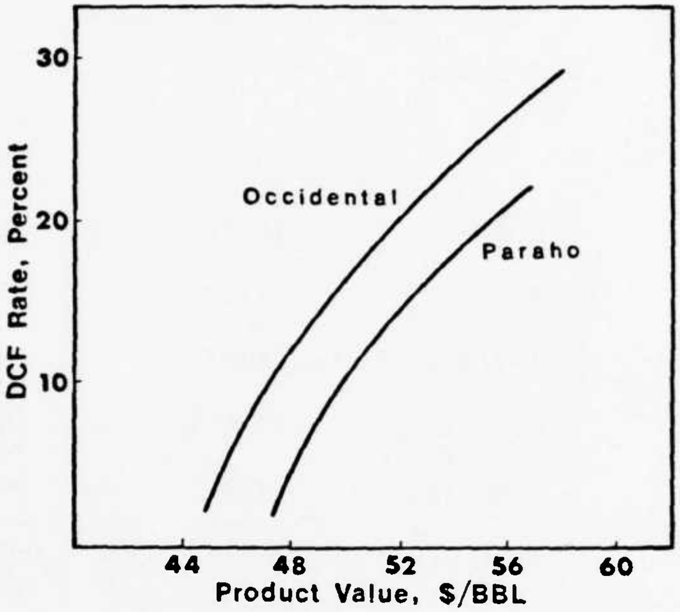
BASIS: 100,000 BPD CRUDE SHALE OIL CHARGE

Slide 47

## BASE CASE PLANT RESULTS COMPARISON

| | OCCIDENTAL | PARAHO |
|---|---|---|
| CAPITAL INVESTMENT, MM $ | 696 | 834 |
| INVESTMENT DISTRIBUTION, % OF TOTAL | | |
| CRUDE SHALE HYDROTREATER | 25 | 21 |
| FLUID CATALYTIC CRACKING | 13 | 16 |
| EXTRACTION | 3 | 3 |
| UPGRADING | 14 | 13 |
| HYDROGEN PLANT | 11 | 14 |
| OFFSITES & OTHER | 34 | 33 |

Slide 48



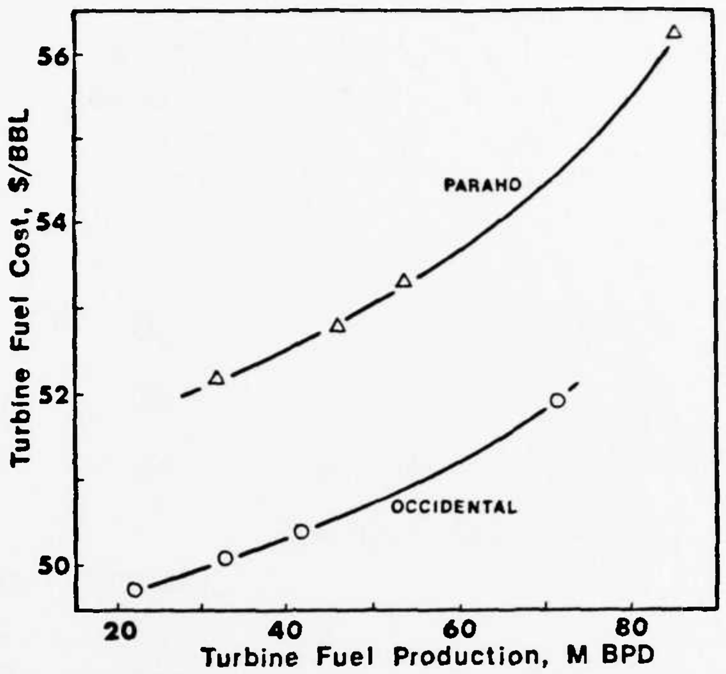
# PRODUCT VALUES
# AS A FUNCTION OF DCF RATE

Slide 49

## OVERALL PRODUCT COST SHEET

| ITEM | COST CONTRIBUTION $/BBL OXY | COST CONTRIBUTION $/BBL PARAHO |
|---|---|---|
| OPERATING COSTS | $ 2.23 | 2.81 |
| BYPRODUCTS | (2.66) | (0.11) |
| WORKING CAPITAL | 0.44 | 0.42 |
| FEEDSTOCK | 43.33 | 42.83 |
| CAPITAL | 6.06 | 6.25 |
| PRIME PRODUCT VALUE | 49.40 | 52.20 |

Slide 50



# INCREMENTAL TURBINE FUEL COST

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### OCCIDENTAL SHALE OIL
### OVERALL PRODUCT COST SHEET
### BASE CASE -- FUEL GAS SALES ALLOWED

| ITEM | WITH GAS SALES | BASE CASE |
|---|---|---|
| CAPITAL INVESTMENT, MM$ | 558 | 595 |
| PRODUCT COST CONTRIBUTIONS, $/BBL: | | |
| OPERATING COST | 2.07 | 2.23 |
| BYPRODUCT | (5.36) | (2.66) |
| WORKING CAPITAL | 0.43 | 0.44 |
| FEEDSTOCK | 45.36 | 43.33 |
| CAPITAL | 5.50 | 6.06 |
| | 48.00 | 49.40 |

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## IMPACT OF TURBINE FUEL AROMATIC SPECIFICATION ON PLANT OPTIMUM

| | | | |
|---|---|---|---|
| SPECIFICATION, VOL % | 15 | 25 | 35 |
| INVESTMENT, MM $ | 670 | 696 | 689 |
| HYDROGEN CONSUMPTION, SCFB | 930 | 910 | 860 |
| DISTILLATE PRODUCT SLATE, BPD: | | | |
| GASOLINE | 41,601 | 41,285 | 41,384 |
| JP-4 | ------ | 3,594 | 3,516 |
| JP-5/8 | ------ | 18,897 | 18,394 |
| DIESEL FUEL | 40,332 | 19,321 | 19,475 |
| PRODUCT COST, $/BBL | 49.40 | 49.40 | 49.30 |

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## OCCIDENTAL SHALE OIL PRODUCT COST COMPONENTS ADDITION OF ALKYLATION/POLYMERIZATION CAPACITY

| | COST CONTRIBUTION, $/BBL | |
|---|---|---|
| ITEM | WITH ADDED CAPACITY | BASE CASE |
| OPERATING COSTS | 2.42 | 2.23 |
| BYPRODUCTS | (0.11) | (2.66) |
| WORKING CAPITAL | 0.40 | 0.44 |
| FEEDSTOCK | 40.33 | 43.33 |
| CAPITAL | 5.86 | 6.06 |
| PRIME PRODUCT VALUE | 48.90 | 49.40 |
| CAPITAL INVESTMENTS, MM $ | 712 | 696 |

Slide 54

AD-A111 217 AIR FORCE WRIGHT AERONAUTICAL LABS WRIGHT-PATTERSON AFB OH F/G 21/4
JET FUEL FROM SHALE OIL - 1981 TECHNOLOGY REVIEW,(U)
DEC 81 H R LANDER
UNCLASSIFIED AFWAL-TR-81-2135 NL

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## OCCIDENTAL SHALE OIL
## PRODUCT SLATE
## ADDITION OF ALKYLATION/POLYMERIZATION CAPACITY

| ITEM | WITH ADDED CAPACITY, BPD | BASE CASE BPD |
|---|---|---|
| GASOLINE | 43,871 | 41,285 |
| JP-4 | 6,705 | 3,594 |
| JP-8/5 | 16,433 | 18,897 |
| DIESEL FUEL | 22,271 | 19,321 |
| RESIDUAL FUEL | 9,910 | 9,224 |
| TOTAL PRIME PRODUCTS | 99,190 | 92,321 |

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## OCCIDENTAL SHALE OIL
## REFINERY VALUES AND PRODUCT SLATE
## FEEDSTOCK VALUE CALCULATION

| ITEM | VALUE, $/BBL | VOLUME, BPD |
|---|---|---|
| LPG | 14.19 | 4,512 |
| PROPYLENE | 17.11 | 3,757 |
| N-BUTANE | 19.09 | 1,075 |
| I-BUTANE | 18.34 | 3,773 |
| BYPRODUCTS | ----- | 13,117 |
| GASOLINE | 40.95 | 49,910 |
| JP-4 | 40.32 | 3,569 |
| JP-5 | 40.32 | 18,636 |
| DIESEL FUEL | 39.80 | 18,650 |
| RESIDUAL FUEL | 28.75 | -0- |
| PRIME PRODUCTS | ----- | 90,675 |

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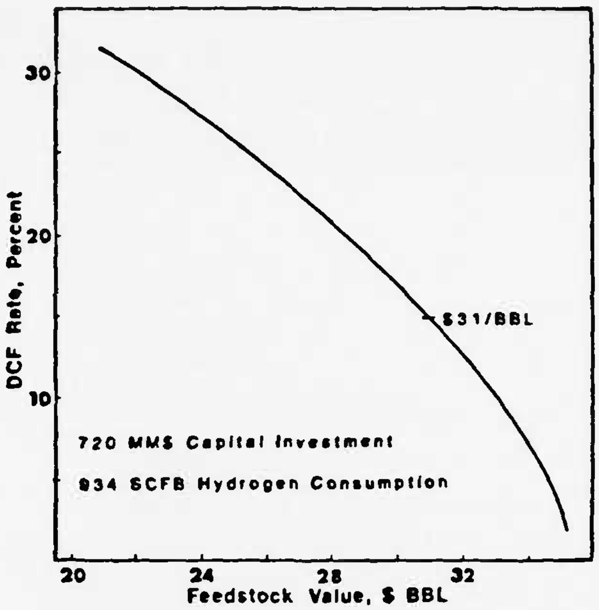

VALUE OF OCCIDENTAL OIL
AT PRESENT MARKET PRICES

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CONCLUSIONS

- REDUCTIONS IN HYDROGEN CONSUMPTION AND CAPITAL COSTS WERE ATTAINED AS PREDICTED.
- MINIMUM HYDROGEN CONSUMPTION AND/OR CAPITAL COST IS NOT OF NECESSITY OPTIMUM.
- OPTIMUM OPERATION FOR OCCIDENTAL OIL IS AT RELATIVELY LOW HYDROGEN CONSUMPTION (ABOUT 900 SCFB).
- OPTIMUM OPERATION FOR THE OCCIDENTAL OIL IS RELATIVELY FLAT IN THE REGION OF 900-1200 SCFB.
- OPTIMUM CONDITIONS FOR THE PARAHO OIL ARE AT HIGHER HYDROGEN CONSUMPTION THAN FOR THE OCCIDENTAL MATERIAL, AND MAY ALSO BE HIGHER THAN PROVIDED IN THIS ANALYSIS.

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## CONCLUSIONS II

- TOTAL VOLUMES OF PRIME MILITARY FUELS PRODUCED EXCEED 90 VOLUME PERCENT OF CRUDE SHALE OIL.
- ON A COMPARABLE BASIS, PRODUCTS FROM THE OCCIDENTAL OIL ARE 2-3 $/BARREL LESS EXPENSIVE THAN THE PARAHO OIL.
- ALLOWING SALES OF FUEL GAS CAN REDUCE PRODUCT COSTS BY $1/BARREL OR MORE.
- TURBINE FUEL YIELDS OF 85 VOLUME PERCENT OR MORE RESULT IN INCREMENTAL COSTS OF UP TO 10¢/GALLON.

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## CONCLUSIONS III

- MODIFICATION OF TURBINE FUEL AROMATIC SPECIFICATION TO 15 VOLUME PERCENT REDUCES PLANT PRODUCTION OF TURBINE FUEL TO ZERO, WHILE EXTENSION TO 35 PERCENT REDUCES TURBINE FUEL COST BY ONLY 10¢/BARREL.
- ADDITION OF ALKYLATION AND POLYMERIZATION CAPACITY REDUCES COSTS ABOUT 50¢/BARREL WHILE INCREASING TOTAL PRIME PRODUCT PRODUCTION BY ABOUT 10%.
- EVALUATION OF THE PROCESS AT TODAY'S MARKET VALUES RESULTS IN A CALCULATED VALUE OF $31/BBL FOR OCCIDENTAL OIL.
- NEITHER ADDITION OF ALKY/POLY CAPACITY NOR USE OF PRESENT MARKET VALUE FOR PRODUCTS SIGNIFICANTLY IMPACTS LOCATION OF THE DEFINED OPTIMUM.

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# MAJOR QUESTIONS REMAINING

1. CSHT Performance With Improved Guard Beds
2. Emissions From The FCC Unit
3. Actual FCC Coke Yields
4. Evaluation Of COHT Addition
5. Response Of Extract To Partial Oxidation
6. Guardcase, Reformer Long Term Aging

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## IV

# PRODUCTION OF SAMPLES OF MILITARY FUELS FROM SHALE OILS

By

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

and A. Schneider

Suntech, Inc.

# PRODUCTION OF SAMPLES OF MILITARY FUELS FROM SHALE OILS

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

SUNTECH, INC.

## Summary

This report covers work performed by Suntech, Inc. in Phase III of our contract with the United States Air Force. The Phase III objectives were to confirm Suntech's process designs and to produce component test samples of military fuels from raw shale oils in existing pilot plant equipment.

Suntech's processing concept for refining raw Occidental shale oil consists of six distinct steps: (1) hydrotreating the whole shale oil to partially reduce the high total nitrogen content (and convert some neutral nitrogen to basic nitrogen), while minimizing hydrogen consumption; (2) distilling the hydrotreated product into appropriate fractions for additional processing; (3) rehydrotreating the light distillate fraction to meet product specifications; (4) treating the wide boiling distillate fraction with anhydrous hydrogen chloride which yields a raffinate and extract phase--the nitrogen content in the HCl raffinate is lowered and concentrated in the extract phase; (5) thermally decomposing the HCl extract to recover anhydrous hydrogen chloride and the recovered HCl-free nitrogen-rich extract fraction is used for generating hydrogen by partial oxidation (this step was not required in Phase III); and (6) hydrocracking the raffinate fraction to maximize the yield of aviation turbine fuels. A total of 475 gallons of specification aviation turbine fuels were prepared--170 gallons of JP-4, 150 gallons of JP-5, and 155 gallons of JP-8.

A modification of Suntech's processing scheme was employed in processing Paraho shale oil. The modified processing route involves severely hydrotreating the raw shale oil followed by hydrocracking the gas oil fraction. Five 5-gallon samples of specification military fuels were produced from Paraho shale oil--JP-4, JP-5, and JP-8 jet fuels, along with Diesel Fuel No. 2 and Marine Diesel Fuel.

A set of tables and figures summarizing the results of the individual processing steps, inspections and analyses of the products are briefly discussed along with the process uncertainties and conclusions.

| | |
|---|---|
| Table 1 | The Phase III objectives are outlined. They are: (1) to confirm Suntech's process designs; and (2) to produce component test samples from both Paraho and Occidental shale oils, utilizing non-proprietary catalysts. Processing problems encountered during the pilot plant operations were to be identified and solved. |
| Figure 1 | Suntech's processing concept for preparing military turbine fuels from raw Occidental shale oil is shown. The first processing step is a relatively mild hydrotreat to partially reduce the high non-hydrocarbon content of the raw shale oil (and convert some neutral nitrogen to basic nitrogen), while minimizing hydrogen consumption. The hydrotreated product is distilled into appropriate fractions for additional processing. The naphtha fraction is rehydrotreated to meet product specifications. The wide boiling gas oil fraction is treated with anhydrous hydrogen chloride which yields a raffinate phase lower in nitrogen content than the feed and a nitrogen-rich extract phase. The raffinate is then hydrocracked to maximize the yield of aviation turbine fuels. JP-4, JP-5, and JP-8 jet fuels were produced in this manner. The extract phase would be used to manufacture hydrogen by partial oxidation. |
| Table 2 | About fifteen hundred gallons of Occidental modified in-situ shale oil were available for use in the Phase III program. Inspections and analyses of raw and hydrotreated Occidental shale oil show that 97% sulfur and 65% nitrogen removal are attained in the main hydrotreater. The presence of water in the hydrotreated product may account for its relatively high oxygen content. |
| Table 3 | Inspections and analyses of the fractions from the hydrotreated shale oil are shown. Nitrogen, sulfur, and aromatic content increase with increasing boiling range. |
| Table 4 | Pilot plant HCl extractions were carried out batchwise. The HCl reacted instantaneously with the gas oil feedstock, the addition time being limited by the vaporization rate of the HCl from the gas cylinder. |
| Table 5 | The purpose of the naphtha hydrotreater is to cleanup the feedstock to meet final product specifications. The stabilized liquid product passed the JFTOT thermal stability test with no pressure drop and a preheater deposit code of zero. |

| | |
|---|---|
| Table 6 | Results from hydrocracking the HCl raffinate are given. Two distinct processing steps were used--R-1 hydrotreating to remove the remaining heteroatoms from the raffinate, and R-2 hydrocracking for molecular weight reduction to produce aviation turbine fuels. A section of the reactor outlet line developed a leak due to chloride stress corrosion. This problem was corrected by substituting a high nickel alloy steel (Inconel 600) for the 304 stainless steel. The bend in the line was stress relieved after fabrication. |
| Table 7 | The three intermediate fractions available for jet fuel blending are characterized. Note that the light hydrocrackate has F-1 clear and F-2 clear octane numbers of 69.5 and 67.9 respectively. This stream would be a suitable feedstock for catalytic reforming. These intermediate streams were distilled in a general purpose continuous distillation column, where we believe they picked up some trace contaminants, causing excessive pressure drop in the JFTOT thermal stability tests on the final fuels. Percolation of these streams through an acidic clay at a dosage of 250 bbl/ton of clay corrected this deficiency. No attempt was made to optimize the clay treat. |
| Table 8 | Inspections and analyses of the 170 gallon sample of JP-4 prepared from Occidental shale oil are given. Since there was little light material in the hydrotreated naphtha, only 27 volume % of the jet fuel blend was hydrotreated naphtha. The remaining 73 volume % was hydrocracked naphtha. |
| Table 9 | The 150 gallon sample of JP-5 jet fuel prepared from Occidental shale oil met all military specifications. The fuel, containing 82 volume % hydrotreated naphtha and 18 volume % hydrocracked naphtha, was precut to insure a minimum jet fuel flash point of 140°F. |
| Table 10 | The 155 gallon sample of JP-8 jet fuel prepared from Occidental shale oil had 57 volume % hydrotreated naphtha and 43 volume % hydrocracked naphtha. The jet fuel was distilled with a relatively low end point to assure obtaining a product meeting all military specifications. |

Figure 2 The Suntech processing scheme used for preparing military fuels from raw Paraho shale oil is shown. This scheme employs a relatively severe hydrotreat, followed by distillation of the hydrotreated product into a naphtha and gas oil fraction. The naphtha is rehydrotreated and the gas oil fraction is hydrocracked to produce lower boiling distillate fuel fractions. Five gallon samples of JP-4, JP-5, and JP-8 jet fuels were prepared along with Diesel Fuel No. 2 and Marine Diesel Fuel.

The relatively severe initial hydrotreat was substituted for the combination of a mild hydrotreat plus HCl extraction. This alternate processing scheme evolved from the successful effort to produce 270 barrels of JP-4 in one step by severe hydrogenation.

Table 11 Properties of the feed and product from the initial hydrotreat of raw Paraho shale oil show that greater than 99% nitrogen and sulfur removal are attained in this step. The use of relatively severe operating conditions account for the large increase in hydrogen content and the lowering of the distillation end point in the hydrotreated product. Again the presence of water in the product may account for its high oxygen content.

Table 12 Inspections and analyses of the fractions from Paraho shale oil hydrotreated to 100 ppm total nitrogen are given. The naphtha and light gas oil were used as feedstock to the cleanup hydrotreater. The 540-650°F boiling gas oil and the 650-1000°F boiling heavy gas oil were used as feedstocks to the gas oil hydrocracker. Overall, the fractions have a relatively low aromatic concentration. The basic nitrogen represents over 50% of the total nitrogen.

Table 13 The I-490°F boiling fraction was given a final hydrotreat to insure passage of all military specifications for JP-4 jet fuel. This step may not have been required, since the feedstock was relatively free of heteroatoms before this final hydrotreat.

Table 14 Typical results from hydrocracking the 650-1000°F boiling heavy gas oil are given. Two separate operations were used in this step--R-1 hydrotreating and R-2 hydrocracking for molecular weight reduction to produce the required samples of military fuels. The overall yield of liquid products was 110 volume % of the 650-1000°F boiling heavy gas oil feed.

| | |
|---|---|
| Table 15 | Inspections and analyses of the 5 gallons of JP-4 prepared from Paraho shale oil are given. The sample has a very low aromatic content and freeze point. |
| Table 16 | Inspections and analyses of the five gallon samples of JP-5 and JP-8 prepared from Paraho shale oil are shown. Both fuels met their respective military specifications. Freeze points on the pilot plant samples were well below the required values. |
| Table 17 | Inspections and analyses of the five gallon sample of Diesel Fuel No. 2 prepared from Paraho shale oil are given. A cetane index of 57, a calculated value, is shown in place of cetane number, a measured value, as given in the specification. |
| Table 18 | Inspections and analyses of the five gallon sample of Marine Diesel Fuel prepared from Paraho shale oil are given. This sample was prepared from 100% hydrocrackate. |
| Table 19 | Phase III uncertainties are stated. |
| Table 20 | Results of the Phase III program are summarized and conclusions are given. |

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge the contributions of E. J. Janoski, J. J. vanVenrooy and K. P. Fogarty in bringing the Phase III program to a successful conclusion.

# TABLE 1

## PHASE III OBJECTIVES

## COMPONENT TEST SAMPLES

1. TO CONFIRM THE PROPOSED FINAL PROCESS DESIGN BASIS FOR UPGRADING RAW SHALE OILS INTO MILITARY FUELS.

2. TO PREPARE LARGE VOLUME SAMPLES OF THREE DIFFERENT MILITARY TURBINE FUELS FROM OCCIDENTAL SHALE OIL IN OUR PILOT PLANTS USING SUNTECH'S PROCESSING CONCEPT - HYDROGENATION, ANHYDROUS HYDROGEN CHLORIDE EXTRACTION AND HYDROCRACKING.

3. TO PRODUCE PILOT PLANT SAMPLES OF FIVE DIFFERENT MILITARY FUELS FROM PARAHO SHALE OIL BASED ON A MODIFIED CONCEPT OF SEVERE HYDROGENATION AND HYDROCRACKING.

4. TO IDENTIFY AND SOLVE PROCESSING PROBLEMS ENCOUNTERED DURING THE SAMPLE PREPARATIONS.

5. TO UTILIZE ONLY NON-PROPRIETARY CATALYSTS IN THE PILOT PLANT OPERATIONS.

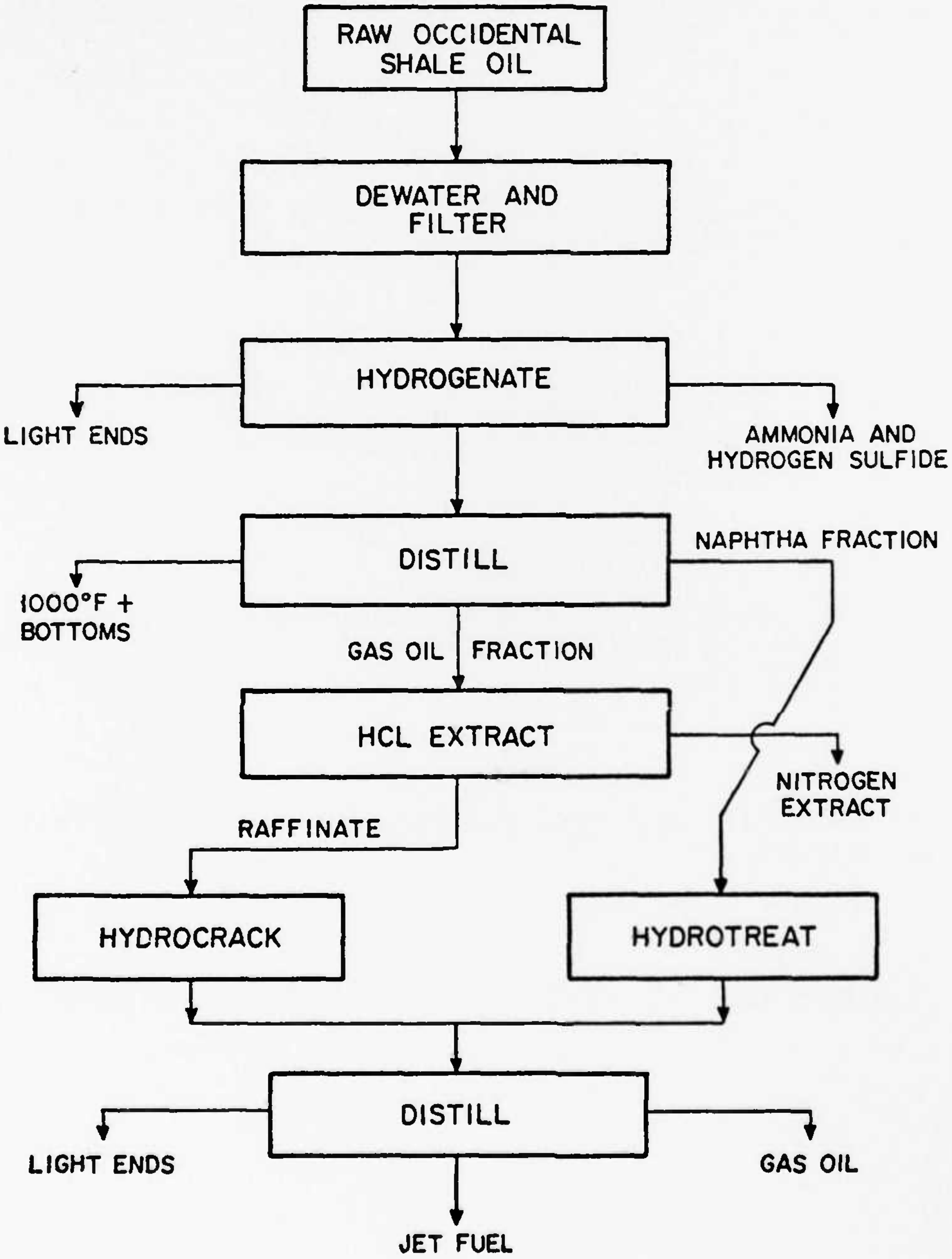

FIGURE 1
BLOCK FLOW DIAGRAM FOR PREPARING JET FUELS FROM OCCIDENTAL SHALE OIL

## TABLE 2

## INSPECTIONS AND ANALYSES OF RAW AND HYDROTREATED OCCIDENTAL SHALE OIL

| | DEWATERED AND FILTERED FEED | HYDROTREATED PRODUCT |
|---|---|---|
| API GRAVITY @ 60°F | 23.0 | 30.9 |
| DISTILLATION, °F | | |
| IBP | 413 | 169 |
| 10 VOL.% | 511 | 422 |
| 50 | 730 | 679 |
| 90 | 959 | 983 |
| EP | - | 1000 |
| RECOVERY | 90 | 97 |
| AROMATICS | 42.5 | 37 |
| POLAR AROMATICS | 23.6 | - |
| ASPHALTENES | 2.4 | - |
| CHEMICAL ANALYSES, WT.% | | |
| CARBON | 84.82 | 86.25 |
| HYDROGEN | 12.04 | 12.77 |
| SULFUR, PPM | 6200 | 159 |
| NITROGEN, TOTAL | 1.46 | 0.50 |
| OXYGEN | 1.18 | 0.11 |
| ARSENIC, PPM | 33 | <1 |
| ASH, WT.% | <0.005 | NIL |

## TABLE 3

## INSPECTIONS AND ANALYSES OF FRACTIONS FROM HYDROGENATED OCCIDENTAL SHALE OIL (0.50 WT.% TOTAL NITROGEN)

| | NAPHTHA | LT. GAS OIL | HVY. GAS OIL |
|---|---|---|---|
| YIELD, VOL. % | 14.8 | 12.2 | 63.4 |
| BOILING RANGE, °F | I-450 | 450-535 | 535-1000 |
| API GRAVITY @ 60°F | 44.0 | 37.5 | 28.9 |
| DISTILLATION, °F | | | |
| IBP | 296 | 460 | 535 |
| 30 | 365 | 477 | 670 |
| 50 | 385 | 481 | 740 |
| 70 | 403 | 487 | 817 |
| EP | 448 | 536 | 1000 |
| POUR POINT, °F | - | - | +43 |
| AROMATICS, % | 19.5 VOL. | 30 WT. | 41 WT. |
| ELEMENTAL ANALYSES, WT.% | | | |
| CARBON | 85.91 | 86.16 | 86.25 |
| HYDROGEN | 14.04 | 13.40 | 13.17 |
| SULFUR, PPM | 46 | 51 | 72 |
| NITROGEN, TOTAL | 0.08 | 0.36 | 0.52 |
| OXYGEN[1] | 0.03 | 0.17 | 0.14 |

[1] HIGH OXYGEN CONTENTS DUE TO PRESENCE OF MOISTURE IN SAMPLE.

## TABLE 4

## TYPICAL RESULTS FROM HCL EXTRACTIONS

FEEDSTOCK: 1275 GALLONS OF 530-1000°F B.R. GAS OIL.
FRACTION FROM HYDROGENATED OCCIDENTAL SHALE OIL.
(4 RUNS)

| | | |
|---|---|---|
| EXTRACTION CONDITIONS: | TEMPERATURE, °F | 110 |
| | PRESSURE, PSIG | 8 |
| | HCL ADDITION TIME, HOURS[1] | 4.5 |
| | ANHYDROUS HCL ADDED, WT.% OF GAS OIL | 2.25 |

| | FEED | RECOVERED RAFFINATE | RECOVERED EXTRACT[2] |
|---|---|---|---|
| YIELD, WT.% | 100 | 84.8 | 13.3 |
| API GRAVITY @ 60°F | 28.9 | 30.6 | 12.9 |
| SPECIFIC GRAVITY | 0.8822 | 0.8728 | 0.9800 |
| NITROGEN, TOTAL, PPM | 5200 | 700 | 3.14 WT.% |
| SULFUR, PPM | 72 | 30 | - |
| CHLORINE, PPM | 0 | 700 | 750 |
| AROMATICS, WT.% | 41 | 33 | - |
| WATER WASH LOSS, WT.% FEED | - | 1.9 | - |

[1] ADDITION TIME LIMITED BY VAPORIZATION RATE OF HCL FROM CYLINDER.

[2] AFTER THERMALLY DECOMPOSING A SMALL SAMPLE IN THE LABORATORY.

# TABLE 5

## FINAL NAPHTHA HYDROTREATING

FEEDSTOCK: IBP-535°F FRACTION FROM SHALE OIL HYDROGENATED TO 0.50 WT% TOTAL NITROGEN

HYDROGENATION UNIT: 10 LITER ADIABATIC REACTOR PILOT PLANT

CATALYST: NI MO ON ALUMINA

OPERATING CONDITIONS:

| | |
|---|---|
| AVERAGE CATALYST BED TEMPERATURE, °F | 760 |
| TOTAL PRESSURE, PSIG | 1500 |
| LIQUID HOURLY SPACE VELOCITY, V/HR/V | 1.4[1] |
| RECYCLE GAS RATE, SCF/B | 4000 |

[1] THROUGHPUT LIMITED BY FEED PREHEATER CAPACITY

| | FEEDSTOCK | STABILIZED LIQUID PRODUCT |
|---|---|---|
| VOLUME, GALLONS | 420 | 420 |
| API GRAVITY @ 60°F | 41.0 | 42.3 |
| DISTILLATION, °F | | |
| IBP | 296 | 306 |
| 10 | 361 | 371 |
| 50 | 454 | 447 |
| 90 | 505 | 499 |
| EP | 536 | 531 |
| AROMATICS, VOL.% | 24 | 15 |
| SULFUR, PPM | 48 | <1 |
| NITROGEN, TOTAL, PPM | 2100 | 3 |

# TABLE 6

## TYPICAL RESULTS FROM HYDROCRACKING HCL RAFFINATE

FEEDSTOCK: 535-1000°F B.R. RAFFINATE FROM HCL EXTRACTION

HYDROGENATION UNIT: 10 LITER ADIABATIC REACTOR PILOT PLANT

CATALYST: R-1 NI MO ON ALUMINA
R-2 NI W ON SILICA ALUMINA

OPERATING CONDITIONS:

| | R-1 | R-2 |
|---|---|---|
| AVG. CATALYST BED TEMP., °F | 760 | 701 |
| TOTAL PRESSURE, PSIG | 1700 | 1700 |
| LIQUID HOURLY SPACE VELOCITY, V/HR/V | 1.4[1] | 1.6[1] |
| RECYCLE GAS RATE, SCF/B | 4000 | 4000 |

| | FEEDSTOCK | R-1 PRODUCT | R-2 LIQUID PRODUCTS | |
|---|---|---|---|---|
| | | | $C_4$ - 300°F | 300°F + BOTTOMS |
| YIELD, VOL.% FEED | 100 | 101 | 47 | 64 |
| API GRAVITY @ 60°F | 30.6 | 31.6 | 71.0 | 38.7 |
| AROMATICS, WT.% | 33.1 | 23.5 | 1 VOL. | 28 |
| SULFUR, PPM | 30 | 2 | 1 | 2 |
| NITROGEN, TOTAL, PPM | 700 | 10 | <1 | 6 |
| CHLORINE, PPM | 700 | 0 | 0 | 0 |

[1] THROUGHPUT LIMITED BY FEED PREHEATER CAPACITY

## TABLE 7

## TYPICAL PROPERTIES OF INTERMEDIATE FRACTIONS FROM OCCIDENTAL SHALE OIL

| | HYDROTREATED NAPHTHA | LIGHT HYDROCRACKATE | HYDROCRACKED BOTTOMS |
|---|---|---|---|
| VOLUME, GALLONS | 420 | 251 | 340 |
| API GRAVITY @ 60°F | 42.3 | 71.0 | 38.7 |
| DISTILLATION, °F | | | |
| IBP | 306 | 84 | 310 |
| 10 | 371 | 129 | 334 |
| 50 | 447 | 204 | 410 |
| 90 | 499 | 257 | 577 |
| EP | 531 | 300 | 658 |
| FREEZE POINT, °F | -31 | -94 | 15 |
| FLASH POINT, °F | 125 | <80 | 130 |
| AROMATICS, VOL.% | 15 | 1 | 28 WT.% |
| SULFUR, PPM | <1 | 1 | 2 |
| NITROGEN, TOTAL, PPM | 3 | <1 | 6 |
| OCTANE NUMBERS | | | |
| F-1 CLEAR | - | 69.5 | - |
| F-2 CLEAR | - | 67.9 | - |

# TABLE 8

## INSPECTIONS AND ANALYSIS OF 170 GALLON SAMPLE OF JP-4 PREPARED FROM OCCIDENTAL SHALE OIL

| | SPEC. | PILOT PLANT SAMPLE |
|---|---|---|
| AROMATICS, VOL. % MAX. | 25.0 | 2.6 |
| OLEFINS, VOL. % MAX. | 5.0 | 2.2 |
| SULFUR, WT. % MAX. | 0.40 | <1.0 PPM |
| NITROGEN (TOTAL), PPM | NA | <1.0 |
| ASTM D-86 DISTILLATION, °F | | |
| IBP | REPORT | 142 |
| 20 VOL. %, MAX. | 293 | 232 |
| 50 VOL. %, MAX. | 374 | 295 |
| 90 VOL. %, MAX. | 473 | 446 |
| EP, MAX. | 518 | 478 |
| GRAVITY, °API MIN./MAX. | 45.0/57.0 | 54.8 |
| RVP, PSIA MIN./MAX. | 2.0/3.0 | 2.6 |
| FREEZE POINT, °F MAX. | -72 | -81 |
| NET HT. OF COMB., MIN. | 18,400 | 18,846 |
| COPPER STRIP CORROSION, MAX. | 1B | 1A |
| THERMAL STABILITY (JFTOT) | | |
| PRESSURE DROP, MM HG, MAX. | 25 | 0 |
| HEATER DEPOSIT, MAX. | 3 | 0 |
| HYDROGEN, WT. % MIN. | 13.6 | 14.46 |
| BLEND COMPONENTS, VOL.% | | |
| HYDROTREATED NAPHTHA | | 27 |
| HYDROCRACKED NAPHTHA | | 73 |

## TABLE 9

## INSPECTIONS AND ANALYSIS OF 150 GALLON SAMPLE OF JP-5 PREPARED FROM OCCIDENTAL SHALE OIL

| | SPEC. | PILOT PLANT SAMPLE |
|---|---|---|
| AROMATICS, VOL. % MAX. | 25.0 | 15.9 |
| OLEFINS, VOL. % MAX. | 5.0 | 2.2 |
| SULFUR, WT. % MAX. | 0.40 | <1.0 PPM |
| NITROGEN (TOTAL), PPM | NA | <1.0 |
| ASTM D-86 DISTILLATION, °F | | |
| IBP | REPORT | 345 |
| 10 VOL. % MAX. | 401 | 373 |
| 20 VOL. % MAX. | REPORT | 385 |
| 50 VOL. % MAX. | REPORT | 417 |
| 90 VOL. % MAX. | REPORT | 461 |
| EP, MAX. | 554 | 487 |
| GRAVITY, °API | 36.0/48.0 | 43.4 |
| FLASH POINT, °F MIN. | 140 | 145 |
| NET HT. OF COMB., MIN. | 18,300 | 18,596 |
| COPPER STRIP CORROSION, MAX. | 1B | 1B |
| THERMAL STABILITY (JFTOT) | | |
| PRESSURE DROP, MM HG MAX. | 25 | 0 |
| HEATER DEPOSIT, MAX. | 3 | 0 |
| HYDROGEN, WT. % MIN. | 13.5 | 14.02 |
| FREEZE POINT, °F MAX. | -51 | -56 |
| BLEND COMPONENTS, VOL.% | | |
| HYDROTREATED NAPHTHA | | 82 |
| HYDROCRACKED NAPHTHA | | 18 |

## TABLE 10

## INSPECTIONS AND ANALYSIS OF 155 GALLON SAMPLE OF JP-8 PREPARED FROM OCCIDENTAL SHALE OIL

| | SPEC. | PILOT PLANT SAMPLE |
|---|---|---|
| AROMATICS, VOL. % MAX. | 25.0 | 11.2 |
| OLEFINS, VOL. % MAX. | 5.0 | 1.4 |
| SULFUR, WT. % MAX. | 0.40 | <1.0 PPM |
| NITROGEN (TOTAL), PPM | NA | <1.0 |
| ASTM D-86 DISTILLATION, °F | | |
| IBP | REPORT | 324 |
| 10 VOL. %, MAX. | 401 | 346 |
| 20 VOL. %, MAX. | REPORT | 360 |
| 50 VOL. %, MAX. | REPORT | 397 |
| 90 VOL. %, MAX. | REPORT | 452 |
| EP, MAX. | 572 | 480 |
| GRAVITY, °API MIN./MAX. | 37/51 | 45.8 |
| FLASH POINT, °F MIN. | 100 | 128 |
| FREEZE POINT, °F MAX. | -58 | -61 |
| NET HT. OF COMB., MIN. | 18,400 | 18,663 |
| COPPER STRIP CORROSION, MAX. | 1B | 1B |
| THERMAL STABILITY (JFTOT) | | |
| PRESSURE DROP, MM HG MAX. | 25 | 0 |
| HEATER DEPOSIT, MAX. | 3 | 0 |
| HYDROGEN, WT. % MIN. | 13.6 | 14.12 |
| BLEND COMPONENTS, VOL.% | | |
| HYDROTREATED NAPHTHA | | 57 |
| HYDROCRACKED NAPATHA | | 43 |

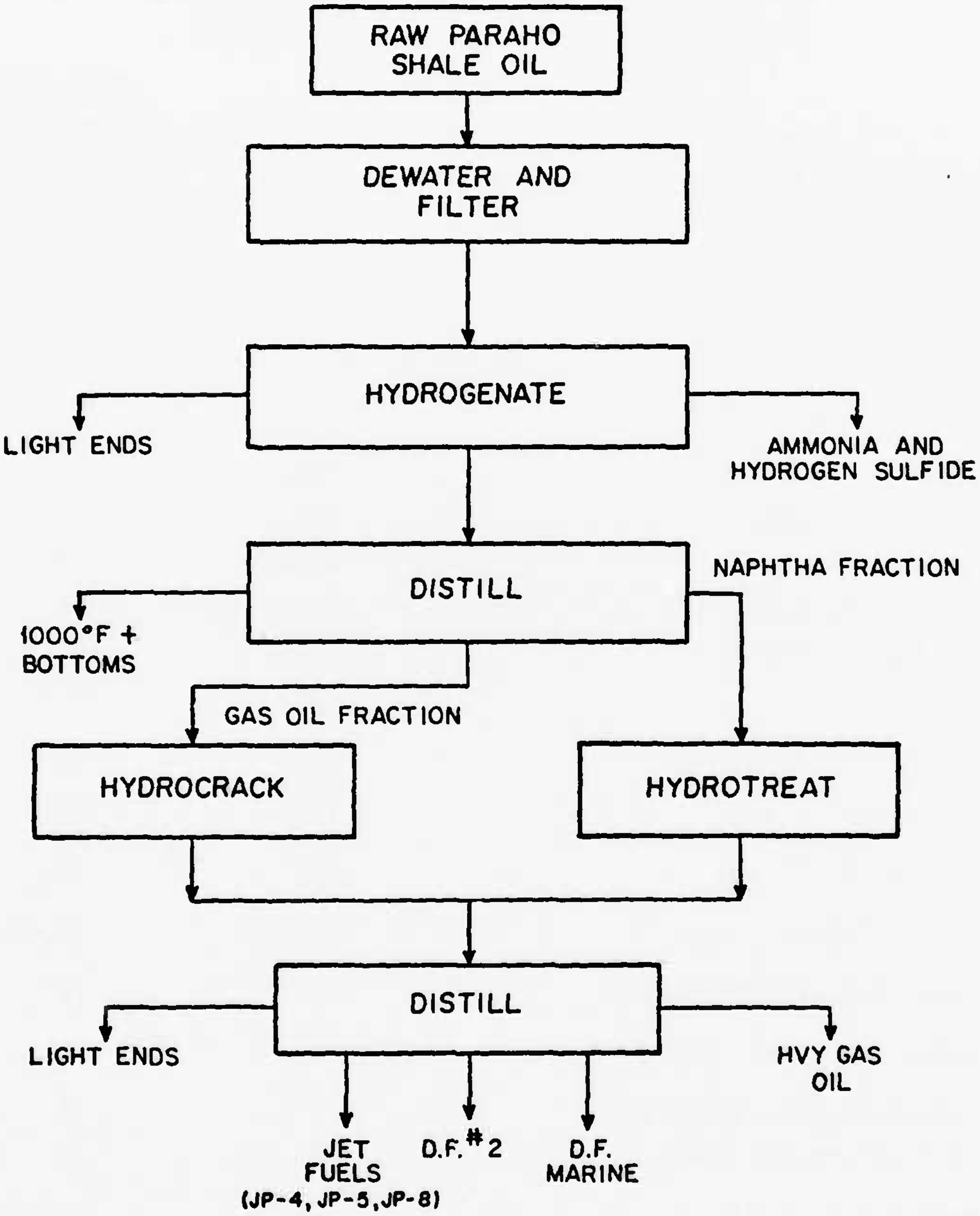

FIGURE 2
BLOCK FLOW DIAGRAM FOR PREPARING MILITARY FUELS FROM PARAHO SHALE OIL

## TABLE 11

## INSPECTIONS AND ANALYSES OF RAW AND HYDROTREATED PARAHO SHALE OIL

| | DEWATERED AND FILTERED FEED | HYDROTREATED PRODUCT |
|---|---|---|
| API GRAVITY @ 60°F | 20.6 | 37.0 |
| DISTILLATION, °F | D1160 | TBP |
| IBP | 133 | 165 |
| 10 VOL. % | 508 | 428 |
| 50 | 798 | 643 |
| 90 | 1057 | 940 |
| EP | 1065 | 1000 |
| RECOVERY | 95 | 97 |
| ASPHALTENES | 2.2 | - |
| CHEMICAL ANALYSES, WT. % | | |
| CARBON | 83.83 | 85.69 |
| HYDROGEN | 11.72 | 13.65 |
| SULFUR, PPM | 7500 | 14 |
| NITROGEN, TOTAL | 2.13 | 100 ppm |
| OXYGEN | 1.31 | 0.39 |
| ARSENIC, PPM | 34 | <1 |
| ASH, WT. % | 0.007 | NIL |

## TABLE 12

## INSPECTIONS AND ANALYSES OF FRACTIONS FROM HYDROGENATED PARAHO SHALE OIL (100 PPM TOTAL NITROGEN)

| | NAPHTHA | LT. GAS OIL | GAS OIL | HVY. GAS OIL |
|---|---|---|---|---|
| YIELD, VOL. % | 22.2 | 8.5 | 22.0 | 45.3 |
| BOILING RANGE, °F (TBP) | I-490 | 490-540 | 540-650 | 650-1000 |
| API GRAVITY @ 60°F | 43.1 | 37.9 | 35.9 | 30.8 |
| AROMATICS, % | 15 VOL. | 20 VOL. | 22 WT. | 28 WT. |
| ELEMENTAL ANALYSES, PPM | | | | |
| NITROGEN, TOTAL | 26 | 27 | 40 | 163 |
| NITROGEN, BASIC | 19 | 18 | 28 | - |
| SULFUR | <1 | <1 | 4 | 21 |

TABLE 13

## FINAL NAPHTHA HYDROTREATING

FEEDSTOCK: IBP-490°F FRACTION FROM SHALE OIL HYDROGENATED TO 100 PPM TOTAL NITROGEN

HYDROGENATION UNIT: 1 LITER ISOTHERMAL REACTOR PILOT PLANT

CATALYST: NI MO ON ALUMINA

OPERATING CONDITIONS:

| | |
|---|---|
| AVERAGE CATALYST BED TEMPERATURE, °F | 730 |
| TOTAL PRESSURE, PSIG | 1500 |
| LIQUID HOURLY SPACE VELOCITY, V/HR/V | 2.0 |
| HYDROGEN TO OIL RATIO, SCF/B | 5000 |

| | FEEDSTOCK | STABILIZED LIQUID PRODUCT |
|---|---|---|
| API GRAVITY @ 60°F | 43.1 | 43.6 |
| AROMATICS, VOL. % | 15 | 4 |
| SULFUR, PPM | 1 | <1 |
| NITROGEN, TOTAL, PPM | 26 | 1 |

## TABLE 14

## TYPICAL RESULTS FROM HYDROCRACKING

FEEDSTOCK: 650-1000°F B.R. SHALE OIL DISTILLATE FROM PARAHO SHALE OIL HYDROGENATED TO 100 PPM TOTAL NITROGEN

HYDROGENATION UNIT: 1 LITER ISOTHERMAL REACTOR PILOT PLANT

CATALYST: R-1 NI MO ON ALUMINA
R-2 NI W ON SILICA ALUMINA

OPERATING CONDITIONS:

| | R-1 | R-2 |
|---|---|---|
| AVG. CATALYST BED TEMP., °F | 750 | 750 |
| TOTAL PRESSURE, PSIG | 1700 | 1700 |
| LIQUID HOURLY SPACE VELOCITY, V/HR/V | 1.0 | 2.0 |
| HYDROGEN TO OIL RATIO, SCF/B | 5000 | 5000 |

| | | | R-2 LIQUID PRODUCTS | | |
|---|---|---|---|---|---|
| | FEEDSTOCK | R-1 PRODUCT | $C_4$-310°F | 310-550°F | 550-675°F |
| YIELD, VOL.% FEED | 100 | 101 | 46 | 29 | 24 |
| API GRAVITY @ 60°F | 30.8 | 31.6 | 75.2 | 43.7 | 38.1 |
| SULFUR, PPM | 21 | 2 | 1 | 2 | 3 |
| NITROGEN, TOTAL, PPM | 163 | <1 | <1 | <1 | <1 |

## TABLE 15

## INSPECTIONS AND ANALYSIS OF 5 GALLON SAMPLE OF JP-4 PREPARED FROM PARAHO SHALE OIL

| | SPEC. | PILOT PLANT SAMPLE |
|---|---|---|
| AROMATICS, VOL.% MAX. | 25.0 | 5.2 |
| OLEFINS, VOL.% MAX. | 5.0 | 1.4 |
| SULFUR, WT.% MAX. | 0.40 | 3 PPM |
| NITROGEN (TOTAL), PPM | NA | <1.0 |
| ASTM D-86 DISTILLATION, °F | | |
| IBP | REPORT | 153 |
| 20 VOL.%, MAX. | 293 | 214 |
| 50 VOL.%, MAX. | 374 | 279 |
| 90 VOL.%, MAX. | 473 | 430 |
| EP, MAX. | 518 | 498 |
| GRAVITY, °API MIN./MAX. | 45.0/57.0 | 56.7 |
| RVP, PSIA MIN./MAX. | 2.0/3.0 | 2.7 |
| FREEZE POINT, °F MAX. | -72 | -80 |
| NET HT. OF COMB., MIN. | 18,400 | 18,794 |
| COPPER STRIP CORROSION, MAX. | 1B | 1B |
| THERMAL STABILITY (JFTOT) | | |
| PRESSURE DROP, MM HG, MAX. | 25 | 0 |
| HEATER DEPOSIT, MAX. | 3 | 0 |
| HYDROGEN, WT.% MIN. | 13.6 | 14.4 |
| BLEND COMPONENTS, VOL.% | | |
| HYDROTREATED NAPHTHA | | 27 |
| HYDROCRACKED NAPHTHA | | 73 |

## TABLE 16

## INSPECTIONS AND ANALYSIS OF 5 GALLON SAMPLES OF JP-5 AND JP-8 PREPARED FROM PARAHO SHALE OIL

| | JP-5 | | JP-8 | |
|---|---|---|---|---|
| | SPEC. | PILOT PLANT SAMPLE | SPEC. | PILOT PLANT SAMPLE |
| AROMATICS, VOL. % MAX. | 25.0 | 23.8 | 25.0 | 23.6 |
| OLEFINS, VOL. % MAX. | 5.0 | 1.7 | 5.0 | 1.3 |
| SULFUR, WT. % MAX. | 0.40 | 3 PPM | 0.40 | 30 PPM |
| NITROGEN (TOTAL), PPM | NA | <0.1 | NA | <0.1 |
| ASTM D-86 DISTILLATION, °F | | | | |
| IBP | REPORT | 335 | REPORT | 306 |
| 10 VOL. % MAX. | 401 | 365 | 401 | 333 |
| 20 VOL. % MAX. | REPORT | 375 | REPORT | 345 |
| 50 VOL. % MAX. | REPORT | 404 | REPORT | 385 |
| 90 VOL. % MAX. | REPORT | 443 | REPORT | 450 |
| EP, MAX. | 554 | 475 | 572 | 489 |
| GRAVITY, °API MIN./MAX. | 36.0/48.0 | 47.1 | 37/51 | 43.7 |
| FLASH POINT, °F MIN. | 140 | 144 | 100 | 118 |
| FREEZE POINT, °F MAX. | -51 | -69 | -58 | -80 |
| NET HT. OF COMB., MIN. | 18,300 | 18,610 | 18,400 | 18,520 |
| COPPER STRIP CORROSION, MAX. | 1B | 1B | 1B | 1B |
| THERMAL STABILITY (JFTOT) | | | | |
| PRESSURE DROP, MM HG MAX. | 25 | 1 | 25 | 0 |
| HEATER DEPOSIT, MAX. | 3 | 0 | 3 | 0 |
| HYDROGEN, WT. % MIN. | 13.5 | 13.5 | 13.6 | 13.7 |
| BLEND COMPONENTS, VOL. % | | | | |
| HYDROTREATED NAPHTHA | | 0 | | 0 |
| HYDROCRACKED NAPHTHA | | 100 | | 100 |

## TABLE 17

## INSPECTIONS AND ANALYSIS OF 5 GALLON SAMPLE OF DIESEL FUEL-2 PREPARED FROM PARAHO SHALE OIL

| DIESEL FUEL PROPERTIES | SPECIFICATION GRADE DF-2 CONUS. | PILOT PLANT SAMPLE |
|---|---|---|
| GRAVITY, °API | REPORT | 40.4 |
| FLASH POINT, °F | 125 | 146 |
| CLOUD POINT, °F MAX. | [1] | -2 |
| POUR POINT, °F MAX. | REPORT | -10 |
| KINEMATIC VISCOSITY @ 100°F, CST | 2.0-4.3 | 2.40 |
| ASTM D-86 DISTILLATION, °F | | |
| IBP | NA | 344 |
| 50% EVAPORATED | REPORT | 494 |
| 90% EVAPORATED, MAX. | 640 | 575 |
| EP, MAX. | 700 | 594 |
| SULFUR, WT. % MAX. | 0.50 | 1 PPM |
| NITROGEN, PPM | NA | 1 |
| COPPER STRIP CORROSION, 3 HRS. @ 122°F, MAX. | 3 | 2A |
| CETANE NUMBER, MIN. | 45 | 57[2] |
| HYDROGEN, WT. % | NA | 13.8 |

[1] VARIES WITH GEOGRAPHICAL AND SEASONAL REQUIREMENTS.

[2] CETANE INDEX

## TABLE 18

## INSPECTION AND ANALYSIS OF 5 GALLON SAMPLE OF MARINE DIESEL FUEL PREPARED FROM PARAHO SHALE OIL

| | SPEC. | PILOT PLANT SAMPLE |
|---|---|---|
| GRAVITY, °API @ 60°F | RECORD | 39.4 |
| FLASH POINT, °F MIN. | 140 | 255 |
| CLOUD POINT, °F MAX. | +30 | +14 |
| POUR POINT, °F MAX. | +20 | -2 |
| KINEMATIC VISCOSITY @ 100°F, CST | 1.8-4.5 | 3.73 |
| ASTM D-86 DISTILLATION, °F | | |
| IBP | NA | 492 |
| 50% | RECORD | 538 |
| 90% | 675 | 580 |
| EP, MAX. | 725 | 601 |
| SULFUR, WT. % MAX. | 1.00 | 30 PPM |
| NITROGEN, PPM | NA | 1 |
| COPPER STRIP CORROSION AT 212°F, MAX. | 1 | 1 |
| HYDROGEN, WT. % | NA | 14.0 |
| CETANE NUMBER, MIN. | 45 | 58[1] |

[1] CETANE INDEX

## TABLE 19

## UNCERTAINTIES

1. CHLORIDE CONTENT IN THE HCL RAFFINATE VARIED OVER A WIDE RANGE FROM RUN TO RUN - 100 TO 800 PPM CL. ADDITIONAL WORK IS NEEDED TO DETERMINE HOW TO MINIMIZE RESIDUAL CONCENTRATION.

2. CONTINUOUS HCL TREATING AND RECOVERY PROCESSES HAVE NOT BEEN DEMONSTRATED. LARGE SCALE RUNS HAD TO BE MADE BATCHWISE DUE TO THE LACK OF SUITABLE CONTINUOUS EQUIPMENT.

3. MAIN HYDROTREATER CATALYST LIFE AT HIGH REACTOR SEVERITY (100 PPM TOTAL NITROGEN IN PRODUCT) WITH PARAHO SHALE OIL WAS NOT DETERMINED.

4. EXTINCTION RECYCLING OF HYDROCRACKED BOTTOMS NOT DEMONSTRATED. TIME PERMITTED ONLY ONCE THROUGH OPERATION WITH THE EQUIPMENT AVAILABLE.

## TABLE 20

## SUMMARY AND CONCLUSIONS

1. A TOTAL OF 475 GALLONS OF SPECIFICATION AVIATION TURBINE FUELS WERE PREPARED IN PILOT PLANTS FROM OCCIDENTAL MODIFIED IN-SITU SHALE OIL USING SUNTECH's PROCESSING CONCEPT. PRODUCT VOLUMES WERE 170 GALLONS OF JP-4, 150 GALLONS OF JP-5 AND 155 GALLONS OF JP-8.

2. SOME TRACE CONTAMINANTS WERE PICKED UP DURING THE FINAL PRODUCT DISTILLATIONS IN A GENERAL PURPOSE STILL WHICH RESULTED IN EXCESSIVE $\Delta P$'s IN THE JFTOT TESTS. THIS PROBLEM WAS CORRECTED BY PERCOLATING THE TURBINE FUELS THROUGH CLAY.

3. A STRESS CORROSION PROBLEM WAS ENCOUNTERED WITH THE HCL RAFFINATE FRACTION (700 PPM CL) EARLY IN THE HYDROCRACKING OPERATION. A LEAK OCCURRED AT AN UNANNEALED 90° BEND IN THE R-1 REACTOR OUTLET LINE. THIS PROBLEM WAS SOLVED BY REPLACING THE 304 TYPE STAINLESS STEEL WITH HIGH NICKEL INCONEL ALLOY 600 TUBING AND STRESS RELIEVING THE BEND AFTER FABRICATION.

4. A TOTAL OF 25 GALLONS OF SPECIFICATION MILITARY FUEL SAMPLES WERE PREPARED FROM PARAHO SHALE OIL USING A MODIFIED PROCESSING SCHEME - SEVERE HYDROGENATION AND HYDROCRACKING (FIVE GALLON SAMPLES EACH OF JP-4, JP-5, JP-8, DF 2 AND DF MARINE). THIS PROCESSING SCHEME WAS AN OUTGROWTH OF THE HIGH SEVERITY HYDROGENATION RUN MADE IN 1980 TO PRODUCE A LARGE VOLUME SAMPLE OF JP-4 IN ONE STEP. HYDROCRACKING WAS ADDED TO INCREASE THE YIELD OF TURBINE FUELS. NO UNUSUAL PROCESSING PROBLEMS WERE ENCOUNTERED DURING PILOT PLANT OPERATIONS.

## V

# OVERALL ECONOMIC OPRIMIZATION STUDY OF SUNTECH'S SHALE OIL UPGRADING PROCESS FOR MILITARY FUELS PRODUCTION

H. E. Reif, J. P. Schwedock,
A. Macris, and A. Schneider

Suntech, Inc.

# OVERALL ECONOMIC OPTIMIZATION STUDY OF SUNTECH'S SHALE OIL UPGRADING PROCESS FOR MILITARY FUELS PRODUCTION

H. E. Reif, J. P. Schwedock, A. Macris, and A. Schneider

SUNTECH, INC.

## SUMMARY

This report covers work performed by Suntech, Inc. in Phase IV of our contract with the United States Air Force. The Phase IV objectives were to establish by computer modelling, the economically optimum processing scheme and plant capacities based on analytical and experimental data from Phases I, II and III.

Using Suntech's processing concepts for refining raw Occidental shale oil and the economic guidelines provided by the USAF, an LP computer program was developed. Due to non-linear yield effects, especially in the HCl-extraction process, the optimization was performed using available experimental processing options. The results from a case-study approach were: 1) the optimal scheme for maximum JP-4 and JP-8 production was with the raw shale oil hydrotreater operating at 2200 ppm total nitrogen content ($N_T$) in the effluent; 2) for the JP-4 and other fuels option was with the raw shale oil hydrotreater operating at 6400 ppm $N_T$ in the effluent.

Detailed process flow sheets of the major process equipment and operating conditions for the three optimal processing schemes were determined. Hydrogen consumption was 2584 SCF/Bbl of raw shale oil for maximum JP-4 production; 2363 SCF/Bbl for maximum JP-8 production; and 1960 SCF/Bbl for the JP-4 and other fuels case. Overall refinery thermal efficiency varied from 81% for the maximum JP-8 production to 87% for the JP-4 and other fuels case. From overall economic analysis we found that the price of liquid products in the maximum JP-4 case was 1.22 $/gal, for the maximum JP-8 case was 1.24 $/gal and for the JP-4 and other fuels case was 1.19 $/gal . Sensitivity analysis on the economic variables, using a computer program, showed that the price of raw shale oil had the largest impact on product prices, that the discounted cash flow and variation in capital expenditure and finally annual interest rate had only a small impact on fuel prices. Examining a more realistic scenario, where the capital investment has to be borrowed at an annual rate of 15% we found that the product prices increase by about 9.5 cents per gallon.

A set of tables and figures have been prepared which outline the LP model work, the plant configuration for the optimal processing schemes and the economic evaluations. Uncertainties and conclusions are stated.

| | |
|---|---|
| Table 1 | The Phase IV objectives are outlined. Using the analytical and experimental data generated in Phases I, II, and III, the economically optimum processing schemes and plant capacities for producing aviation turbine fuels from raw Occidental shale oil were to be established by modeling. Remaining problems and uncertainties were to be defined. |
| Figure 1 | Suntech's processing concept for preparing military turbine fuels from raw Occidental shale oil is shown. The first processing step is a relatively mild hydrotreat to partially reduce the high non-hydrocarbon content of the raw shale oil (and convert some neutral nitrogen to basic nitrogen), while minimizing hydrogen consumption. The hydrotreated product is distilled into appropriate fractions for additional processing. The 1000°F+ bottoms fraction is excluded from anhydrous hydrogen chloride extraction, since it causes emulsion problems. The naphtha fraction is rehydrotreated to meet product specifications. The wide boiling gas oil fraction is treated with anhydrous hydrogen chloride which yields a raffinate phase lower in nitrogen content than the feed and a nitrogen-rich extract phase. The raffinate is then hydrocracked to maximize the yield of aviation turbine fuels. The extract phase would be used to manufacture hydrogen by partial oxidation. |
| Figure 2 | Hydrogen consumption in the raw shale oil hydrotreater is plotted as a function of nitrogen content in the hydrotreated product. Hydrogen consumption is greater when producing lower nitrogen levels in the hydrotreated product. Data obtained at nitrogen levels of 2200, 5000, and 6400 ppm were used as inputs to Suntech's computer model. |
| Figure 3 | The yield of 1000°F+ bottoms decreases with increasing severity in the raw shale oil hydrotreater. This fraction is blended into heavy fuel, used for refinery fuel or for manufacturing hydrogen by partial oxidation. |
| Figure 4 | The yield of extract from the HCl treating step goes through a maximum at a total nitrogen level of about 6500 ppm in the gas oil feed. At this level, the severity of the raw shale oil hydrotreat was sufficient to convert neutral nitrogen to basic nitrogen more rapidly than basic nitrogen was converted to ammonia gas. Hydrogen consumption can be conserved when operating in this fashion. |
| Figure 5 | Suntech's linear program decision model is shown schematically. Raw Occidental shale oil is introduced into the main hydrotreater, where it can be processed to three levels of effluent nitrogen, and then distilled to yield four liquid products: a) $C_4$-450°F cut, b) 450°-550°F cut, c) 550°-1000°F cut, and d) 1000°F+ bottoms. Note that the 450°-550°F cut can go to the naphtha hydrotreater or the HCl extraction plant, depending on which product is maximized. The 1000°F+ bottoms |

can be used for $H_2$ production in the Texaco Partial Oxidation (TPO) plant, for refinery fuel or be sold directly as product.

The naphtha hydrotreater products are sent for aviation turbine fuel blending, or are treated as direct products. HCl raffinate goes to the hydrocracker unit, while HCl extract can be sent to the TPO plant, used as refinery fuel or sold directly as product. The hydrocracker products are sent for jet-fuel blending or are treated as direct products, depending on the option considered.

Light ends from the hydroprocessing units are sent to the steam reforming plant for $H_2$ production. Waste water from the same plant is sent to a combination of plants (Chevron Waste Water plant, $NH_3$ plant, and Sulfur Recovery plant) to produce $NH_3$ and S by-products. The hydrogen balance is closed by using additional Occidental shale oil, if needed, in the TPO plant.

Table 2 Hydrogen consumptions for the three optimized cases are shown, ranging from 1960 SCF/Bbl of raw shale oil in the JP-4 and other fuels case to 2584 SCF/Bbl of raw shale oil in the maximum JP-4 case.

Table 3 Material balance summaries are shown for the three optimized cases:

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

Yields and overall refinery thermal energy efficiencies are greater than those reported in Phase II, due to optimization of processing schemes and plant capacities.

Table 4 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 vacuum 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 5 Guidelines for developing Suntech's Phase IV economics are given. A first quarter 1981 cost base is used with 100% equity financing. Crude shale oil is valued at $40/Bbl and all product fuels are equally valued at actual cost.

| | |
|---|---|
| Table 6 | Plant capacities and investments are presented for the three optimized cases. As in Phases I and II, the main hydrotreater and the TPO hydrogen plant account for the majority of the on-site costs. Total capital investments were $878.6 million for maximum JP-4 production; $862.5 million for maximum JP-8 production; and 804.1 million for the JP-4 plus other fuels case. |
| Table 7 | Total product costs including the adjusted crude costs are 122.3¢/gal of product for maximum JP-4 production; 124.4¢/gal of product for maximum JP-8 production; and 118.5¢/gal of product for the JP-4 plus other fuels case. Total manufacturing costs ranged from $9.94/Bbl of product for the JP-4 plus other fuels case to $10.38/Bbl of product for maximum JP-8 production. |
| Figure 6 | The sensitivity of fuel cost to changes in the investment rate of return (IRR) is shown. Due to the uncertainties associated with investing in a new technology, we feel that an IRR of at least 20% would be needed to attract capital. This would increase the product fuel cost an additional 9 ¢/gal. |
| Figure 7 | The sensitivity of fuel cost to changes in the price of raw shale oil is shown. Changes in the price of raw shale oil has a significiant impact on the product fuel cost . An increase in the cost of raw shale oil from $40 to $45/Bbl would cause the product fuel cost to rise an additional 12¢/gal. |
| Figure 8 | The effect of changes in capital investment on product fuel cost is shown. A contingency was not included in the Phase IV economic evaluation. We recommend a contingency of at least 25% for new technology energy process plants such as a raw shale oil upgrading facility. An additional cost of 4.5¢/gal of product results from the use of this contingency factor. |
| Figure 9 | The effect of changes in the annual interest rate of working capital on product fuel cost is shown. Since interest charges are only associated with working capital and not plant investment, the product fuel cost is not overly sensitive to changes in the annual interest rate. Increasing the annual interest rate from 15% to 20% adds 0.4¢/gal to the product cost. |
| Table 8 | If 100% debt financing is used, the increase in product cost is 9.1 to 9.5¢/gal of product. |
| Table 9 | Yields, costs, and thermal efficiencies are summarized for the three processing routes. Based on total energy input to the refinery, 94.4 volume % jet fuel is produced when maximizing |

| | |
|---|---|
| | JP-4; 54.3 volume % jet fuel when maximizing JP-8; and 79.1 volume % jet fuel in the JP-4 plus other fuels case. Overall thermal efficiencies range from 80.7 to 86.7%. Plant investments for the three shale oil refineries are between 8041 and 8786 \$/SDB of capacity. The plant investment for a conventional petroleum fuels refinery of similar capacity is less than half of the above figures. |
| Table 10 | Phase IV uncertainties are stated. |
| Table 11 | Results of the Phase IV program are summarized and conclusions are given. |

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge the contributions of G. F. Frey and J. W. Ruth in bringing the Phase IV program to a successful conclusion.

# TABLE 1

## PHASE IV OBJECTIVES

### OVERALL ECONOMIC OPTIMIZATION STUDY

1. ESTABLISH BY COMPUTER MODELLING THE ECONOMICALLY OPTIMUM PROCESSING SCHEME AND PLANT CAPACITIES BASED ON ANALYTICAL AND EXPERIMENTAL DATA FROM PHASES I, II, AND III.

2. DETERMINE THE ECONOMIC AND YIELD TRADE-OFFS FOR PRODUCING JP-4 OR JP-8 TURBINE FUELS AS PRIMARY PRODUCTS.

3. COMPUTER MODEL THE OVERALL PROCESSES. PROVIDE DETAILED PROCESS FLOW SHEETS OF THE MAJOR PROCESS EQUIPMENT AND OPERATING CONDITIONS FOR THE OPTIMIZED SHALE OIL PROCESSING SCHEME.

4. ESTIMATE EXTERNAL RESOURCES REQUIRED FOR EACH PROCESS INVESTIGATED - I.E., WATER, ELECTRICITY, AND HYDROGEN.

5. DEFINE REMAINING PROBLEMS AND/OR UNCERTAINTIES.

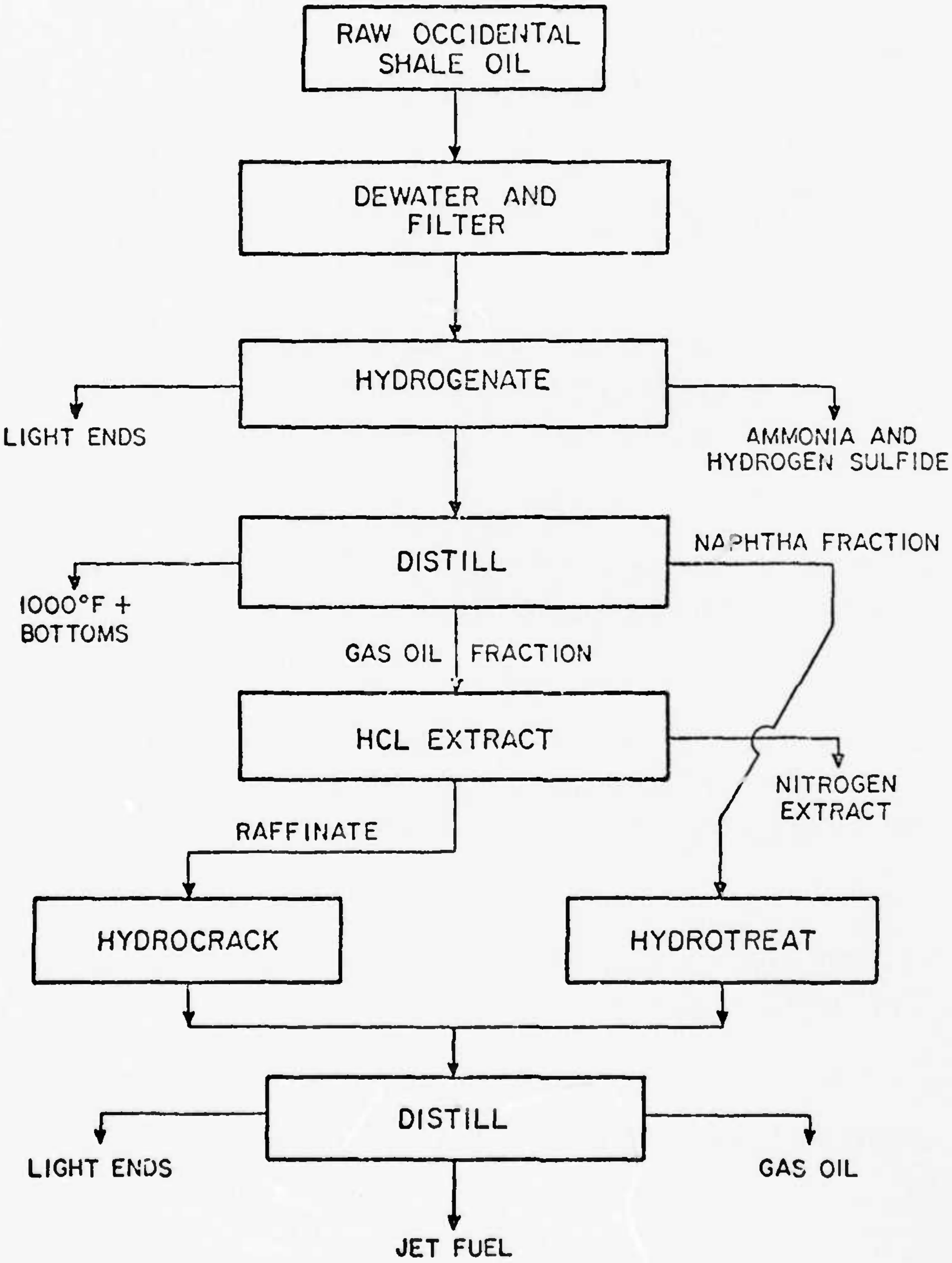

FIGURE 1
BLOCK FLOW DIAGRAM FOR PREPARING
JET FUELS FROM OCCIDENTAL SHALE OIL

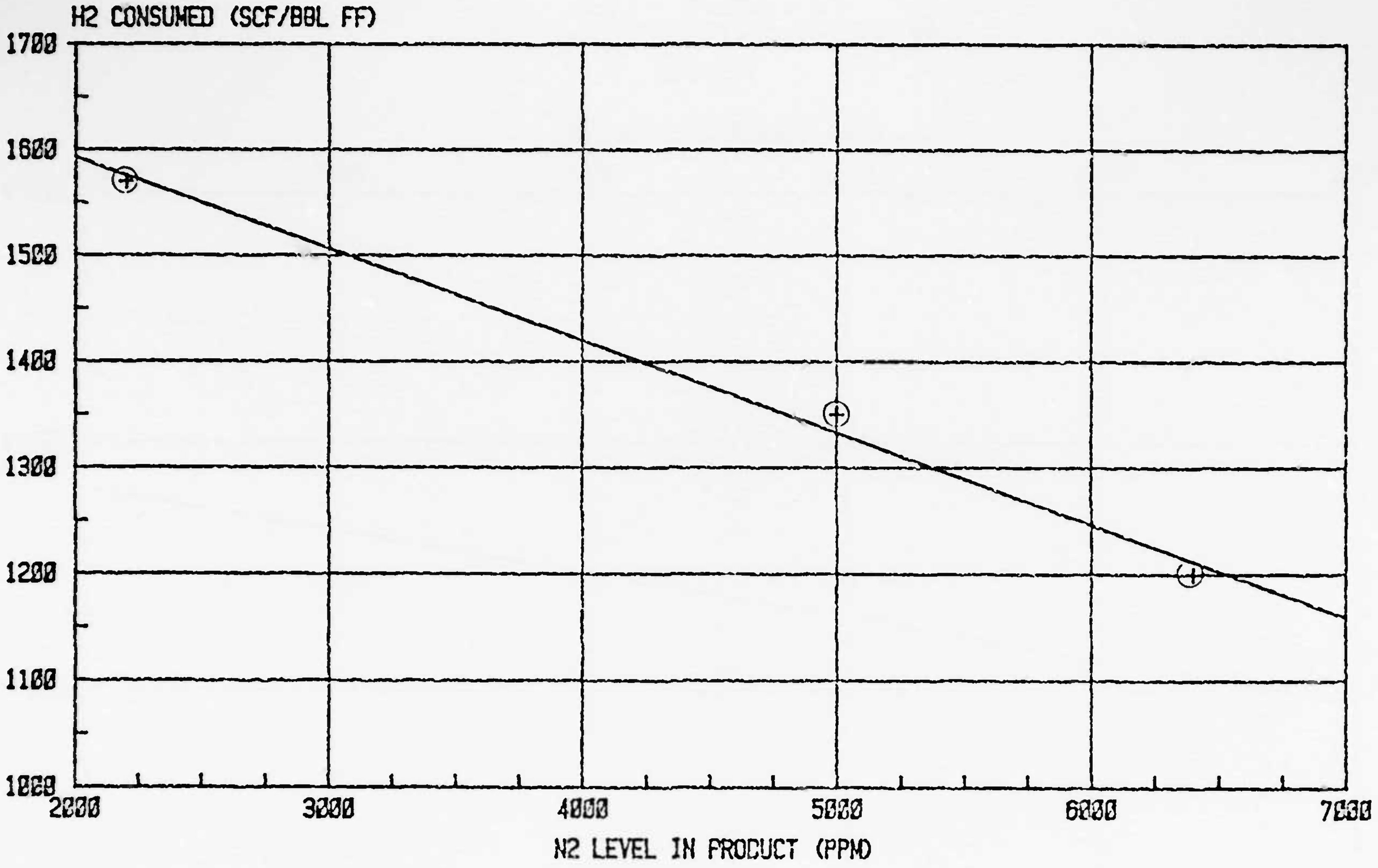

FIGURE 2

NITROGEN REMOVAL VS. HYDROGEN
CONSUMPTION (CHEMICAL) AT MAIN HYDROTREATER

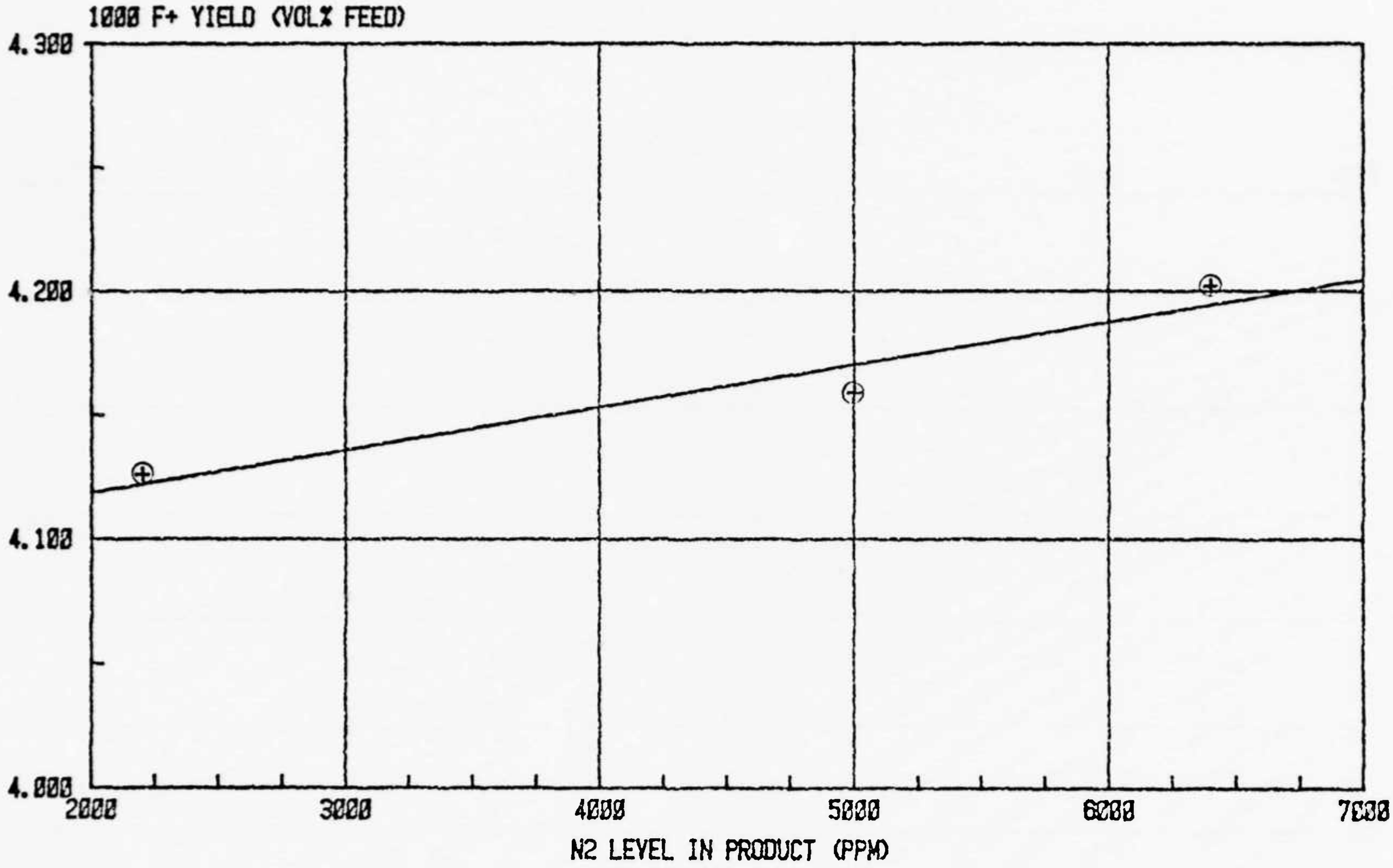

FIGURE 3

EFFECT OF HYDROTREATING SEVERITY ON
1000°F + BOTTOMS YIELD

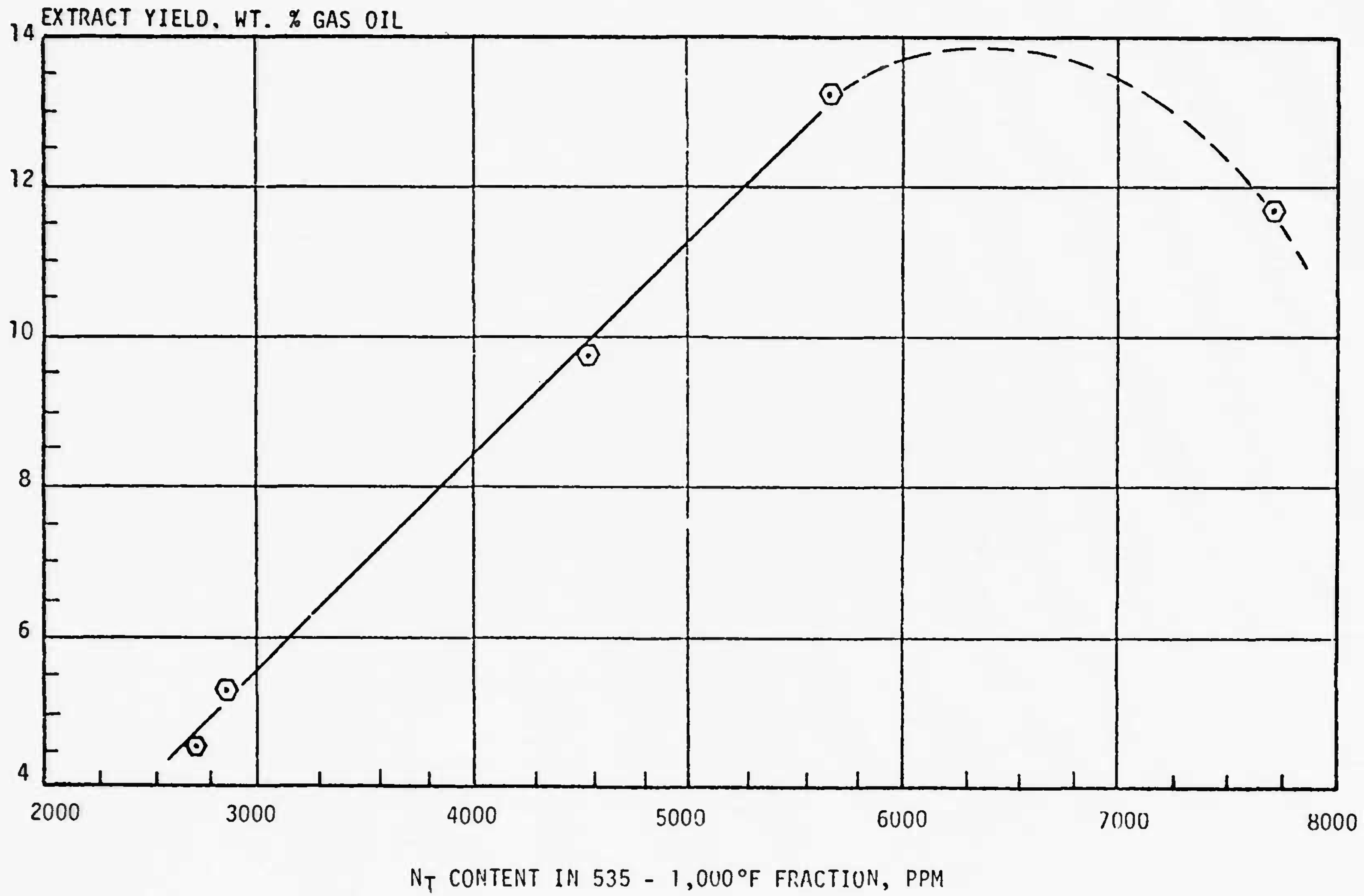

FIGURE 4

EFFECT OF NITROGEN CONTENT IN GAS OIL
FRACTION ON HCL EXTRACT YIELD

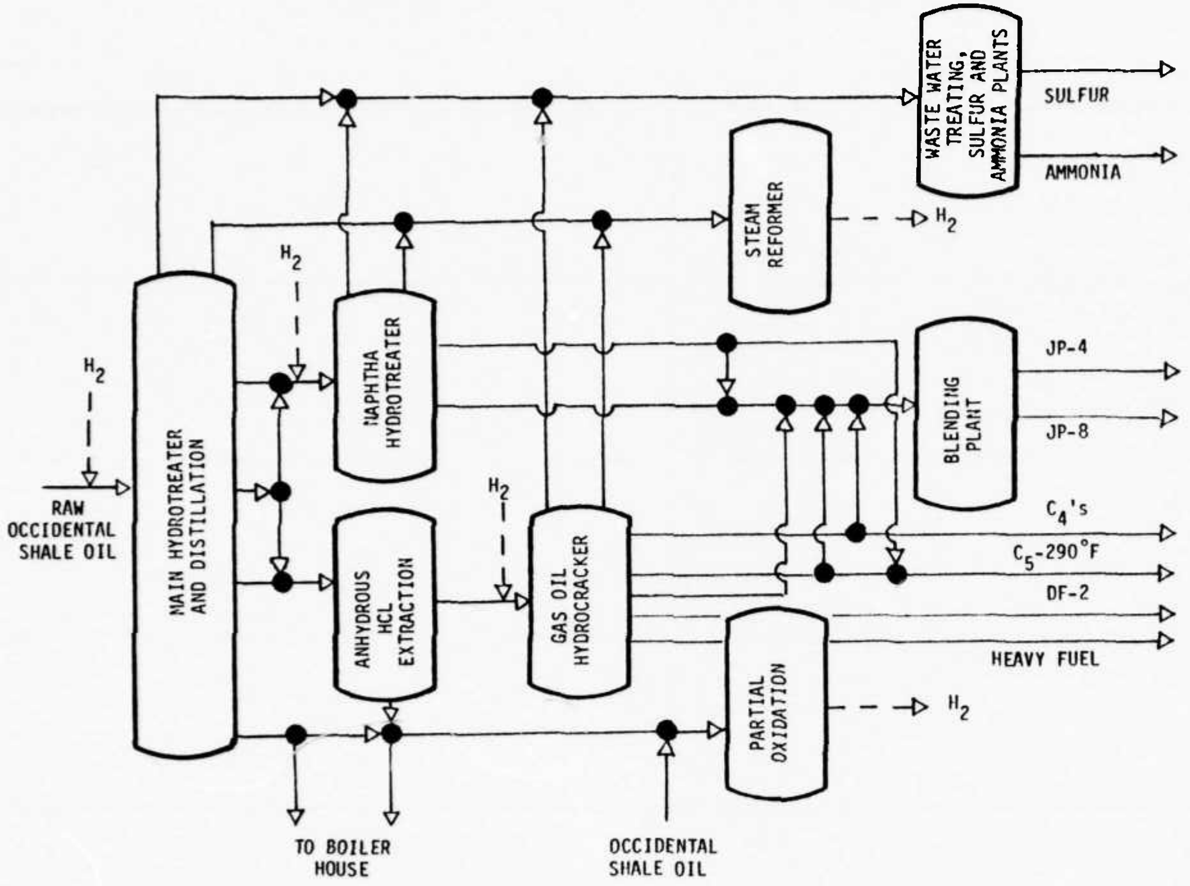

FIGURE 5

SCHEMATIC DIAGRAM OF LINEAR PROGRAM MATHEMATIC MODEL FOR MAXIMIZING YIELDS OF MILITARY FUELS

## TABLE 2

## TOTAL HYDROGEN CHEMICALLY CONSUMED IN OPTIMIZED CASES

BASIS: 100,000 BPSD RAW OCCIDENTAL
SHALE OIL FEEDSTOCK TO THE MAIN HYDROTREATER

| | SCF 100% HYDROGEN X $10^6$ CONSUMED PSD | | |
|---|---|---|---|
| | MAX JP-4 | MAX JP-8 | JP-4 & OTHER FUELS |
| OPTIMUM MAIN HYDROTREATER SEVERITY, PPM $N_T$ IN LIQUID | 2200 | 2200 | 6400 |
| RAW SHALE OIL HYDROTREATER | 157.0 | 157.0 | 120.0 |
| NAPHTHA HYDROTREATER | 7.6 | 8.8 | 8.4 |
| GAS OIL RAFFINATE HYDROCRACKER | 93.8 | 70.5 | 67.6 |
| TOTAL | 258.4 | 236.3 | 196.0 |
| TOTAL HYDROGEN CONSUMED PER BBL OF RAW SHALE OIL, SCF | 2584 | 2363 | 1960 |

## TABLE 3

## MATERIAL BALANCE SUMMARY

BASIS: OPTIMIZED 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 | --- | 43,716 | --- |
| $C_4$-490°F B.R. JP-4 | 108,504 | --- | 83,810 |
| 290-550°F B.R. JP-8 | --- | 62,141 | --- |
| 450°+ HC recycle Drag. | 3,464 | 3,367 | --- |
| 490-675°F B.R. DF-2 | --- | --- | 16,454 |
| 675-1000°F B.R. Heavy Fuel | --- | --- | 5,777 |
| TOTAL FUELS | 111,968 | 109,224 | 106,141 |
| Other Products, STPSD | | | |
| Liquid Ammonia | 245.9 | 254.2 | 199.4 |
| Sulfur | 119.6 | 112.5 | 110.7 |
| Ammonium Chloride | 2.8 | 2.7 | 3.2 |
| Liquid Fuel Yields | | | |
| Total Products as Vol. % Process Feeds | | | |
| Naphtha | --- | 43.7 | --- |
| JP-4 | 108.5 | --- | 83.9 |
| JP-8 | --- | 62.1 | --- |
| DF-2 | --- | --- | 16.5 |
| Heavy Fuel | 3.5 | 3.4 | 5.8 |
| TOTAL REFINERY INPUT (CRUDE, FUEL & UTILITIES CONVERTED TO FOE), BPSD | 114,973 | 114,334 | 105,677 |
| TOTAL PRODUCTS AS VOL. % REFINERY INPUT | | | |
| Naphtha | --- | 38.2 | --- |
| JP-4 | 94.4 | --- | 79.0 |
| JP-8 | --- | 55.2 | --- |
| DF-2 | --- | --- | 15.6 |
| Heavy Fuel | 3.0 | 2.9 | 5.5 |
| Overall Refinery thermal Energy Efficiency, % | 81.5 | 80.7 | 86.7 |

# TABLE 4

## TYPICAL PRODUCT INSPECTIONS AND ANALYSES

| CHEMICAL AND PHYSICAL TEST DATA | JP-4 | JP-8 | I-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 | - |
| 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 | 0.0001 | 0.0011 | 0.06 |
| NITROGEN (TOTAL), PPM | 5 | 3 | 1 | 3 | 3600 |
| FLASH, °F | - | 100 | - | 210 | - |
| FREEZE POINT, °F | -72 | -70 | -76 | -10 | - |
| NET HT. OF COMB., BTU/LB | 18,760 | 18,610 | 19,050 | 18,730 | 18,500 |
| $H_2$ CONTENT, WT. % | 14.16 | 13.85 | NA | NA | NA |

# TABLE 5

## BASIS FOR PHASE IV ECONOMICS

### CAPITAL INVESTMENT

PLANT LOCATION - SALT LAKE CITY, UTAH

REFINERY CAPACITY - 100,000 BPSD RAW SHALE OIL

COST BASE - 1st QUARTER 1981

PLANT OFFSITES - 45% PLANT ONSITES MINUS COST OF SPECIFIED TANKAGE CAPACITY FOR STORING CRUDE AND PRODUCTS

FINANCING - 100% EQUITY

- INVESTMENT TIMING OVER THREE-YEAR CONSTRUCTION PERIOD

25% FIRST YEAR
50% SECOND YEAR
25% THIRD YEAR

INVESTMENT TAX CREDIT @ 10%

### WORKING CAPITAL

CRUDE INVENTORY - 21 DAYS STORAGE CAPACITY/14 DAY INVENTORY

PRODUCT INVENTORY - 14 DAYS STORAGE CAPACITY/ 7 DAY INVENTORY

CRUDE SHALE OIL - $40.00 PER BARREL

PRODUCT PRICE - PRODUCT VALUED AT ACTUAL COST

DEBT FINANCING - 15% (INCLUDING COST OF INITIAL CATALYST LOADING)

### CAPITAL RETURN

DISCOUNTED CASH FLOW RATE - 15%

PLANT SALVAGE VALUE - ZERO

PLANT DEPRECIATION - 13 YEARS SUM OF YEARS DIGITS

# TABLE 5 (CONT'D)

## BASIS FOR PHASE IV ECONOMICS

### OPERATING BASES

| | | |
|---|---|---|
| PLANT LIFE | - | 16 YEARS |
| PLANT OPERATING FACTORS | - | 50% OPERATING CAPACITY 1st YEAR |
| PLANT ON STREAM FACTOR | - | 90% |

### OPERATING COST BASES

| | | |
|---|---|---|
| PROCESS HEAT | - | REQUIREMENTS GENERATED INTERNALLY |
| COOLING WATER | - | 3¢/1000 GALLONS |
| ELECTRICITY | - | 4.5¢ KWHR |
| OPERATOR(1) | - | $12.00/MANHOUR |
| HELPERS(1) | - | $10.50/MANHOUR |
| SUPERVISION | - | 25% OF DIRECT LABOR |
| OVERHEAD | - | 100% OF DIRECT LABOR |
| TAXES | - | FEDERAL & STATE COMBINED @ 50% |
| MAINTENANCE, LOCAL TAXES & INSURANCE | - | 4.5% OF FIXED INVESTMENT |
| PRODUCT VALUES | - | ALL FUELS ARE EQUAL VALUE |
| BY-PRODUCT VALUES | - | AMMONIA $155.00 PER SHORT TON<br>SULFUR $105.00 PER LONG TON |

(1) BASED ON 4.2 SHIFT POSITIONS PLUS 10% RELIEF FOR CONTINUOUS OPERATION.

## TABLE 6

## PLANT CAPACITIES AND ESTIMATED FIRST QUARTER 1981 INVESTMENTS (PHASE IV)

| | MAX. JP-4 | | MAX. JP-8 | | JP-4 + OTHER FUELS | |
|---|---|---|---|---|---|---|
| | CAPACITY PSD | $\$ \times 10^6$ | CAPACITY PSD | $\$ \times 10^6$ | CAPACITY PSD | $\$ \times 10^6$ |
| $H_2$ PLANT (TPO), MMSCF/SD (100% $H_2$ BASIS) | 155.9 | 120.8 | 174.5 | 127.5 | 139.4 | 112.4 |
| $H_2$ PLANT (STEAM REFORMING), MMSCF/SD | 102.5 | 39.5 | 61.8 | 29.0 | 56.7 | 27.9 |
| SULFUR RECOVERY ST/SD | 112.2 | 11.3 | 112.5 | 11.0 | 110.7 | 10.9 |
| WASTE WATER TREATING, ST/SD, $NH_3$ | 246.0 | 15.7 | 246.4 | 16.0 | 119.4 | 14.0 |
| MAIN HYDROTREATER & $H_2S$ RECOVERY, MBPSD | 100.0 | 183.8 | 100.0 | 183.8 | 100.0 | 183.8 |
| ATM. & VAC. DISTN., MBPSD | 103.9 | 49.7 | 103.9 | 49.7 | 103.9 | 49.7 |
| DIST. HYDROTREATER, MBPSD | 27.1 | 37.3 | 29.1 | 47.8 | 19.8 | 30.9 |
| HCl TREATER, MBPSD | 71.9 | 2.6 | 69.9 | 2.5 | 76.0 | 2.7 |
| HYDROCRACKER & ATM. DISTN., MBPSD FRESH FEED | 69.3 | 107.7 | 67.3 | 103.5 | 68.3 | 97.7 |
| SUBTOTAL | | 581.4 | | 570.5 | | 530.0 |
| TANKAGE, MM BBLS. | 3.6 | 35.6 | 3.6 | 35.3 | 3.6 | 35.6 |
| TOTAL ON-SITES | | 617.0 | | 605.8 | | 565.6 |
| OFF-SITES (45% ON-SITES LESS TANKAGE) | | 261.6 | | 256.7 | | 238.5 |
| TOTAL CAPITAL INVESTMENT | | 878.6 | | 862.5 | | 804.1 |

## TABLE 7

## PHASE IV COST COMPARISON FOR MANUFACTURING MILITARY FUELS FROM RAW OCCIDENTAL SHALE OIL

BASIS: OPTIMIZED 100,000 BPSD REFINERY CRUDE CAPACITY (90,000 BPCD)

| | MAX. JP-4 | MAX. JP-8 | JP-4 AND OTHER FUELS |
|---|---|---|---|
| TOTAL PLANT INVESTMENT, $ $10^6$ | | | |
| Plant | 878.6 | 862.5 | 804.1 |
| Catalysts | 19.3 | 19.0 | 16.8 |
| Working Capital | 98.1 | 97.1 | 91.0 |
| TOTAL | 996.0 | 978.6 | 911.9 |
| MANUFACTURING COSTS - $/CD | | | |
| Direct Labor | 15,538 | 15,538 | 15,538 |
| Purchased Power and Cooling Water | 91,140 | 91.701 | 74,081 |
| Catalyst, Chemicals & Royalties | 47,052 | 47,160 | 44,038 |
| Overhead @ 100% Direct Labor | 15,538 | 15,538 | 15,538 |
| Maint., Local Taxes & Insurance | 76,064 | 74,689 | 69,730 |
| Depreciation (Average 13 years) | 188,535 | 185,121 | 172,835 |
| Subtotal | 433,867 | 429,747 | 391,760 |
| Less $NH_3$ & S (Credit) | (50,673) | (51,214) | (42,531) |
| Direct Costs | 383,194 | 378,533 | 349,229 |
| Liquid Product, $/Bbl | 3.80 | 3.85 | 3.66 |
| TOTAL LIQUID FUELS, BPCD | 100,771 | 98,306 | 95,527 |
| TOTAL MANUFACTURING COSTS, $/Bbl Product[1] | 10.30 | 10.38 | 9.94 |
| Adjusted Crude Cost, $/Bbl Product | 41.07 | 41.87 | 39.83 |
| TOTAL PRODUCT COST | | | |
| $/Bbl | 51.37 | 52.25 | 49.77 |
| ¢/Gal | 122.3 | 124.4 | 118.5 |

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[1] Total Manufacturing Costs Computed on the Basis Shown in Table 5 for Developing Phase IV Economics

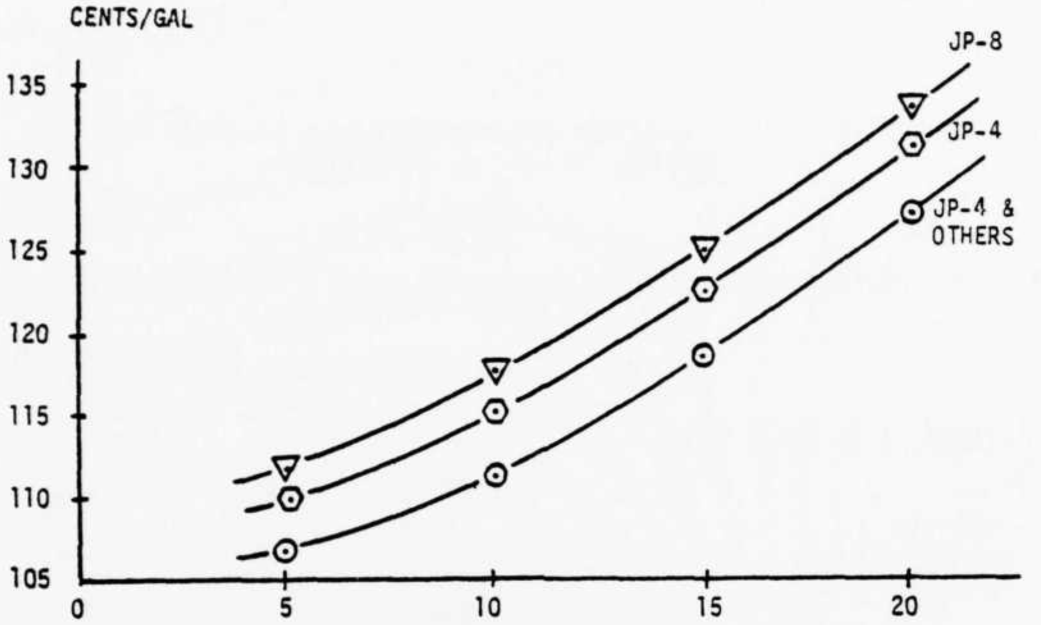

FIGURE 6

SENSITIVITY OF FUEL COST TO
CHANGES IN INTEREST RATE
OF RETURN (IRR)

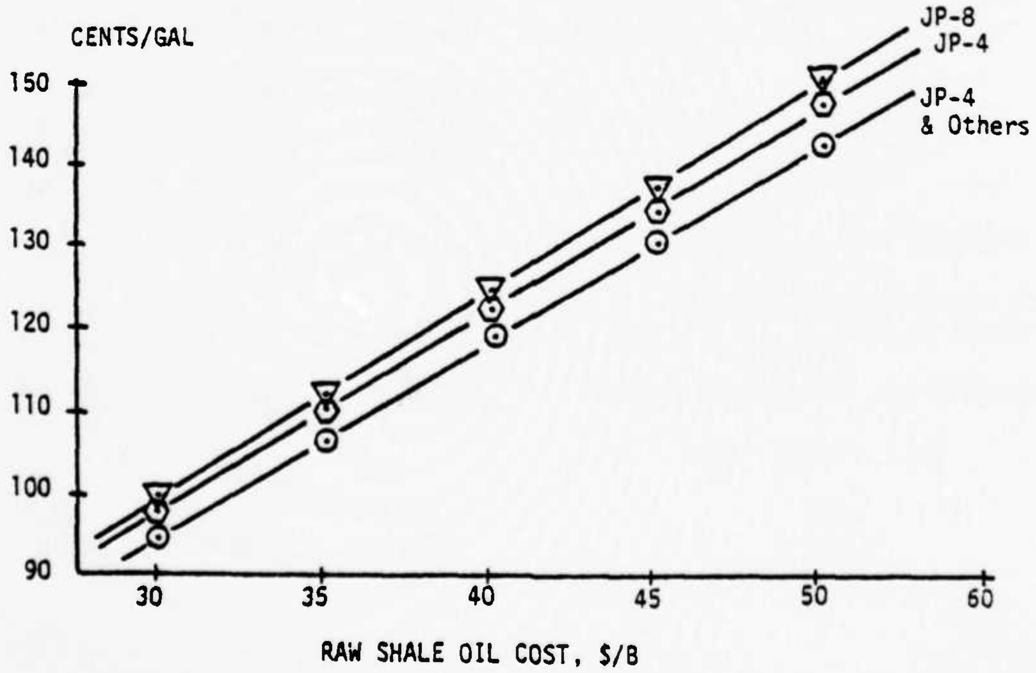

FIGURE 7

SENSITIVITY OF FUEL COST TO
CHANGES IN PRICE OF RAW SHALE OIL

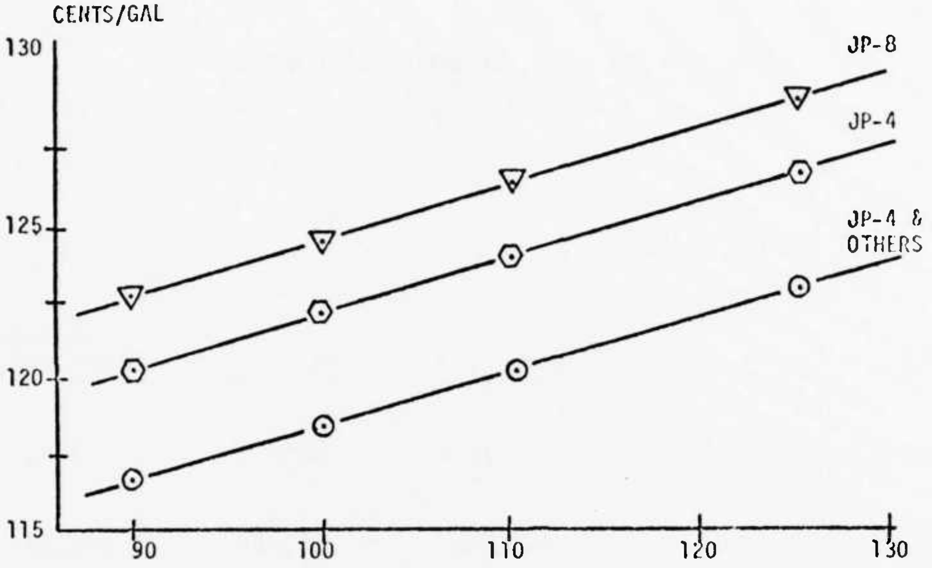

FIGURE 8

SENSITIVITY OF FUEL COST TO
CHANGES IN CAPITAL INVESTMENT

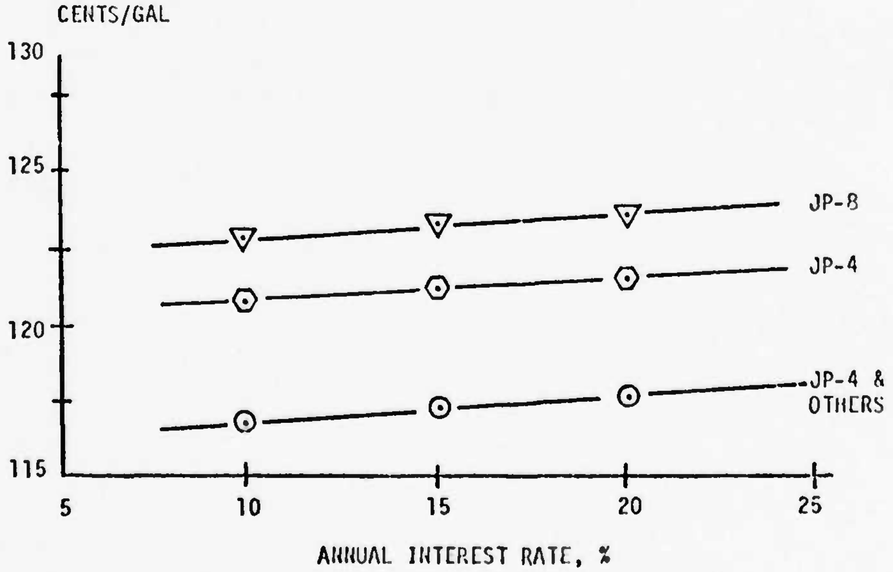

FIGURE 9

SENSITIVITY OF FUEL COST TO CHANGES IN
ANNUAL INTEREST RATE OF WORKING CAPITAL

## TABLE 8

## EFFECT OF INTEREST ON BORROWED CAPITAL ON PRODUCT COSTS

BASIS: PHASE IV ECONOMICS BASIS

| Major Products | MAX. JP-4 | MAX. JP-8 | JP-4 AND OTHER FUELS |
|---|---|---|---|
| Plant Investment, $\$ \times 10^6$ | 878.6 | 862.5 | 804.1 |
| Total Liquid Fuels, BPCD | 111,968 | 109,224 | 106,141 |
| Product Cost, ¢/Gallon Working Capital Only @ 15% Interest Rate | 122.3 | 124.4 | 118.5 |
| Working Capital and 100% Plant Investment @ 15% Interest Rate | 131.7 | 133.9 | 127.6 |
| Δ Cost | 9.4 | 9.5 | 9.1 |

# TABLE 9

## SUMMARY

BASIS: PHASE IV ECONOMICS

| Processing Route For | MAX. JP-4 | MAX. JP-8 | JP-4 AND OTHER FUELS |
|---|---|---|---|
| Raw Shale Oil Input to Main Hydrotreater, BPSD | 100,000 | 100,000 | 100,000 |
| TOTAL REFINERY INPUT | 114,973 | 114,334 | 105,677 |
| Products, BPSD | | | |
| JET FUEL | 108,504 | 62,141 | 83,910 |
| TOTAL LIQUID PRODUCTS | 111,968 | 109,224 | 106,141 |
| Liquid Fuel Yields as Vol % Crude Processed | | | |
| JET FUEL | 108.5 | 62.1 | 83.9 |
| TOTAL FUELS | 112.0 | 109.2 | 106.1 |
| Products as vol % Total Energy Input (Crude + Fuel + Utilities Converted to FOE) | | | |
| JET FUEL | 94.4 | 54.3 | 79.1 |
| TOTAL LIQUID PRODUCTS | 97.4 | 95.5 | 100.7 |
| Product Cost, $/B | 51.37 | 52.25 | 49.77 |
| ¢/gal | 122.3 | 124.4 | 118.5 |
| Overall Thermal Efficiency, % | 81.5 | 80.7 | 86.7 |
| Plant Investment, $/SDB | 8786 | 8625 | 8041 |

## TABLE 10

## UNCERTAINTIES

1. ARSENIC DISPOSAL - SPENT CATALYST FROM GUARD REACTOR WILL HAVE A HIGH ARSENIC CONTENT. DISPOSAL OR REGENERATION OF CATALYST MAY PRESENT PROBLEMS.

2. RAW SHALE OIL IS PROBABLY NOT SUITABLE FOR USE AS FUEL TO FURNACES FOR MANUFACTURING HYDROGEN BY STEAM REFORMING.

3. CONTINUOUS HCl EXTRACTION PROCESS NOT DEMONSTRATED IN THE PILOT PLANT.

4. RESIDUAL CHLORIDE CONTENT IN HCl RAFFINATE VARIED FROM 70 TO 800 PPM. ADDITIONAL WORK NEEDED TO MINIMIZE AND CONTROL CONCENTRATION. EFFECT OF CHLORIDE CONTENT IN FEED ON CATALYST LIFE IN R-1 OF HYDROCRACKER NOT DETERMINED.

5. EXTINCTION RECYCLE OF HYDROCRACKER BOTTOMS NOT DEMONSTRATED IN PILOT PLANT. IT PROBABLY CAN BE DONE TO MAXIMIZE JP-4, BUT NOT FOR JP-8 DUE TO BUILD UP OF AROMATICS AND WAX ON RECYCLE STREAM. YIELDS AND OPERATING CONDITIONS WERE OBTAINED FROM SUNTECH'S HYDROCRACKING MATH MODEL.

6. THE LP OPTIMIZATION PROGRAM IS PRICE DRIVEN AND THE OPTIMIZED RESULTS ARE ONLY AS REALISTIC AS THE ECONOMICS USED. THE USE OF MARKET VALUES FOR PRODUCTS WILL GIVE A MORE REALISTIC OPTIMIZED PROCESSING SCHEME.

7. A CONTINGENCY WAS NOT INCLUDED IN THE PHASE IV ECONOMICS. A MINIMUM CONTINGENCY OF 25% IS RECOMMENDED FOR NEW TECHNOLOGY ENERGY PROCESS PLANTS SUCH AS A SHALE OIL UPGRADING FACILITY.

## TABLE 11

## SUMMARY AND CONCLUSIONS

1. LP RESULTS SHOWED THAT THE OPTIMAL PROCESSING SCHEME FOR MAXIMIZING JP-4 AND JP-8 WAS WITH THE RAW SHALE OIL HYDROTREATER OPERATING AT 2200 PPM TOTAL NITROGEN IN THE EFFLUENT, AND FOR JP-4 AND OTHER FUELS WAS WITH THE RAW SHALE OIL HYDROTREATER OPERATING AT 6400 PPM TOTAL NITROGEN IN THE EFFLUENT.

2. TOTAL PRODUCT YIELDS AS PERCENT OF TOTAL REFINERY INPUT FOR MAX JP-4, MAX JP-8 AND JP-4 AND OTHER FUELS WERE 97.4, 95.5 AND 100.7 RESPECTIVELY.

   HYDROGEN CONSUMPTION WAS 2584, 2363 AND 1960 SCF/Bbl FOR THE THREE CASES.

   OVERALL REFINERY THERMAL EFFICIENCIES WERE 81.5, 80.7 AND 86.7 RESPECTIVELY.

3. ECONOMICS WERE DEVELOPED FOR A 100,000 BPSD REFINERY USING A FIRST QUARTER 1981 COST BASE AND $40 PER BBL FOR RAW SHALE OIL. TOTAL PRODUCT COST VARIED FROM $1.24 TO $1.19 PER GALLON, DEPENDING ON THE REFINERY PRODUCT SLATE.

4. SENSITIVITY ANALYSIS SHOWED THAT PRODUCT PRICE WAS SENSITIVE TO THE FOLLOWING IN THE ORDER PRESENTED:

   - RAW SHALE OIL PRICES
   - DISCOUNTED CASH FLOW (IRR)
   - VARIATIONS IN CAPITAL INVESTMENT
   - ANNUAL INTEREST RATE

5. FINANCING 100% OF CAPITAL INVESTMENT AT 15% ANNUAL INTEREST RATE INCREASED PRODUCT PRICES BY 9.5¢/GALLON.

## VI

# JET FUELS FROM SHALE OIL BY SINGLE-STAGE HYDROCRACKING

By

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# JET FUELS FROM SHALE OIL BY SINGLE-STAGE HYDROCRACKING

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## ABSTRACT

Extensive screening of novel catalysts has led to the development of a single catalyst capable of the direct upgrading of a whole shale oil into high yields of jet fuels on a once-through basis. To maximize jet fuels a catalyst must have the ability to sequentially saturate, denitrogenate, and hydrocrack the feedstock in the presence of high levels of contaminants such as organic nitrogen compounds and ammonia while maintaining high selectivity toward jet fuel boiling-range material. Catalysts incorporating these functions, along with high temperature stability, were developed by optimization of both chemical and physical properties. The effectiveness of the final single catalyst for the direct upgrading of an Occidental shale oil has been demonstrated in a 100-day test. The feed, containing approximately 15 wt% JP-4 material and 13,000 ppm nitrogen, was upgraded to a water-white product containing approximately 75 wt% JP-4 material and 1 to 3 ppm nitrogen. The hydrogen consumption was 1800 to 1900 SCFB.

## INTRODUCTION

Development of new processes and catalysts to enable U.S. refiners to produce conventional products from unconventional raw materials such as shale oil, tar sands, coal liquids, and heavy petroleum residues is especially important now because of national concerns for the price, quality, and stability of supply of petroleum products. Various sources have estimated that U.S. reserves of shale and tar sands oil are more than four times that of conventional oil and could provide a secure source of energy for about 100 years if economic means can be found to convert these reserves to usable products.

Given this impetus, the U.S. Air Force and Wright-Patterson Air Force Base entered into a 19-month contract with Amoco Oil late in 1979 to develop a catalyst for increased jet fuel production from shale oil. Although other companies have conducted more extensive process and design work, Amoco's investigation was limited to the development of improved catalysts. However, in order to test catalysts, a processing scheme was required, and we chose to develop a single catalyst capable of the direct conversion of the shale oil into jet fuel boiling-range material on a once-through basis.

The contract called for four major tasks:

I. A process variable study on existing proprietary catalysts.

II. A catalyst composition study, i.e., metals concentration and support.

III. A catalyst physical properties study.

IV. An activity maintenance test on the preferred catalyst.

Results have been presented previously for the first two tasks.

Table I shows analytical data for three shale oils. Although such oils are basically similar to petroleum crudes with respect to chemistry (i.e., the same types of compounds are present but in different relative amounts), they do exhibit some unique properties.

Shale oils typically have high pour points dictating on-site processing or the use of wax modifiers or heated transportation pipelines for off-site processing. The H/C atomic ratios are on the low end of the scale for petroleum crudes and hence upgrading will require additional hydrogen to produce equivalent product qualities. The high nitrogen content of up to two or more percent is an order of magnitude higher than for petroleum crudes and represents the major upgrading difficulty since organic nitrogen compounds act as severe poisons for downstream catalytic cracking and reforming processes and cause product instability.

Thus, to maximize jet fuels from shale oils, a catalyst must have the ability to sequentially saturate, denitrogenate, and hydrocrack the feedstock in the presence of high levels of contaminants such as organic nitrogen compounds and ammonia while maintaining high selectivity towards the jet fuel boiling-range material.

## RESULTS AND DISCUSSION

The Occidental shale oil was used throughout the study. Although the oil contained 26 ppm arsenic and about 60 ppm iron plus nickel, it was not pretreated nor was a guard chamber used to remove these contaminants.

The initial process variable study on existing proprietary catalysts indicated that a catalyst containing cobalt, chromium, and molybdenum salts on an alumina support could effectively remove nitrogen and effect moderate conversion of the feed into JP-4 jet fuel boiling-range material. Initial product qualities at one set of processing conditions are shown in Table II. For this catalyst, nitrogen removal was found to be first order in nitrogen and hydrogen pressure.

The next study on catalyst composition included optimization of the metal oxide concentrations and the support composition. Catalysts were prepared with various combinations of metal oxides on alumina and screened at 780°F, 1800 psig and 0.5 LHSV. The optimized metal oxide loadings were determined to be 1.5% cobalt oxide, 10% chromium oxide and 15% molybdenum oxide. Although the presence of the chromium oxide actually lowered denitrogenation activity, the 10% level was required to impart high temperature stability to the catalyst.

For the support composition, catalysts with the optimized metal loadings were prepared on different supports. The most active catalysts were prepared on supports of alumina, 20% silica on alumina, and 30% Ultrastable (US) sieve on alumina. Results are shown in Figure 1 in a plot of relative activity for denitrogenation versus days on oil. The activities given are based on first-order kinetics and are relative to the 1.5% CoO/10% $Cr_2O_3$/10% $MoO_3$ catalyst (Activity - 100) prepared on the same alumina as was used for the catalysts previously mentioned. These results indicate a 60% to 100% increase in nitrogen removal activity when acid functions are introduced into the support.

Table III shows how the increased activity affects product qualities for these three systems. Compared to the alumina system, the 20% silica/alumina and the 30% US sieve/alumina catalysts gave almost complete nitrogen removal. The presence of silica did not, however, affect other product qualities whereas incorporation of the US sieve resulted in a significant increase in cracking activity, resulting in a lower pour point and a high yield of JP-4 boiling-range material.

Based on these results, the US sieve-containing catalyst appeared promising for the direct hydrocracking of the shale oil. Consequently, additional catalysts with various US sieve contents and the optimized metal loadings were prepared and screened at 780°F, 1800 psig and 0.5 LHSV. Figures 2 and 3 summarize pertinent results.

The effect of increasing sieve content from 20 to 50 wt% was to almost double the JP-4 yields from approximately 40 to 77 wt% with a corresponding decrease in both the diesel and gas oil fractions. The $C_1$-$C_4$ gas make increased moderately from 3.7 to 5.6 wt%. It should be noted that the yield structures for the catalyst containing 20 wt% sieve were not much different from the pure alumina based catalyst. At the 50% sieve level, approximately 95% of the product boiled below 650°F. As expected, the increase in JP-4 yield was accompanied by a smooth increase in the hydrogen consumption from approximately 1400 SCFB to approximately 1900 SCFB, Figure 3.

For the three sieve catalysts, activity maintenance for jet fuel production is detailed in Figure 4. Both the 20% and 30% sieve-containing catalysts initially give high yields of JP-4 but rapidly lost activity to give lined out yields of approximately 50 and 35 wt% JP-4. For comparison, the nonsieve-containing catalyst yielded a constant 38 wt% JP-4 over the same time period. The 50% US sieve catalyst maintained the higher activity for JP-4 production and appeared to undergo a less severe loss in activity.

The estimated JP-4 yields used in Figure 4 were obtained from Figure 5, which represents a correlation between JP-4 yields from simulated distillation data and whole product API gravities. The solid data points represent all previously tested US sieve-containing catalysts whereas the open points represent all other catalysts previously tested, independent of support type or metals loading, and all 50% US sieve alumina catalysts tested subsequently. The correlation can be represented by:

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

Simulated distillation data agreed within one to two percentage points with actual distillation data for all samples so that Figures 4 and 5 represent actual yields of JP-4 to a high degree of accuracy. This correlation proved valuable for monitoring catalyst cracking activities on a daily basis.

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

To this point, catalyst physical properties were kept within fairly narrow ranges for sets of catalyst within each task. With the metals optimized, and the support type and composition determined, the next task was designed to optimize the support physical properties.

Eight supports, consisting of 50% US sieve in alumina, were prepared to give a range for each of three physical properties as detailed in Table IV. These variations were achieved by modification of the alumina component, since modification of the sieves themselves could destroy their original nature and their inherent activity for cracking.

Data for the screening runs at 780°F and 1800 psig are given in Table V. Since the previous tasks had demonstrated that high sieve-containing catalysts could reduce the nitrogen content to less than 10 ppm at 0.5 LHSV, the possibility existed that all eight of the above-detailed catalysts could exhibit similar high nitrogen removal at that space velocity and hence negate the purpose of the task. To avoid that possibility, each catalyst was additionally tested at the higher space velocity. At constant sieve content, the relationship between JP-4 yield and hydrogen consumption for these eight catalysts is shown in Figure 6. Hydrogen consumption appears to increase linearly with JP-4 yields in the range of approximately 40 to 70 wt%. (See also Figure 3.) Below approximately 40 wt% JP-4, hydrogen consumption increased with little increase in product JP-4, probably as a result of saturation reactions required prior to cracking reactions. Above approximately 70 wt% JP-4, hydrogen usage appears to increase more rapidly than JP-4 content, probably as a result of additional long-chain paraffin cracking which, in addition, reduces product pour point.

A relationship between pour point and JP-4 yield for these eight US sieve-containing catalysts is given in Figure 7, which indicates a rapid drop in JP-4 yield for whole products with pour points greater than about 40°F. Data for the 20%, 30%, and 50% US sieve catalysts tested previously can also be represented by Figure 7.

The effect of product nitrogen on JP-4 yield is shown in Figure 8. The results indicate that JP-4 yield remained at approximately 30 wt% for product nitrogen above 600 ppm and increased with decreasing nitrogen content. To produce a product with approximately 50 wt% percent JP-4, product nitrogen must be reduced to approximately 10 ppm. Product nitrogen must be virtually eliminated to produce JP-4 yields of approximately 70 wt% or more.

Hydrogen usage to achieve these levels of product nitrogens is shown in Figure 9. About 1550 SCFB of hydrogen was required for 10 ppm product nitrogen (50% JP-4 yield). About 400 SCFB additional hydrogen was required to decrease product nitrogen to near zero and to increase JP-4 yields to 80%. These results are instructive in that correlations important to the overall hydrocracking scheme have been developed within this set of catalysts.

Nitrogen removal kinetic plots for these catalysts are shown in Figure 10. Of the eight catalysts tested, only one, 3838-023, performed well at both 0.5 and 0.75 LHSV with respect to nitrogen removal in particular, conversion, and activity maintenance at the lower throughput. Nitrogen removal for this catalyst appears to be first order as shown in Figure 10, whereas all other catalysts display less than first-order (or mixed-order) kinetics. This type of kinetic behavior is perhaps a reflection upon nitrogen removal efficiency and suggests an axial dependence on nitrogen content, or an accelerating nitrogen removal reaction promoted by the sieve itself.

In general, it is difficult to obtain correlations between the physical properties of catalysts containing molecular sieves and catalyst performance because of the complexity of the systems. Figure 11, however, does reflect a correlation between catalyst average pore diameters (calculated as $4V \times 10^4/A$) and product nitrogen. At 0.75 LHSV, the correlation is reasonable but is somewhat less so at 0.5 LHSV. Both sets of results indicate that greatest nitrogen removal occurs with the catalysts of smallest average pore diameters. The two best catalysts in the series, 3838-023 and 3838-039, have APD's close to 70°A, but only the former is "efficient" at both space velocities and has the highest cracking activity and best activity maintenance. Comparison of the pore size distributions for these two catalysts indicates a sharper distribution of pores for catalyst 3838-023 when compared to catalyst 3838-039. All other catalysts in this series, with one exception, have broader pore size distributions. Other catalyst physical properties, namely surface area and pore volumes, did not show any correlation with product nitrogens.

Results from the catalyst physical properties study indicated that for high denitrogenation and cracking activity the preferred support of 50% US sieve in alumina should have pores of average pore diameters near 70°A combined with a high surface area and a sharp pore size distribution.

Some data for an activity maintenance test using the preferred catalyst are detailed in Table VI. Start-of-run conditions were 0.4 LHSV, 2000 psig hydrogen, and 770°F and were chosen to maximize hydrogenation and hydrocracking reactions while allowing for an increase in reactor temperature in case catalyst deactivation occurred.

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

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

Figure 12 shows product nitrogens as a function of days on oil. With the exception of those upsets which affected product nitrogens (shown as solid points), product nitrogens were maintained generally in the 1 to 3 ppm range throughout the test. As indicated previously (Figure 8), 10 ppm product nitrogen would reduce JP-4 yields to approximately 50 wt% or less whereas a JP-4 yield of $\geq 70$ wt% would require $\leq 2$ ppm nitrogen in the product. High cracking activity to produce JP-4 is critically dependent upon very low product nitrogen levels.

Daily JP-4 yields, estimated from product API gravities and Figure 5, are shown in Figure 13. The solid symbols represent upsets affecting JP-4 yields or cracking activity. The following points can be drawn from Figure 13.

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

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

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

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

In order to calculate catalyst life at a specified JP-4 yield, temperature response factors need to be calculated. This was done by using the data at the end of the test at 785°F (period 93), 790°F (period 96), and 780°F (period 101) assuming zero-order kinetics, no nitrogen inhibition in the actual cracking zone, and constant activity. Hydrocracking reactions in the presence of nitrogen are generally zero order over the total catalyst system, and in this case all samples contained $<10$ ppm nitrogen.

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

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

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

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

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

## CONCLUSIONS

A single-catalyst system capable of direct hydrocracking of a whole shale oil containing large amounts of nitrogen has been developed. The novel catalyst, consisting of cobalt, chromium, and molybdenum salts on a base of 50% US sieve in alumina is multifaceted in that it combines both the saturation and denitrogenation activity of alumina with the cracking activity of the sieve. The combination is more effective than alumina alone for hydrocracking with the cracking zone confined to that part of the bed at the bottom where the nitrogen content has been reduced to <10 ppm. This cracking zone would vary with changes in process conditions.

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

* * *

# 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 |
| O, Wt% | 1.39 | 1.16 | 1.33 |

# Table II

## Initial Product Qualities

### Co/Cr/Mo on Alumina

(1800 psig, 0.55 LHSV, 790°F)

| | Product | Feed |
|---|---|---|
| API° | 39 | 23.8 |
| Pour Point, °F | 80 | 60 |
| Nitrogen, ppm | 116 | 13,200 |
| JP-4, Wt%* | 37 | 15.5 ** |
| 650°F-, Wt% | 74 | 44 |
| SCFB Hydrogen | 1400 | - |

* 20% distilled at 290°F, 90% distilled at 470°F

** Heavy JP-4 fraction, IBP of 290°F

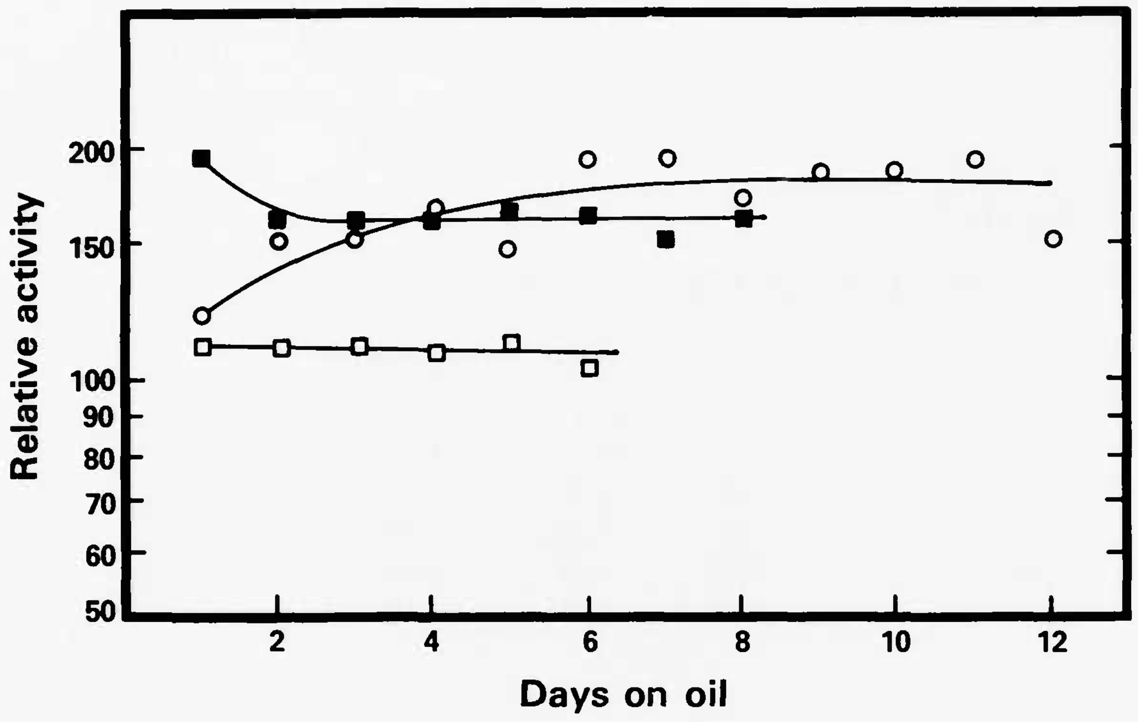

Figure 1 — Effect of Support Type on Relative Denitrogenation Activity for 1.5/10/15 Catalysts, □, Alumina; ○, 30% US Sieve Alumina; ■, 20% Silica Alumina

## Table III

## Effect of Support Composition on Product Qualities

| | $Al_2O_3$ | 20% $SiO_2$/ $Al_2O_3$ | 30% US Sieve/ $Al_2O_3$ |
|---|---|---|---|
| API° | 39.2 | 39.7 | 44.6 |
| Nitrogen, ppm | 83 | <10 | < 5 |
| Pour Point, °F | 80 | 65 | 30 |
| JP-4, Wt% | 38 | 38 | 54 |
| 650°F-, Wt% | 76 | 77 | 87 |
| SCFB Hydrogen | 1400 | 1400 | 1660 |

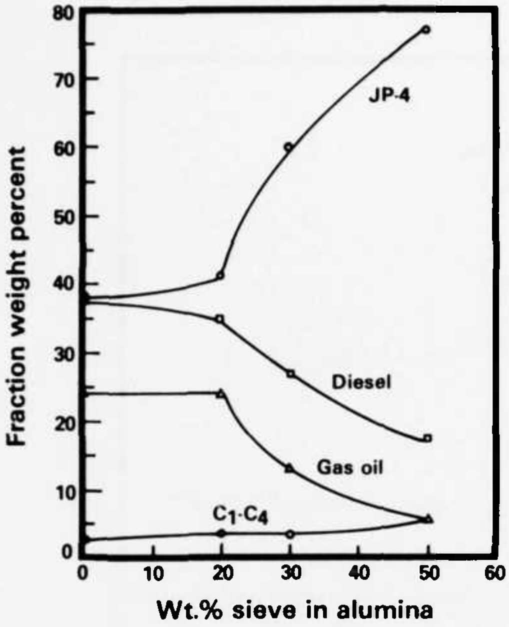

Figure 2 — Product Yield Structures as a Function of US Sieve Content in the Support

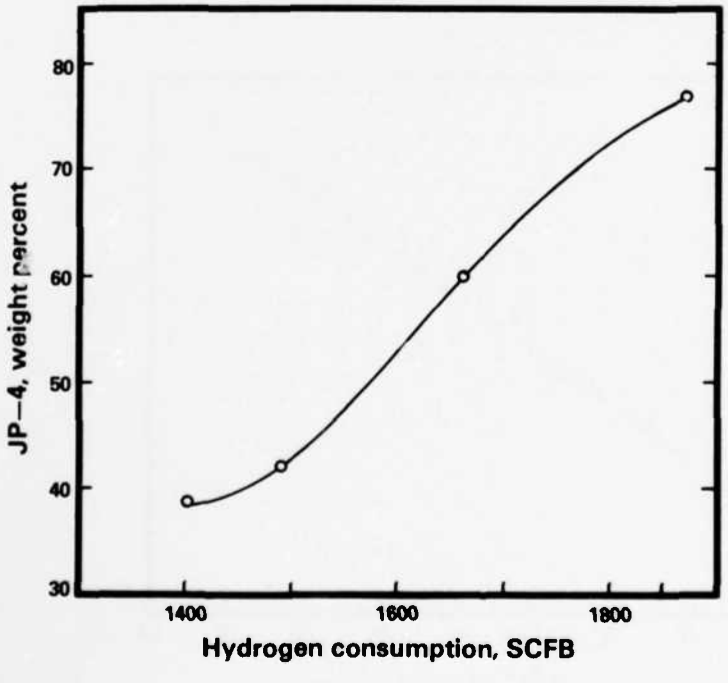

Figure 3 — Correlation Between JP-4 Yields and Hydrogen Consumption for Catalysts Containing 0, 20, 30, and 50% US Sieve

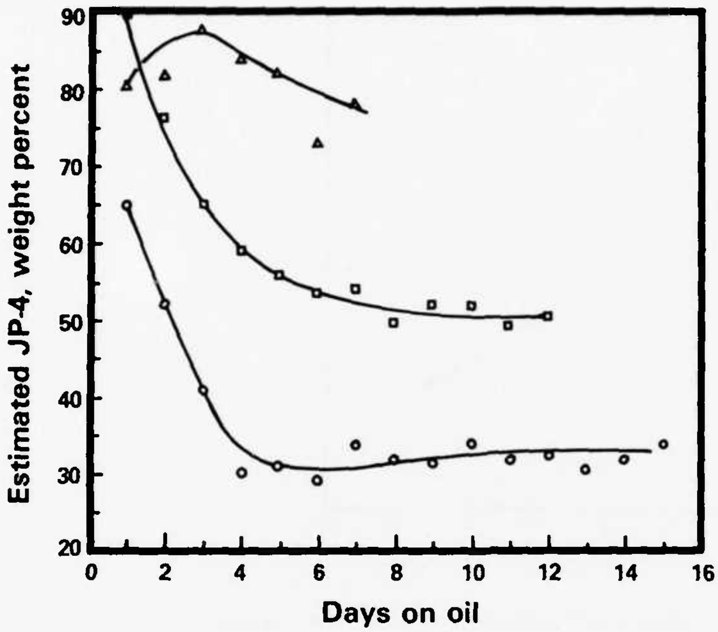

Figure 4 — Estimated Daily Yields of JP-4 for Catalyst of Different Sieve Content, ○, 20%; □, 30%; and △, 50% US Sieve

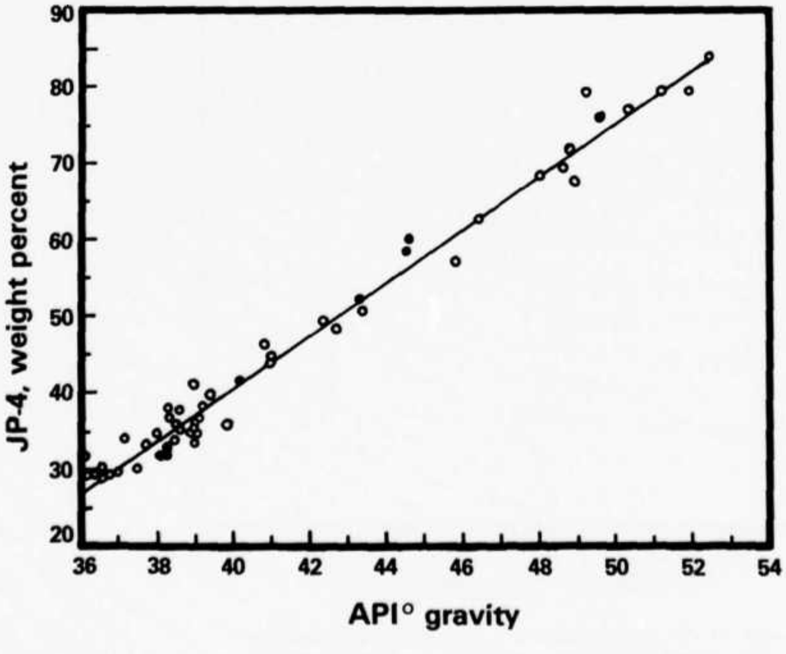

Figure 5 — Correlation Between Product API° Gravities and JP-4 Yields

## Table IV

## Catalyst Physical Properties

(50% US Sieve/alumina)

| Catalyst ID 3838- | Surface Area m²/g | Pore Volume cc/g | Avg Pore Diameter (4 V/A), °A |
|---|---|---|---|
| 023 | 280.5 | 0.477 | 68.0 |
| 028 | 255.2 | 0.545 | 85.5 |
| 030 | 222.4 | 0.505 | 90.8 |
| 031 | 312.5 | 0.824 | 105.4 |
| 034 | 305.0 | 0.589 | 77.2 |
| 035 | 276.3 | 0.784 | 113.4 |
| 037 | 280.4 | 0.710 | 101.3 |
| 039 | 234.0 | 0.417 | 71.4 |

## Table V

## Product Qualities from Catalysts with Different Physical Properties

| Catalyst ID 3838- | Nitrogen, ppm | Pour Point °F | 650°F-, Wt% | JP-4, Wt% | SCFBH |
|---|---|---|---|---|---|
| **0.5 LHSV** | | | | | |
| 023 | 1 | -50 | 92.5 | 79.5 | 1930 |
| 028 | 4 | 35 | 86.5 | 62.7 | 1670 |
| 030 | 600 | 75 | 65.6 | 29.6 | 1190 |
| 031 | 76 | 70 | 72.5 | 36.8 | 1390 |
| 034 | 5 | 55 | 71.2 | 50.6 | 1520 |
| 035 | 46 | 65 | 75.6 | 43.9 | 1380 |
| 037 | 77 | 70 | 74.0 | 39.9 | 1360 |
| 039 | 1 | 40 | 79.5 | 57.1 | 1660 |
| **0.75 LHSV** | | | | | |
| 023 | 44 | 75 | 67.5 | 33.8 | 1310 |
| 028 | 1510 | 75 | 63.0 | 30.1 | 1300 |
| 030 | 1240 | 75 | 65.5 | 29.4 | 1190 |
| 031 | 985 | 75 | 62.6 | 30.1 | 1200 |
| 034 | -- | -- | -- | -- | -- |
| 035 | 1950 | 75 | 64.5 | 29.3 | 1120 |
| 037 | 1560 | -- | 66.4 | 28.3 | 1150 |
| 039 | 289 | 75 | 60.4 | 33.3 | 1260 |

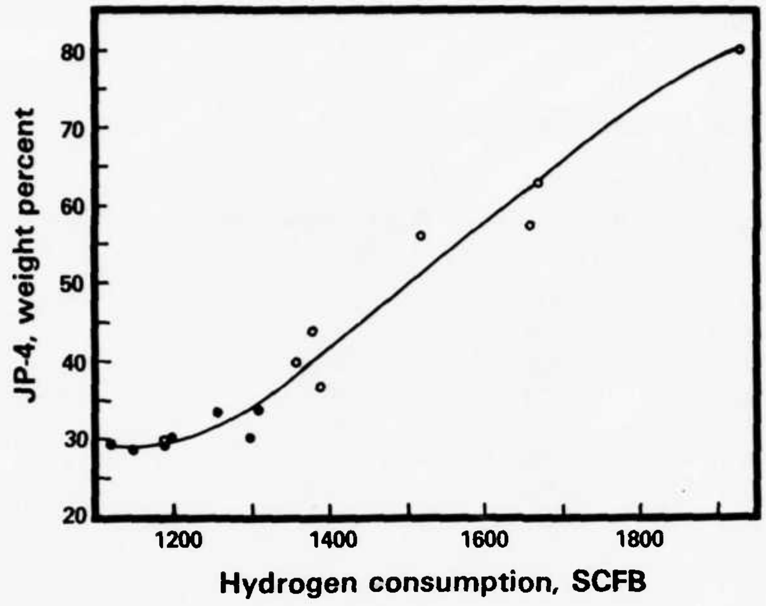

Figure 6 — Correlation Between JP-4 Yields and Hydrogen Consumption for Catalysts Containing 50% US Sieve, ●, 0.75 LHSV; ○, 0.5 LHSV

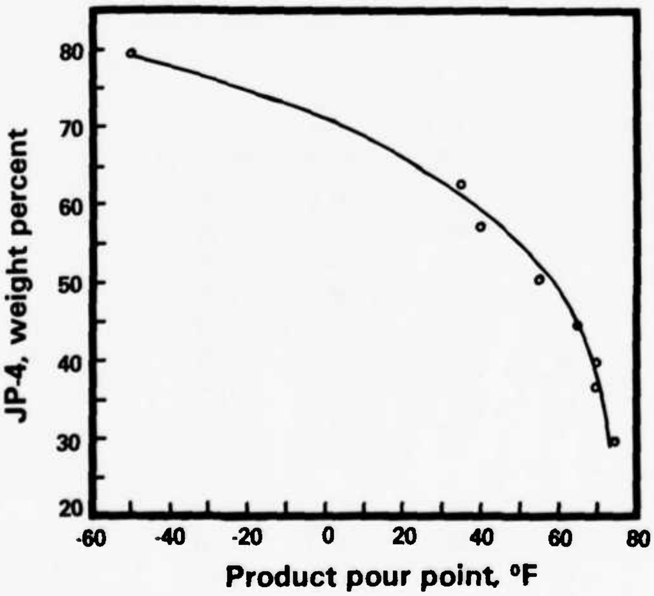

Figure 7 — Correlation Between Product Pour Point and JP-4 Yields for Catalysts Containing 50 % US Sieve

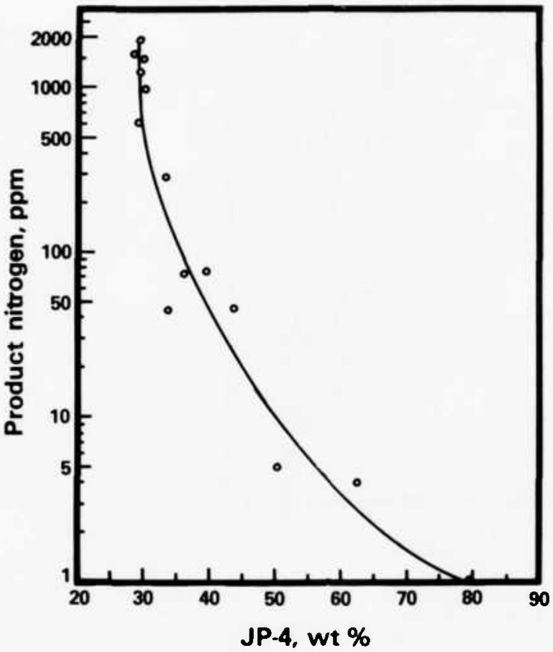

Figure 8 — JP-4 Yields as a Function of Product Nitrogen for Catalysts Containing 50% US Sieve

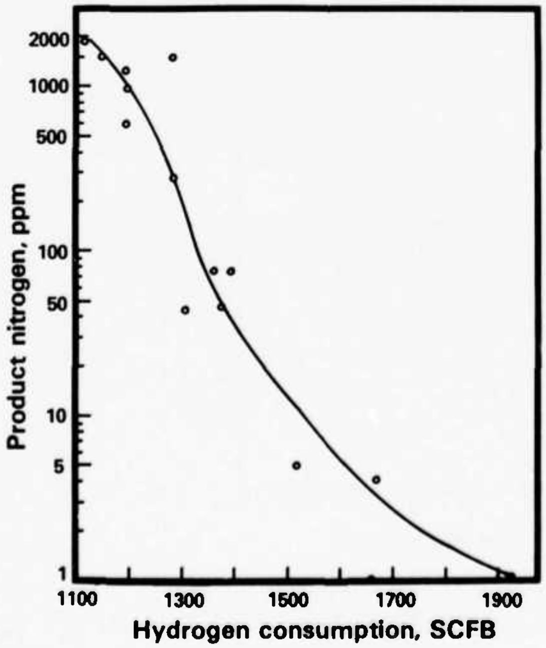

Figure 9 — Hydrogen Consumption as a Function of Product Nitrogen for Catalyst Containing 50% US Sieve

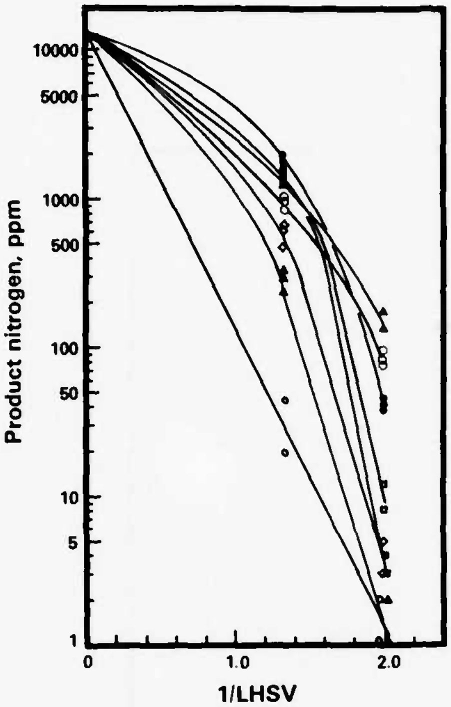

Figure 10 — Effect of Space Velocity on Product Nitrogens for Catalyst with Different Physical Properties.
Catalysts 3838-023 ( ○ ); -028 ( □ ); -030 ( △ ); -031 ( ○ ); -034 ( ◇ ); -035 ( ● ); -037 ( ■ ); -039 ( ▲ ).

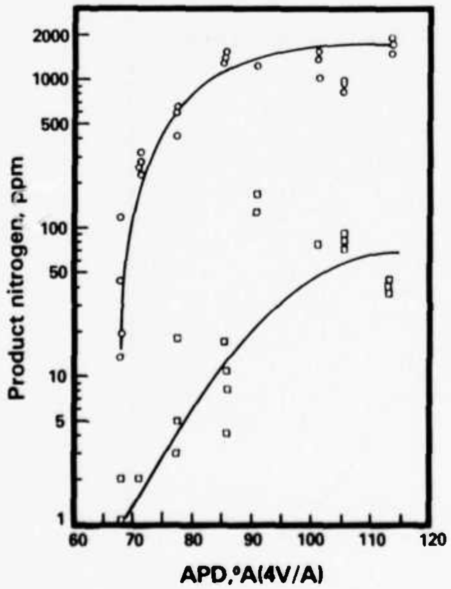

Figure 11 — Correlation Between Catalyst Average Pore Diameters and Product Nitrogen for 50% US Sieve Alumina Catalysts, ○, 0.75 LHSV; □, 0.5 LHSV.

## Table VI

## Product Qualities from the Activity Maintenance Test

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

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

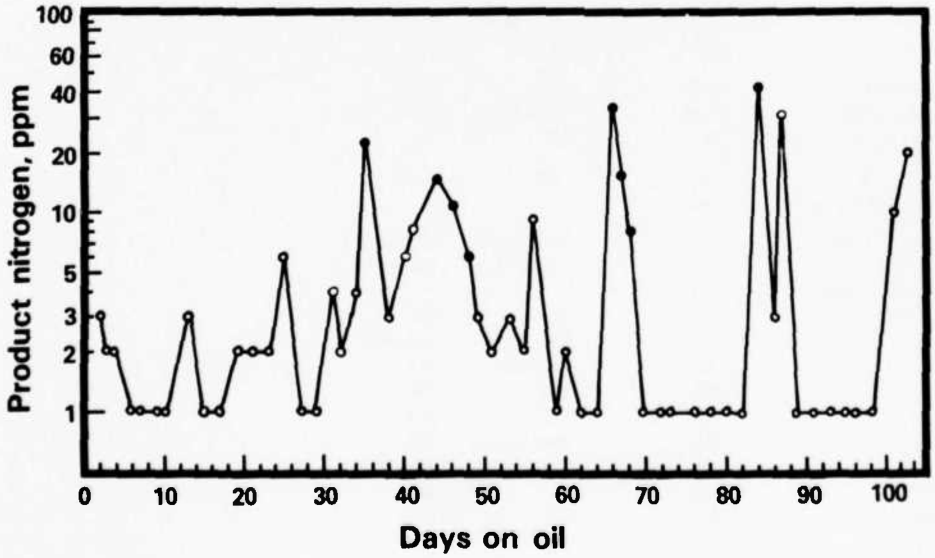

Figure 12 — Product Nitrogen as a Function of Days on Oil for the Activity Maintenance Test

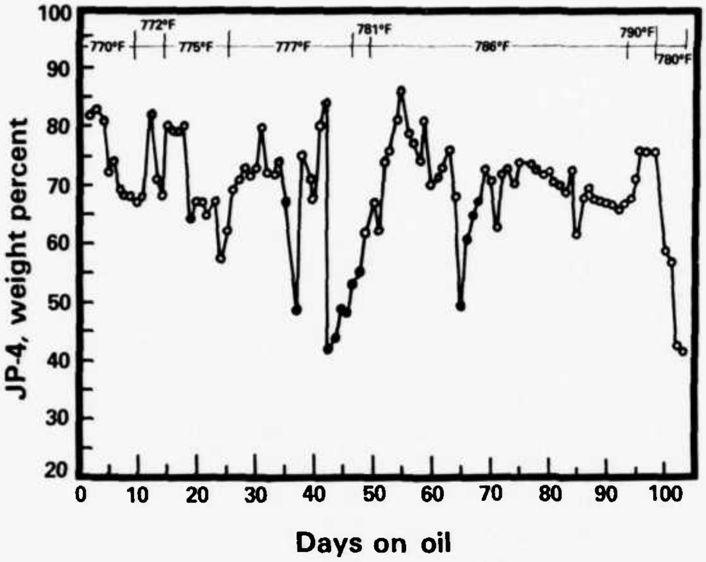

Figure 13 — Daily JP-4 Yields for the Activity Maintenance Test

## Table VII
## *Jet Fuel Qualities*

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

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

## VII

# AIR FORCE FUEL MAINBURNER/TURBINE EFFECTS PROGRAMS

By

Thomas A. Jackson

Aero Propulsion Laboratory

Wright-Patterson Air Force Base

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

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Wright-Patterson Air Force Base, Ohio 45433

## 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 has been 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 manufacturers 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.

## 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

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[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).

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 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 was obtained in standard combustor component test rigs. Special rigs were 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 were instrumented supplements the rig test generated data base. In addition the engine tests were used to perform the transient evaluations. 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 were conducted exclusively in standard combustor component test rigs and in a turbine erosion 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 were retained in these current combustion efforts but less emphasis was 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 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 eight test fuels are prepared from actual refinery process streams. They are not combinations of specification fuels and component additives.

## Conclusions

The shale oil derived JP-4 behaves as expected in terms of its combustion performance. In those areas where it closely matched the petroleum based JP-4, the response of the combustor in terms of performance and hot section durability was identical, within experimental variations. In those areas where it differed from the baseline, such as hydrogen content and viscosity, the performance deviations were predictable. The lower hydrogen content created slightly higher liner temperatures and some additional smoke. The higher viscosity caused the fuel spray to degrade and accounted for some higher low power emissions and poorer ignition at some conditions. The more broad program conclusions are apparent. Low power emissions and ignition/relight performance are affected mostly by fuel physical properties, viscosity and volatility. Fuel nozzle durability is sensitive to fuel thermal stability. It was also shown that combustor liner temperature and smoke emissions decrease with increasing hydrogen content.

# REFERENCES

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

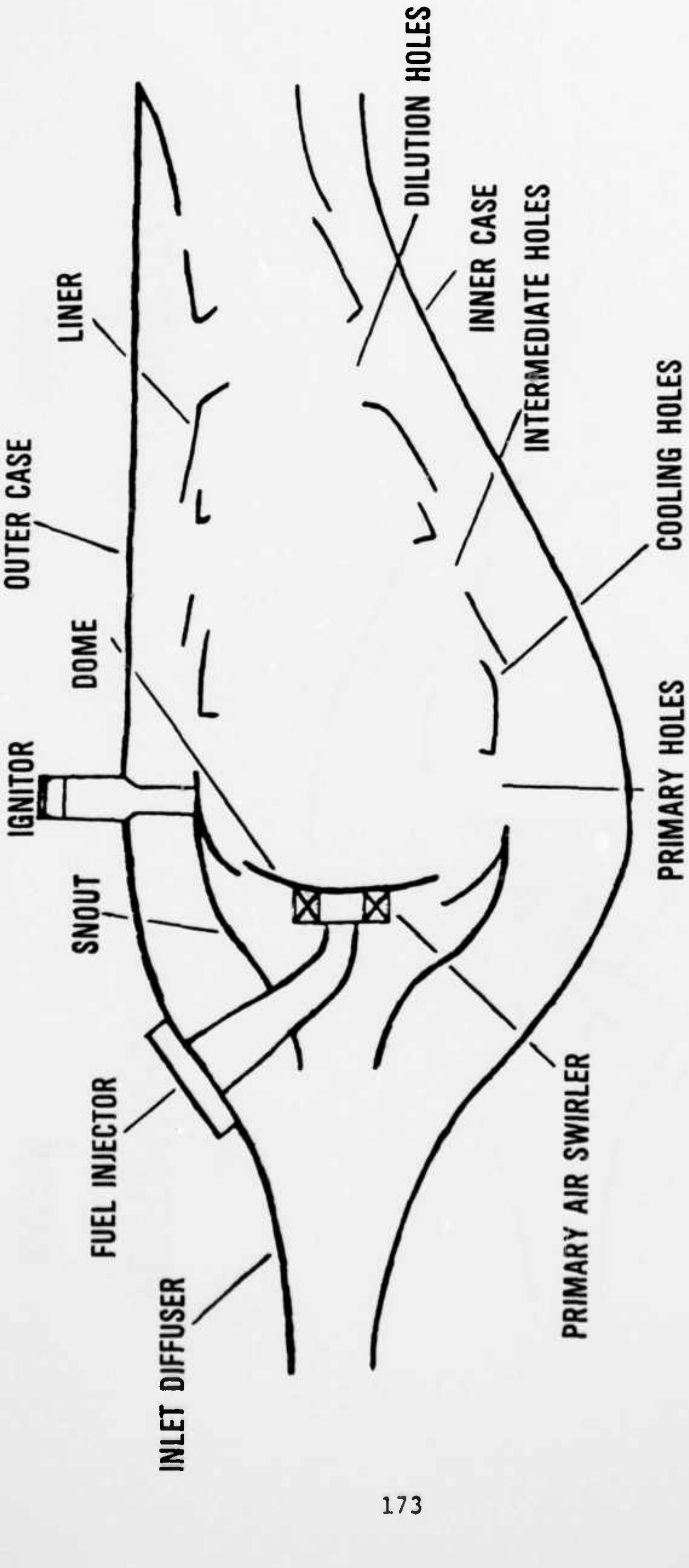
2. Jackson, T. A., "The Evaluation of Fuel Property Effects on Air Force Gas Turbine Engines - Program Genesis", to be presented at the ASME Gas Turbine Conference in Houston, TX, March 1981 and subsequently published as an ASME paper.

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

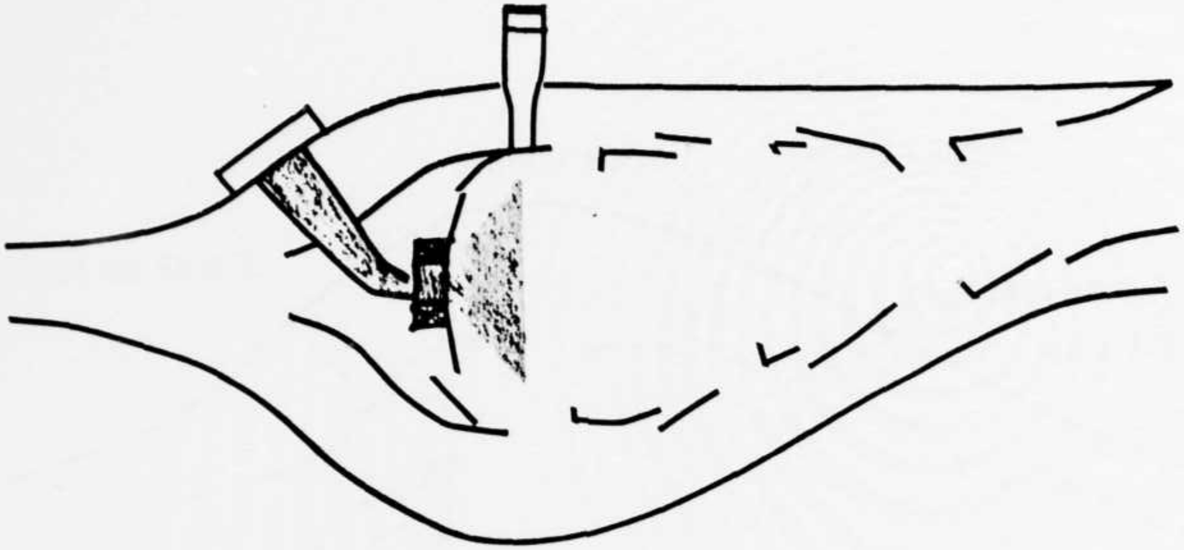
4. Gleason, C. C., et al, "Evaluation of Fuel Character Effects on the F101 Engine Combustion System", AFAPL-TR-79-2018, June 1979.

# OBJECTIVE

- QUANTIFY THE RELATIONSHIP BETWEEN FUEL PROPERTY VARIATIONS AND THE PERFORMANCE AND DURABILITY OF AIRCRAFT GAS TURBINE MAINBURNER AND TURBINE SYSTEMS
- DETERMINE THE IMPACT OF USING SHALE OIL DERIVED JP-4 IN EXISTING AIRCRAFT GAS TURBINE ENGINES


INLET DIFFUSER
FUEL INJECTOR
SNOUT
IGNITOR
DOME
OUTER CASE
LINER
PRIMARY AIR SWIRLER
PRIMARY HOLES
COOLING HOLES
INTERMEDIATE HOLES
INNER CASE
DILUTION HOLES

# FUEL INJECTION



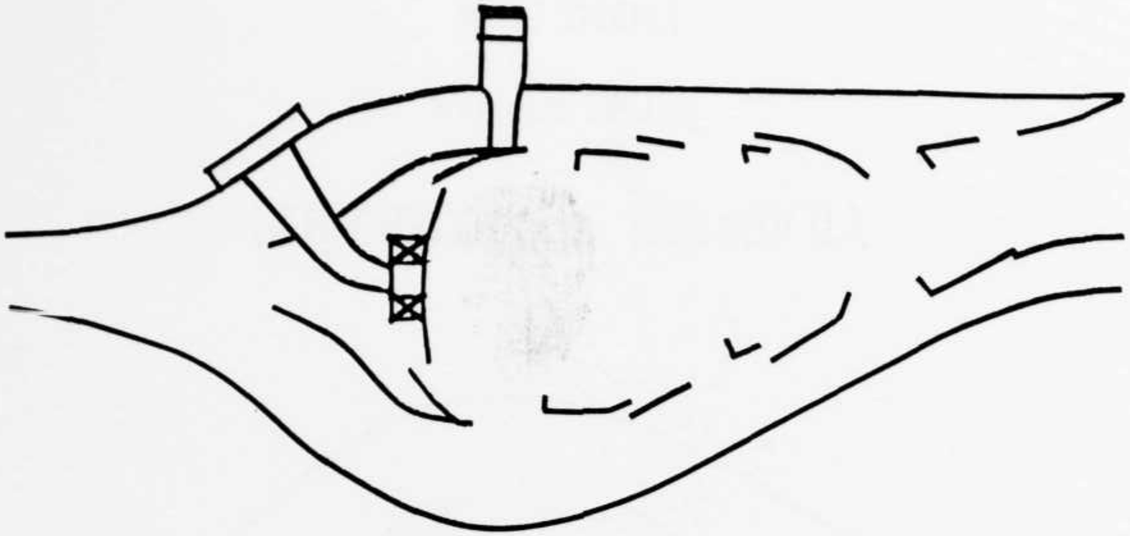
**PERFORMANCE**

- IGNITION
- LOW POWER EMISSIONS

**DURABILITY**

- FOULING
- CARBONING

# PRIMARY COMBUSTION ZONE



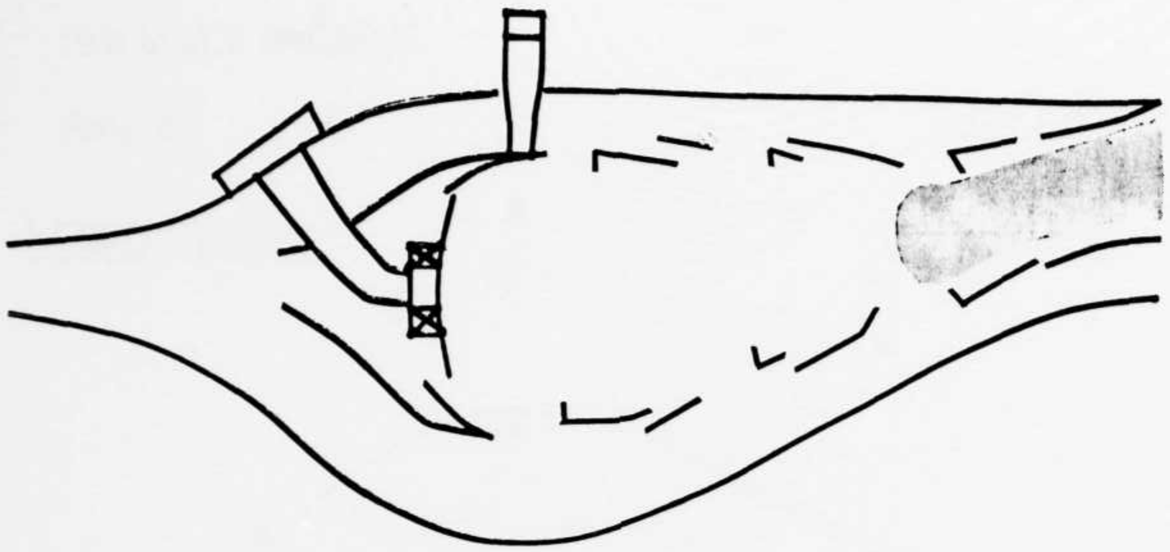
**PERFORMANCE**

- IGNITION
- LOW POWER EMISSIONS
- NOX
- SMOKE

**DURABILITY**

- LINER TEMPERATURE

# DILUTION ZONE/COMBUSTOR EXIT



**PERFORMANCE / DURABILITY**

PATTERN FACTOR

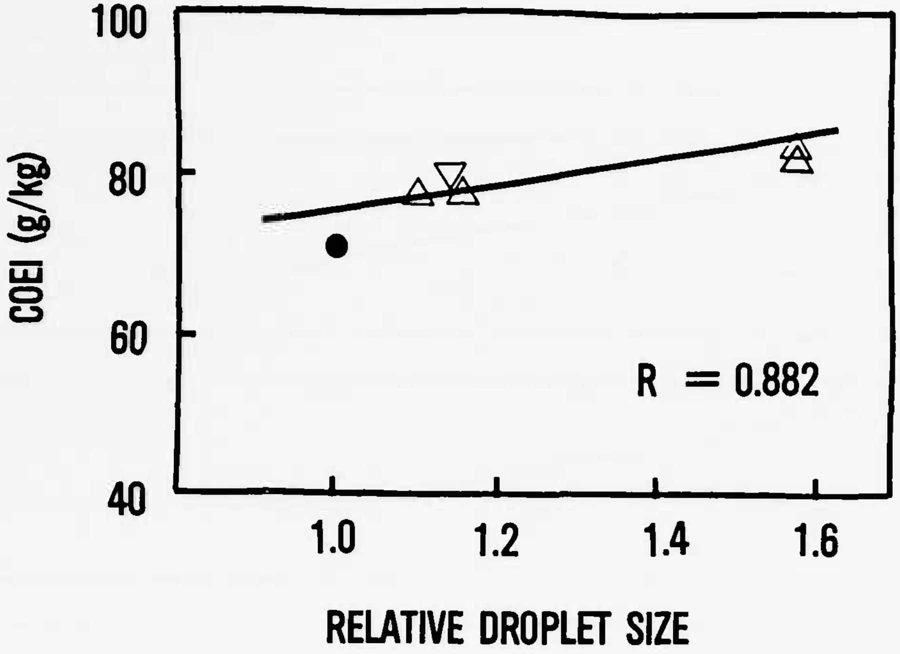
SOLID CARBON

# 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 |

## SHALE OIL JP4

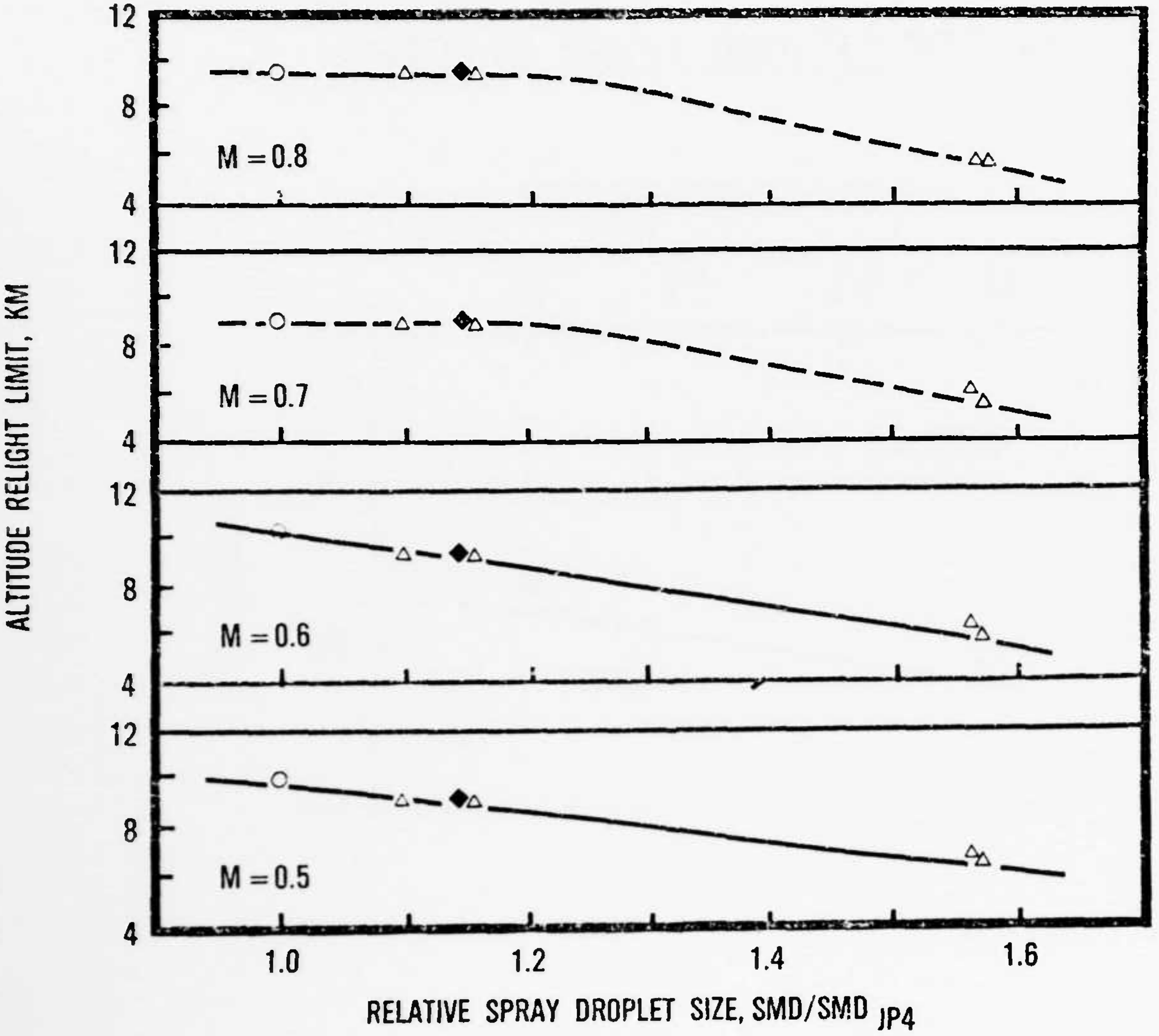
| | MIL SPEC | GE-OH | GE-MA | PW |
|---|---|---|---|---|
| GRAVITY (°API) | 45 - 57 | 49.7 | 48.5 | 49.8 |
| FREEZE POINT (K) | 215 MAX | 213 | 253 | 214 |
| NET HT OF COMBUSTION (MJ/kg) | 42.8 MIN | 43.42 | 43.24 | 43.48 |
| AROMATICS (VOL %) | 25 MAX | 11.0 | 10.6 | 11.7 |
| HYDROGEN (WT %) | 13.6 MIN | 14.30 | 14.29 | 14.29 |
| KINEMATIC VISCOSITY $mm^2/s$ at 294 K | — | 1.24 | 1.36 | 1.28 |
| DISTILLATION (K) | | | | |
| 10% | REPORT | 376 | 392 | 389 |
| 50% | 458 MAX | 461 | 469 | 461 |
| 90% | 523 MAX | 521 | 529 | 508 |
| 99.5% | 593 MAX | 601 | 617 | 574 |



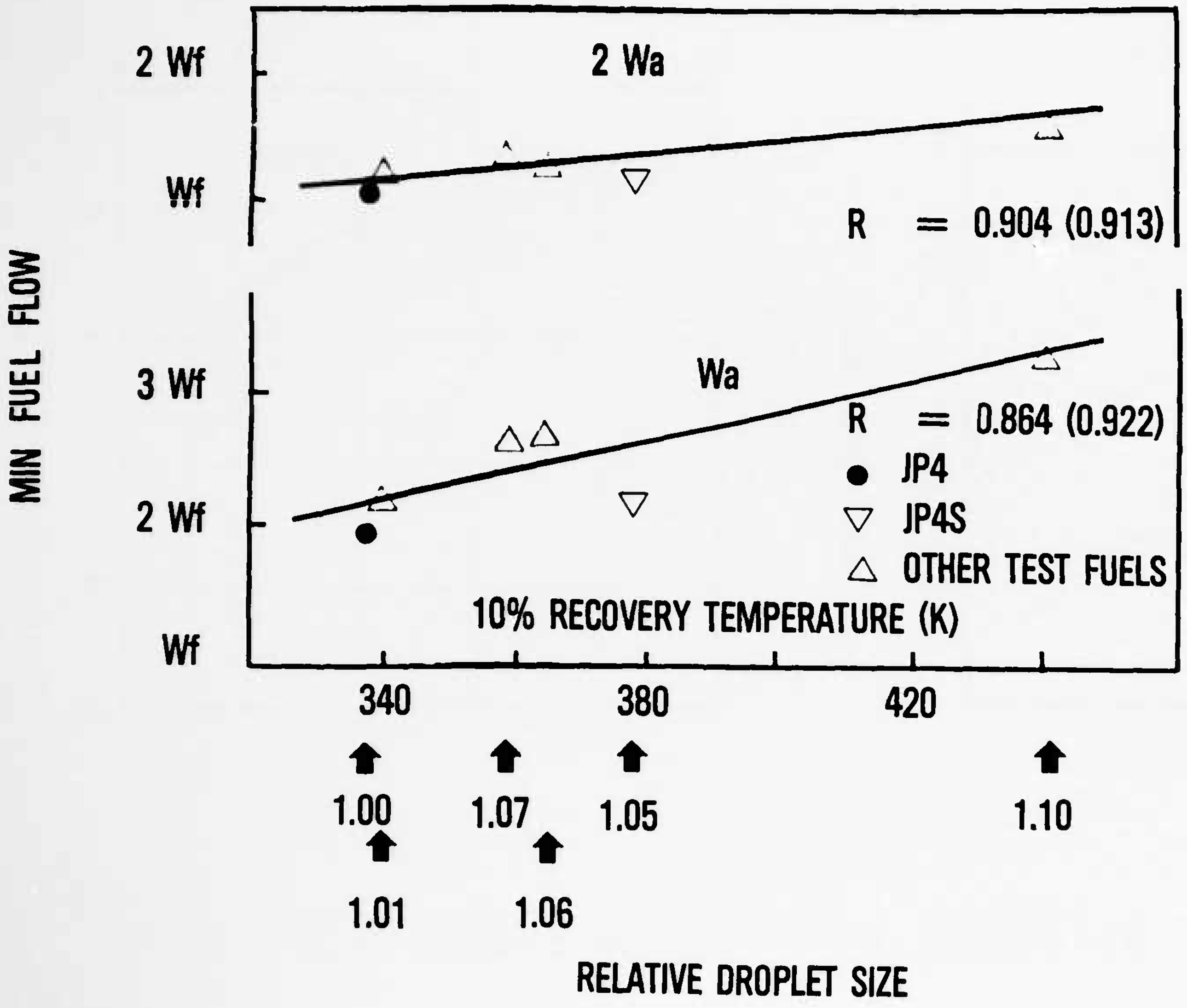
EFFECT OF SPRAY DROPLET SIZE ON

CO EMISSION LEVELS AT IDLE, TF39 RIG

# ALTITUDE IGNITION
## TF39



# VOLATILITY EFFECTS ON F100 COLD DAY GRD START



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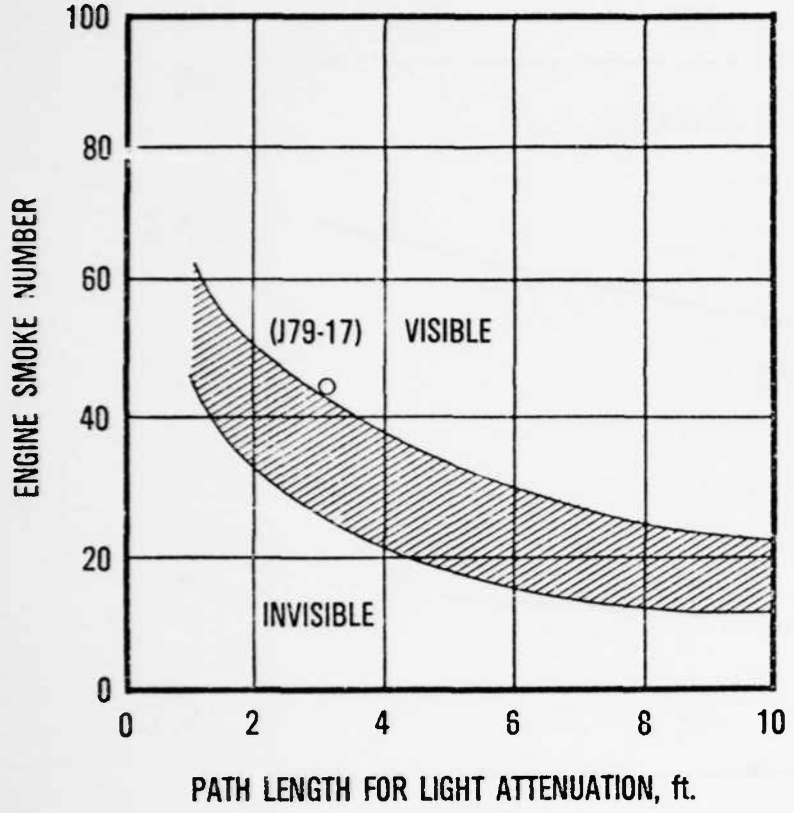

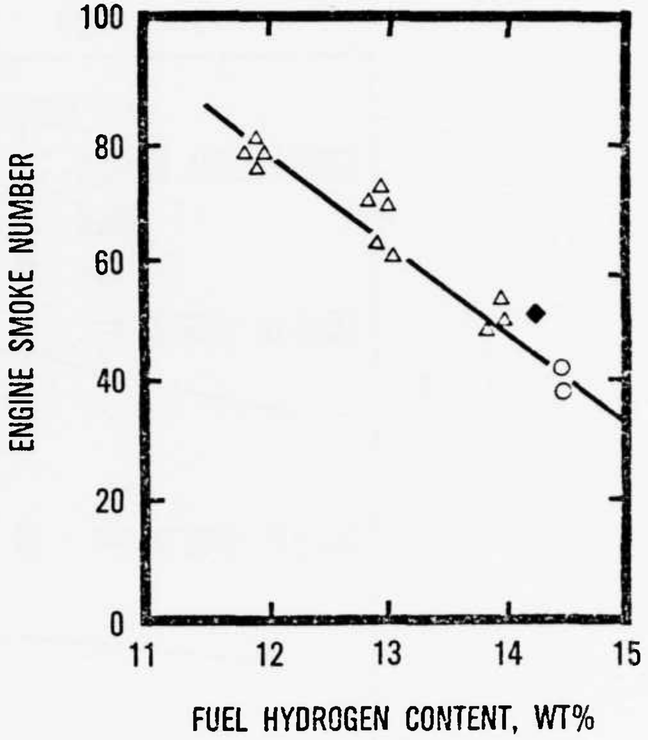

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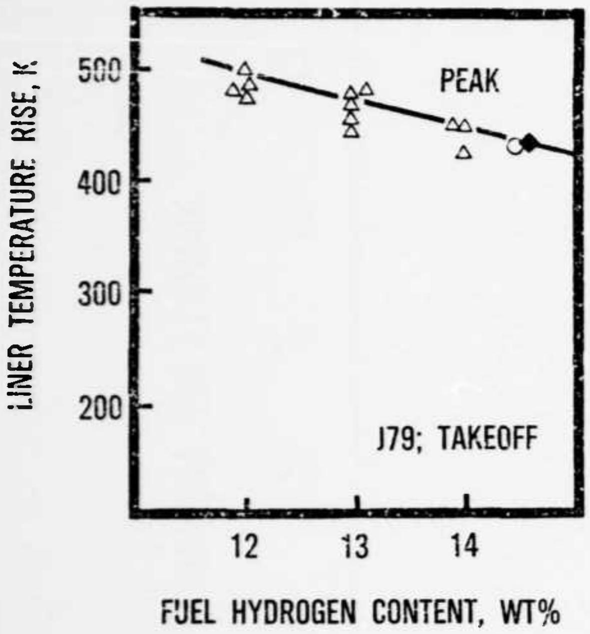
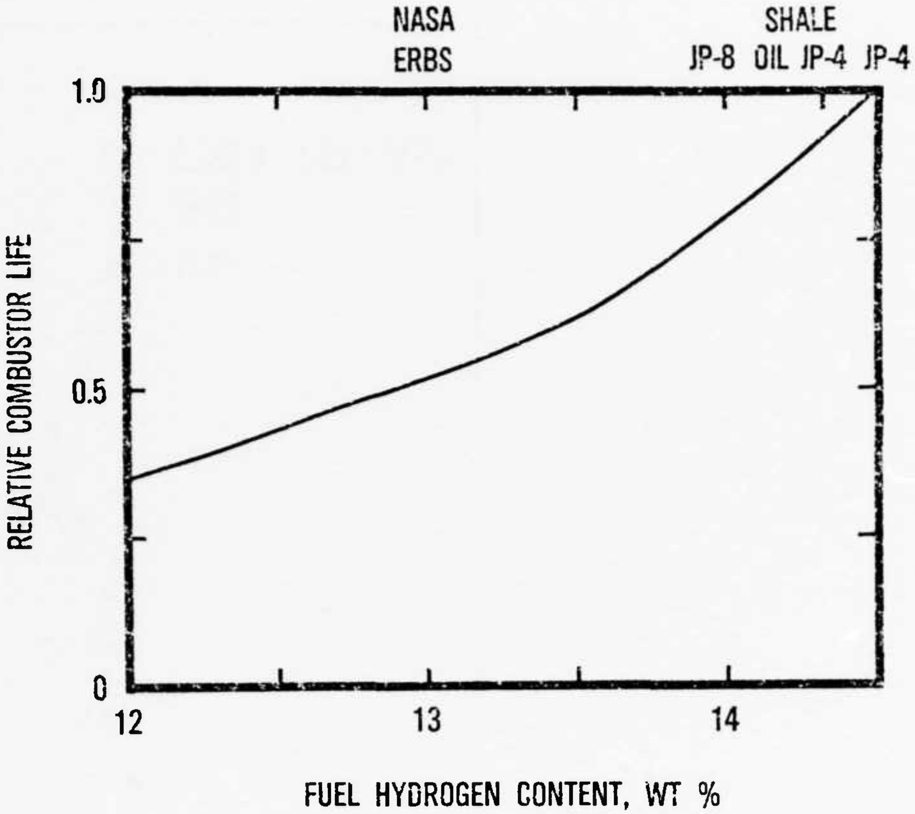
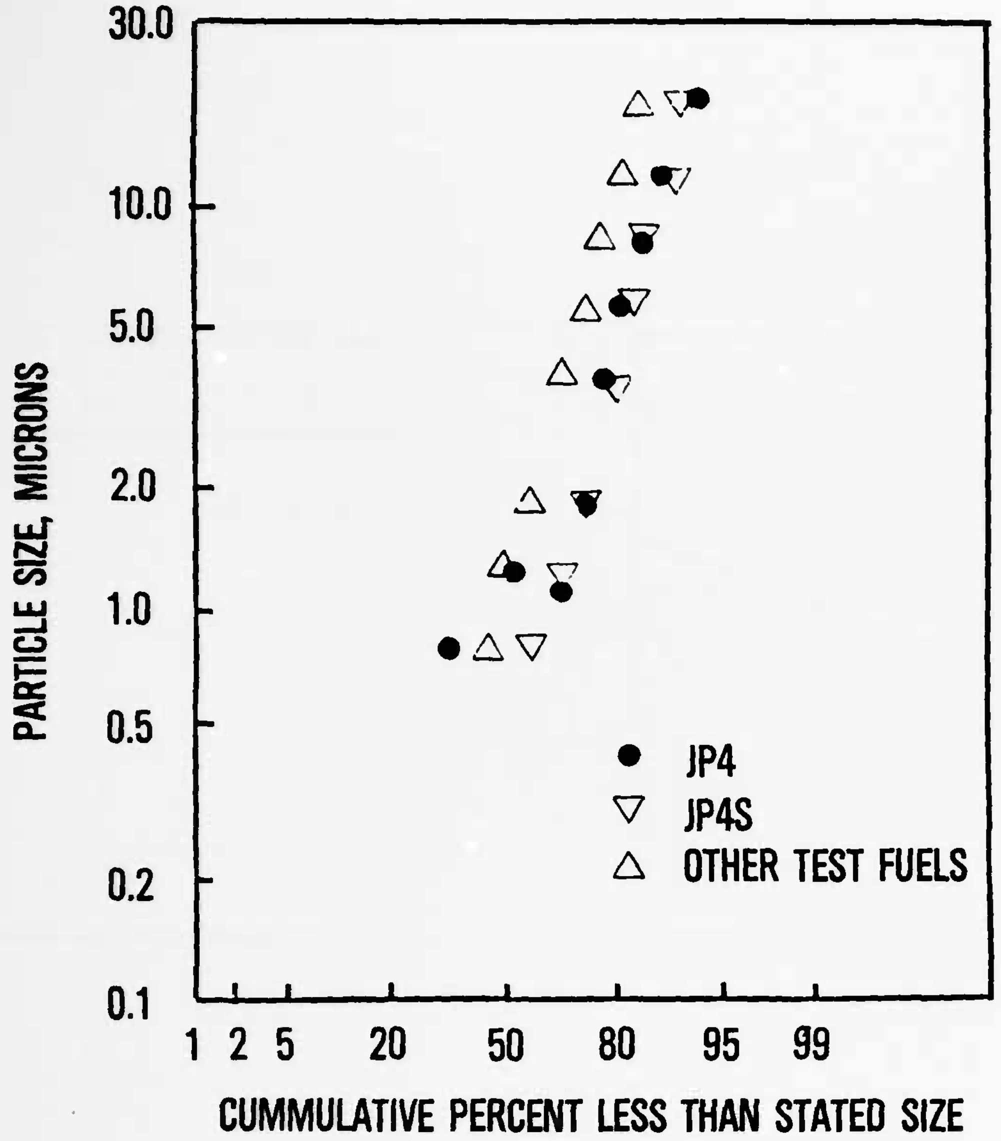
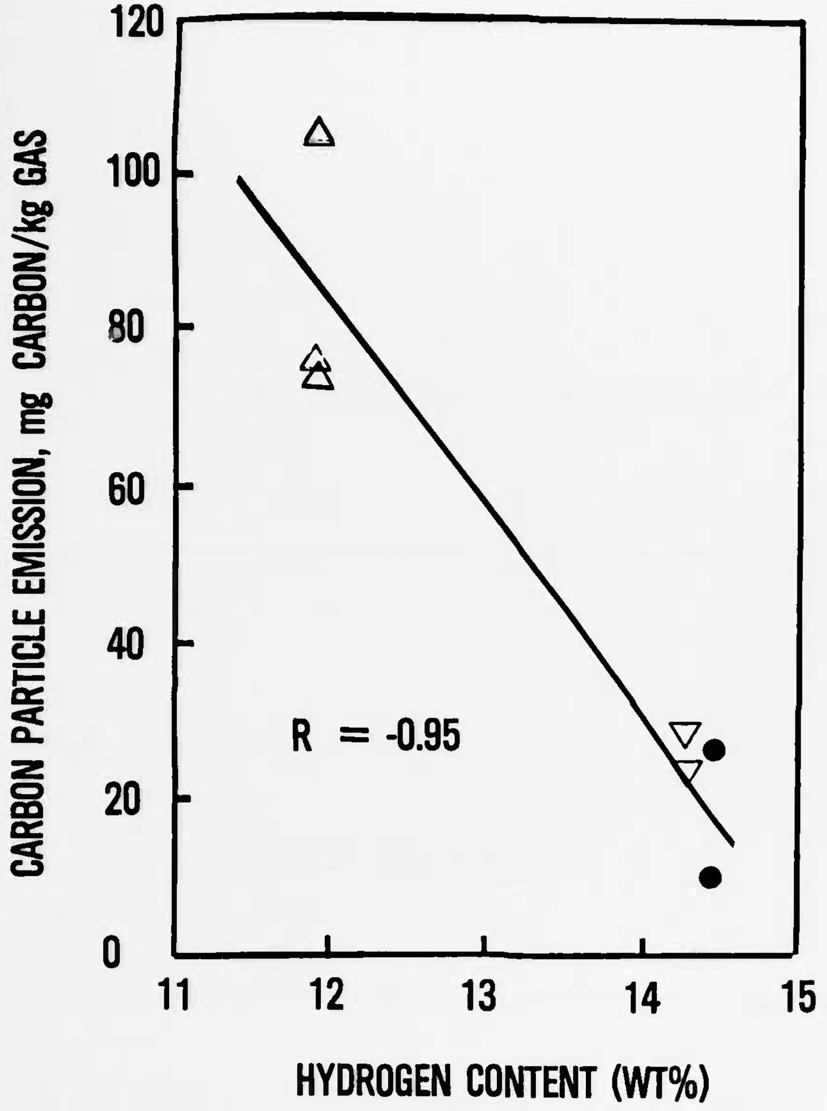




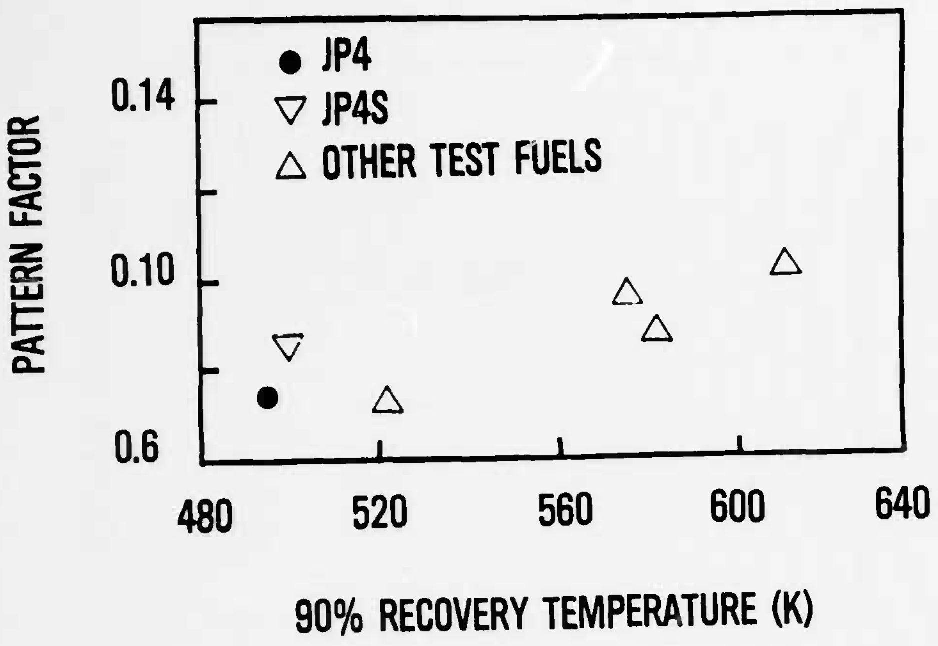


CARBON PARTICLE SIZE DISTRIBUTION, J79 CRUISE



EFFECT OF HYDROGEN CONTENT ON
CARBON EMISSIONS LEVELS, J79 CRUISE

# VOLATILITY EFFECT ON TF33 PATTERN FACTOR



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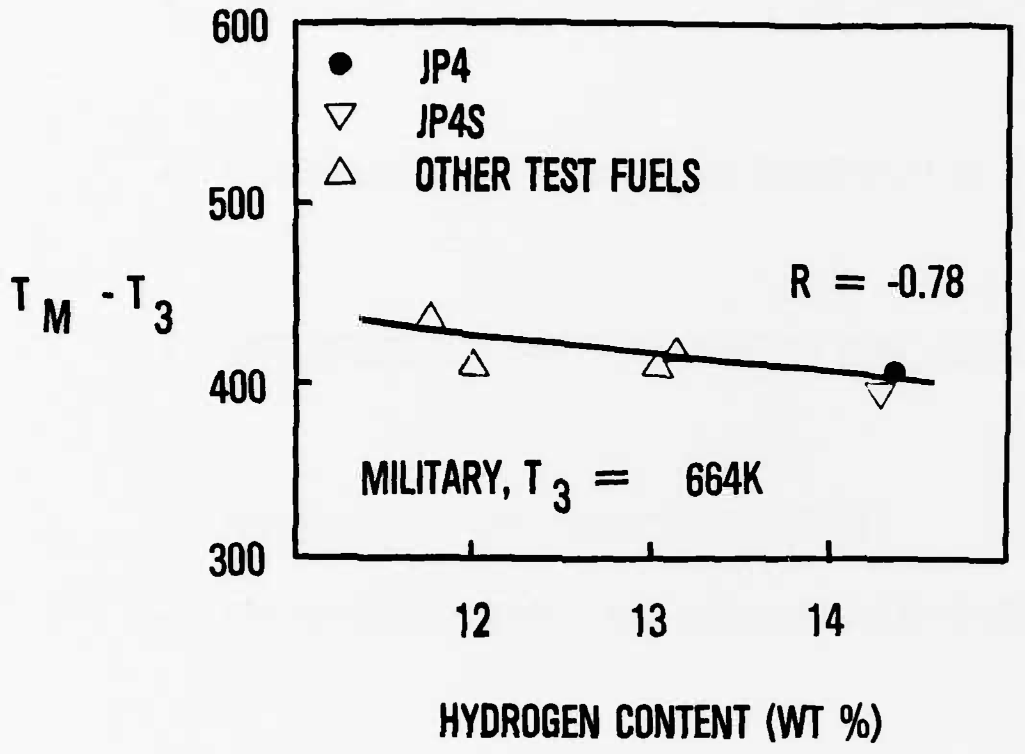

EFFECT OF HYDROGEN CONTENT ON J85
FIRST STAGE TURBINE NOZZLE, L.E.

# CONCLUSIONS

- SHALE DERIVED JP4 FUEL BEHAVES ACCORDING TO ESTABLISHED TRENDS
- LOW POWER EMISSIONS AND IGNITION /RELIGHT PERFORMANCE DOMINATED BY FUEL PHYSICAL PROPERTIES
- FUEL NOZZLE DURABILITY SENSITIVE TO FUEL THERMAL STABILITY
- COMBUSTOR LINER TEMPERATURE DOMINATED BY FUEL CHEMICAL PROPERTIES
- COMBUSTOR SMOKE EMISSION SENSITIVE TO FUEL CHEMICAL PROPERTIES

# VIII

# COMPOSITION OF SHALE-DERIVED FUEL SAMPLES

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# COMPOSITION OF SHALE-DERIVED FUEL SAMPLES

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Previous papers have described in detail the technology and economics of the methods used to obtain high yields of jet fuel from shale-derived crudes. The Air Force interest in alternate sources of jet fuel arose in response to the shortages experienced during the 1973 Oil Embargo. Studies conducted for the Air Force by Exxon showed that oil shale is an immense resource and that technology for conversion of oil shale into transportation fuels in general and jet fuel in particular was closer to commercial scale operation than the corresponding technology for conversion of coal. Studies conducted by Chevron under sponsorship of the United States Department of Energy (DOE) reached similar conclusions. Table 1 shows the sources of shale-derived jet fuels to be described in this paper. The initial large scale attempt to obtain transportation fuels from shale-derived crude (shale oil) was the processing of Paraho crude at the Gary Western Refinery in Fruita, Colorado. Fuels from this program (known as Shale I) were tested by the Department of Defense (DOD). In June 1975, General James Stewart, Commander of the Aeronautical Systems Division (ASD), flew a T-39 jet aircraft powered by shale-derived JP-4 from Wright-Patterson Air Force Base, Ohio to Carswell Air Force Base, Texas. There the aircraft was refueled with petroleum-derived JP-4; the return flight was made on a mixture of petroleum and shale-derived JP-4s. Extensive clay treatment was required before the Gary Western shale-derived JP-4 could be certified acceptable for the historic flight of the T-39.

Examination of the yields and fuel properties from the process used at the Gary Western Refinery showed that the search for alternate sources of jet fuel should include investigation of improved methods to obtain higher yields and better properties of jet fuel from shale oil. The high nitrogen content and high normal paraffin (wax) content, together with the low hydrogen content of shale oil, when compared with petroleum crude, presented the greatest technical challenge. In the fall of 1978, the Navy managed a major refining effort (known as Shale II) at the Sohio Toledo Refinery to convert approximately 63,000 barrels of shale-derived Paraho crude into transportation fuels. The Shale II operation produced JP-8, JP-5, diesel fuels and heavy products, but no JP-4. In early 1979, the Air Force awarded contracts to Ashland, Suntech, and UOP for processing studies to develop methods to obtain high yields of jet fuel from shale oil, to evaluate economics of those methods, and to provide fuel samples from those processing methods. The crudes used in the processing studies were Occidental shale oil from Retort 6 and Paraho shale oil from the Shale II program. Late in 1979, the Air Force awarded a contract to Amoco for the development of a catalyst optimized for removal of nitrogen from shale oil and high jet fuel yield with minimum hydrogen consumption in a single-pass hydrotreating operation. In early 1980, Hydrocarbon Research, Inc. (HRI), under subcontract to Suntech, produced for Air Force testing 270 barrels of JP-4 from Geokinetics shale-derived crude. The HRI program, which deserves to be called Shale III, achieved a 30 percent yield of JP-4 from shale oil. In October 1981, the last samples were received from the processing studies begun in 1979.

We have conducted extensive chemical analyses of the fuels obtained from each of these programs. The objective of this paper is to present the results of those analyses and to relate the chemical composition of the fuel samples to the processing technologies from which they were derived. Some of the fuel analyses were conducted by nonstandard methods; some of the standard methods are not truly applicable to fuels with the boiling ranges encountered. Although the absolute accuracy of the values obtained from such methods has not been demonstrated, the relative values are useful for comparison of different fuel samples with the same boiling range. Also, in some cases, different analytical methods were used for JP-4s than for JP-8s and diesel fuels. Thus, caution is advised when comparing compositional data among different fuel types. Nevertheless, the relative values obtained do provide useful information about compositional differences between fuels from the various programs.

Detailed chemical analyses of fuels were obtained by the methods listed in Table 2 and discussed below.

Hydrogen content was determined by wide-line Nuclear Magnetic Resonance spectrometry (NMR) using a method based on ASTM D3701. Hydrogen content is reported as weight percent.

Fuel composition by chemical compound class was determined by mass spectrometry (MS) and reported as weight percent. Figure 1 shows the compound classes determined by MS and gas chromatography (GC). For JP-4 samples, ASTM D2789 was modified to extend its applicability from its originally intended boiling range to the slightly higher boiling range of JP-4. JP-8 and diesel fuel samples were analyzed by a Monsanto mass spectrometric method which uses the same physical procedures as ASTM D2789, but significantly different software for calculation of chemical composition from the raw mass spectrometric data. The paraffin determinations from these mass spectrometric methods were further categorized into branched and normal paraffins. Thus, six hydrocarbon classes are reported as weight percent for each fuel, cycloparaffins, branched paraffins, normal paraffins, single ring aromatics, indans and tetralins, and naphthalenes. The concentrations of individual normal paraffins were determined by high-resolution temperature-programmed gas chromatography (GC) using a capillary column with more than 200,000 theoretical plates. A sample chromatogram is shown in Figure 2. The specific normal alkanes were identified by retention time and quantitated as area percent of flame ionization detector response. The total weight percentage of normal alkanes was assumed to be the sum of the area percents of the individual normal alkanes. The normal alkane concentrations thus determined were subtracted from paraffins (determined by MS) to obtain the concentration of branched alkanes. For comparison, aromatics, olefins, and saturates were determined by fluorescent indicator adsorption (FIA) (ASTM D1319) and reported as volume percent. In fuels of very low olefin content, FIA may overestimate olefin concentration while mass spectrometry ignores olefins entirely.

Boiling range information for these fuels was obtained by the same high-resolution gas chromatography runs used to determine normal paraffins. In this method, the fuel boiling range is reported as the integral (Area %) of the GC peaks grouped by carbon number (Figure 3). For example, all of the peaks eluting after normal heptane (C-7) up to and including normal octane (C-8) are reported as being in the carbon number eight (C-8) boiling range. This reporting method has a sound theoretical basis, as most eight-carbon paraffins will, in fact, elute in the C-8 boiling range. However, eight-carbon aromatic compounds will elute in the C-9 boiling range. The fuels analyzed have significant concentrations of hydrocarbons in the C-4 through C-24 boiling ranges. The most appropriate presentation for such integrated GC data for a single fuel would be an histogram such as the one shown in Figure 4 which depicts the boiling range distribution for the Shale I JP-4 from the Gary Western Refinery. However, in order to present more than one fuel on a single graph, we have chosen to use line graphs which merely connect the dots at the end of each carbon number group (Figure 5). On such a graph, the y value at each carbon number represents the percentage of the fuel in that particular boiling range. Since the y value represents the integral of the GC trace over a single carbon number interval, the area under the curve has no physical significance. This grouping of boiling range, integrated by carbon number, allows a graphical presentation which readily portrays differences in fuel volatility and composition by carbon number (Figure 6).

Sulfur content was determined by the standard ASTM method D1266 and reported as weight percent sulfur.

High-resolution NMR, both proton and Carbon-13 , was used to determine a number of measures of fuel composition (Table 3). These include fraction aromatic carbon (the number of carbon atoms in aromatic rings divided by the total number of carbon atoms in the fuel), fraction aromatic hydrogen (the number of hydrogen atoms attached to aromatic carbon atoms divided by the total number of hydrogen atoms in the fuel), hydrogen to carbon aromatics ratio (number of aromatic hydrogen atoms divided by the number of aromatic carbon atoms), number of hydrogens on an average aromatic ring (hydrogen to carbon aromatics ratio multiplied by six), and the calculated values for mole percent total paraffins, mole percent total naphthalenes, mole percent alkyl benzenes, mole percent total aromatics, and mole percent paraffins. Significant advances have been made in high-resolution NMR technology; the method has only recently been applied to detailed analysis of fuel composition.

Before proceeding to a detailed comparison of the composition of the various shale-derived samples, it is useful to highlight some of the differences between the three methods of determining fuel composition by hydrocarbon class (Table 4). Mass spectrometric data is reported by weight percent. FIA analyses are reported as volume percent. Simple conversions can be made from weight to volume percent using assumed densities for each compound class. Mass spectrometric and FIA methods are subject to fuel boiling range limitations. FIA is not really applicable to diesel fuels. No standard mass spectrometric method is strictly applicable to JP-4. NMR is not subject to the boiling range limitations of MS and FIA; a single NMR method is applicable to the entire range of liquid fuels. While the MS methods measure molecular ions and fragments, NMR determines the chemical environment of the atoms in the fuel. Thus, the raw data of NMR is expressed in atomic ratios of carbon or hydrogen in various chemical environments. The atomic ratio nature of NMR data makes it fundamentally different from that obtained by MS or FIA. Consider, for example, the effect of hexyl benzene in a fuel (Figure 7). FIA would categorize hexyl benzene as 100 percent aromatic. That is, addition of hexyl benzene to a fuel would increase the aromatic content of the fuel in an additive fashion according to volume added. MS should consider hexyl benzene as aromatic, but depending upon the mode of fragmentation, MS could identify the six-carbon side chain as coming from a paraffin. Thus, MS might find hexyl benzene in a fuel to be either 100% aromatic, 50% aromatic, or any value in between. Of course a skilled mass spectrometrist would be able to apply empirically derived corrections to obtain results close to the true value, but these ambiguities are present in the standard MS methods and must be considered. High-resolution NMR on the other hand is a nondestructive technique which measures the relative amounts of carbon (or hydrogen) atoms in each type of chemical environment. Thus, the hexyl benzene molecule $C_{12}H_{18}$ could be considered by NMR to consist of two parts: the aromatic part ($C_6H_5$) and the nonaromatic part ($C_6H_{13}$). Carbon-13 NMR would find hexyl benzene to be 50% aromatic. Proton NMR would find hexyl benzene to be 28% aromatic (five aromatic hydrogen atoms divided by 18 total hydrogen atoms per molecule). The debate continues about which measures of fuel composition are most relevant to engine performance and durability. The combination of proton NMR and Carbon-13 NMR together with a determination of hydrogen content would show that five of the six aromatic carbons have a hydrogen attached. Prior separation of the fuel into saturate and aromatic fractions can allow the NMR to reveal a wealth of structural information about each fraction. High-resolution NMR presents compositional data in an unfamiliar format, but it is essentially insensitive to fuel boiling range. Each of the methods (FIA, MS, NMR) provides useful information if we understand the theoretical basis for the differences in the values obtained and appreciate the limitations of each method. Table 5 lists the shale-derived JP-4 samples we analyzed. The table lists the Air Force sample code, the refiner's sample code, and the shale crude from which the jet fuel was derived.

The detailed fuel analyses showed that significant advances have been made as a result of the processing studies. For purposes of comparison, we will use the Shale I Gary Western fuel (GWR 77-11) as the reference shale JP-4 produced with minimal processing. We will compare it to the Shale III Hydrocarbon Research Institute fuel (HRI 61) and to the UOP fuel (UOP 149). The UOP fuel was chosen as representative of the Phase III JP-4s because it has, in general, properties intermediate between those of the Ashland and Suntech Phase III JP-4 samples. Figure 8 shows the hydrogen content of these three fuels, GWR 77-11, HRI 61, and UOP 149. The hydrogen contents are quite similar; both the Gary Western fuel and the UOP fuel have a hydrogen content of 14.5. The HRI fuel has a slightly lower hydrogen content of 14.3 weight percent. This is somewhat surprising, since the HRI fuel was severely hydrotreated and the Gary Western fuel was not. We should remember that there are three fundamental chemical features which can result in a fuel with a low hydrogen content (Table 6). The first and most obvious is the presence of double bonds in the molecules, especially in aromatic rings. Single-ring aromatic compounds in the jet fuel boiling range have hydrogen contents ranging from 7.7 percent for benzene to 11.9 weight percent for decyl benzene. Saturated molecules in the jet fuel boiling range have hydrogen contents varying from 17.2% for butane to 15.0 for hexadecane. The second structural feature which lowers hydrogen content is the presence of saturated rings; single ring saturated compounds all have a hydrogen content of 14.37 weight percent. Another, more subtle way in which the hydrogen content may be lowered is by increasing the average carbon number (boiling range) of a paraffinic fuel. Recall that hydrogen content decreases from 17.2 for butane to 15.0 for hexadecane, the highest boiling component of significant concentration in jet fuel. Hydrogen content, in contrast, increases with boiling point for single-ring aromatic compounds, but because jet fuels are primarily paraffins, hydrogen content of jet fuel tends to increase as boiling range decreases.

Figure 9 shows the fraction aromatic carbon for these three fuels as determined by high-resolution NMR. Note the relatively high aromatic content of the Gary Western fuel, a fact that appears inconsistent with its high hydrogen content.

Figure 10 shows hydrocarbon compound class distribution by weight percent for the three fuels, as determined by mass spectrometry and high-resolution gas chromatography. The aromatic contents of the three fuels are 12.9 for GWR 11, 12.4 for HRI 61, and 9.2 for UOP 149. Thus, mass spectrometry confirms the NMR results. Obviously some other factor or factors must account for the high hydrogen content of the Gary Western fuel when compared with the UOP fuel which has a significantly lower aromatic content. The cycloparaffin concentration of the three fuels provides part of the explanation; cycloparaffins have a lower hydrogen content than either branched or normal paraffins. The cycloparaffin concentrations for the HRI and UOP fuels are both high, 42.2 and 44.4 percent respectively; the Gary Western fuel has only 22.9 percent cycloparaffins accounting, at least partially, for its relatively high hydrogen content. This figure shows that the Gary Western fuel is unique in another way; the normal paraffin concentration is 41.0 percent, extremely high when compared to the 23.8 percent for the HRI fuel and 13.1 percent for the UOP JP-4. This is an operationally significant difference; normal paraffins, especially those with more than 13 carbons tend to increase the freezing point of the fuels. A high normal paraffin content is one of the features which distinguishes shale oil from petroleum derived fuels. Thus, Figure 10 shows the progress which has been made to reduce the normal paraffin concentration to acceptable levels and, in the case of the UOP fuel, below that ordinarily found in petroleum-derived JP-4.

Figure 6 shows the boiling ranges of the three fuels. The Gary Western fuel shows the narrowest boiling range, boiling only as high as C-13 (tridecane) due to the high normal paraffin content of this fuel. It was necessary to limit the boiling range of this fuel in order to meet the -72°F specification maximum freeze point. The other two fuels have a broader boiling range; the HRI fuel has significant material in the C-15 boiling range, while the UOP fuel includes a similar amount of C-16 compounds. Thus, the reduction of normal alkane concentration by improved processing methods has allowed the boiling range to be extended by three carbon numbers, allowing increased yields of JP-4.

Now that we have focused on the progress made in improving the properties and yield of JP-4 from shale oil, we will turn our attention to a detailed comparison of samples from the various processes.

The most important fuel type produced from the shale fuel program is JP-4, the standard jet fuel used by the Air Force. A typical petroleum JP-4 is a broad-range naptha-kerosene fuel. The shale fuels produced by this program fall into this classification.

Table 5 lists the shale-derived JP-4 samples we analyzed. The table lists the sample number assigned by the Air Force for management purposes, the refiners code number, and the shale crude type.

Hydrogen content not only yields a clue to processing, but also correlates with aircraft gas turbine engine performance and durability parameters. Figure 11 illustrates the weight percent hydrogen of the fuels produced in Phase III of the program. Numerical data is provided in Table 7. The hydrogen content range for the JP-4 samples produced in Phase III is between 14.0 and 14.7 weight percent hydrogen which is well within specifications. The fuel sample with the highest hydrogen content is SUN 155. The other samples in order of decreasing hydrogen content are UOP 149, SUN 150, GWR 77-11 with 14.5 weight percent hydrogen, HRI 61 at 14.3 weight percent, and ASH 141 and Amoco 158 at 14.0 percent.

The high hydrogen content of the fuel samples is due to a variety of physical and chemical properties. The high hydrogen content of the JP-4 samples is attained in two distinct ways: (1) the fuel is composed of a quantity of narrow-cut blend streams consisting of low molecular weight, high hydrogen content compounds or (2) the fuel consisted of broad boiling range, high hydrogen content material which has small quantities of olefinic and aromatic materials. High-resolution gas chromatography best illustrates the boiling range distribution of the sample (Figure 12 and Table 8).

Samples consisting of narrow-cut high hydrogen content blend streams were SUN 150P, SUN 155, and ASH 141. The other samples consist of a high hydrogen content broad-range material.

The amount and type of chemical compound classes cause differences in hydrogen content. The samples analyzed were low in olefins as measured by FIA and will be discussed as containing only paraffins and aromatics. Paraffins have a higher weight percent hydrogen than do aromatics with similar numbers of carbons.

The fraction of the carbon atoms in aromatic rings is small (Figure 13) as determined by high-resolution NMR, and ranged between 0.0564 (UOP 149) and 0.1359 (Amoco 158). The high hydrogen content of the samples is due to lack of high concentrations of aromatic compounds.

The concentrations of specific aromatic compound classes in the samples were determined by mass spectrometry. The total aromatic content for the samples ranged from 6.3 to 19.2 percent by weight (Figure 14). The types of aromatics identified are naphthalenes, indans and tetralins, and single ring aromatics. All JP-4 samples had a very low naphthalene content. This is due to two reasons: (1) most naphthalene compounds fall outside the boiling range of JP-4; and (2) most naphthalenes were removed by hydrotreating.

Most naphthalenes were hydrotreated to structures containing both a saturated and an unsaturated ring such as indans and tetralins. As hydrotreating severity increases, the indan and tetralin structures are hydrogenated to a cycloparaffin structure.

To illustrate this, sample Amoco 158 has rather low hydrogen content, wide boiling range, and more indans and tetralins (6.1%) than the other fuels, all of which indicates rather mild hydrotreating. If this sample is compared to sample UOP 149, a rather broad boiling sample, the indans and tetralins content is lower (3.7%). The cycloparaffin content of UOP 149 is higher, 42.2% compared to 35.9% for Amoco 158, yielding a higher hydrogen content representative of more severe hydrotreating. Because other samples either contained multiple process streams or were produced from shale crudes other than Occidental, comparison of relative severity of hydrotreating may be misleading.

Single ring aromatic compounds ranged from 4.7 to 12.6 percent by weight. The concentration of single ring compounds in the fuel is influenced by three things: (1) boiling range of single ring aromatics; (2) amount of reformate material in the blend stocks; and (3) the relative amount of cracking. Many single ring aromatics fall in the boiling range of JP-4, however, if a large amount of low boiling compounds was used to increase hydrogen content, for example Sun 155, this could limit the amount of single ring aromatics (4.7%) compared to a broader range fuel such as Amoco 158 (12.6%). Reforming increases the single ring aromatic content. Cracking of indan and tetralin structures can increase single ring aromatic content.

The structure of the single ring aromatics was investigated by high resolution NMR. This method determined that the average aromatic ring had three to four hydrogens attached to it (Figure (15).

The paraffinic content of the fuels was analyzed by mass spectrometry and high-resolution gas chromatography. All fuels had paraffin contents of 86.4 to 93.7 percent by weight except for sample Amoco 158 which had a paraffin content of 80.3% by weight.

The paraffinic fraction of the fuel was analyzed to determine three structural types, normal paraffins, branched paraffins and cycloparaffins. Samples produced by Ashland, Suntech, UOP and Amoco all had similar concentrations of normal paraffins (13.1 - 14.2%) indicating, when compared to the HRI or GWR sample concentration that hydrocracking is occurring. The amount of branched paraffins in the fuel sample is increased by cracking of the fuel. An example is sample SUN 155 which has a higher concentration of branched paraffins (37.8%) than does the Amoco 158 sample (30.8%). The cycloparaffin concentration is similar for all fuel samples (41.2 to 45.4% by weight), except for the sample Amoco 158 which has a lower cycloparaffin concentration (35.9%) and GWR 77-11 (22.9% cycloparaffins). The hydrotreating for all samples (except GWR 77-11 which had undergone minimal processing) was severe enough to hydrogenate naphthalenes and single ring aromatics to cycloparaffins.

A final specification property investigated was smoke point. Smoke point correlates to engine parameters and, in general, increases with increased paraffin content. All fuels were within specifications and illustrate this general trend.

A second type of jet fuel produced in Phase III was JP-8, a candidate NATO fuel. JP-8 is a kerosene base fuel similar to commercial Jet A.

JP-5 samples were also analyzed with the JP-8 samples. JP-5 is used by the Navy; like JP-8, it is a kerosene based fuel. It differs from JP-8 primarily in flash point with the JP-5 having a flash point above 140°F, while JP-8 is required to have a flash point greater than 100°F.

Table 9 lists the shale-derived JP-8 and JP-5 samples we analyzed. The table lists the sample number assigned by the Air Force, the refiners code, and shale crude type.

Figure 16 illustrates the weight percent hydrogen for the JP-8 and JP-5 samples. Numerical data is presented in Table 10. The hydrogen content range for these fuels is between 13.6 and 14.4 weight percent. The UOP 164 sample had a hydrogen content of 14.4%. The other samples in decreasing hydrogen content are SUN 156 - 14.2%, SUN 157-5 - 14.1%, Sohio 62 - 13.9%, Amoco 159 - 13.8%, and SUN 151P-5, SUN 152P, ASH 145 with 13.6% hydrogen.

The high hydrogen contents of the JP-8 and JP-5 samples were attained in two ways: (1) the fuel is composed of a large quantity of a narrow-cut blend stream consisting of relatively low molecular weight, high hydrogen content compounds or (2) the fuel consisted of broad boiling range, high hydrogen content material with small quantities of olefinic and aromatic compounds. High-resolution gas chromatographic data illustrates the boiling range distribution of these fuels (Figure 17 and Table 11).

Samples consisting of narrow-cut high hydrogen content blend streams were SUN 151P-5, SUN 156, SUN 157-5, and SOH 62 samples. The other samples consisted of high hydrogen content, broad range materials. The Amoco 159 sample is a very wide cut fuel with a carbon number range from 5 to 21; it is a "JP-8 boiling range" cut which was not required to meet freeze point.

The aromatic content of the JP-8 and JP-5 samples is higher than that of the JP-4 samples. The carbon aromaticities of the JP-8 and JP-5 samples are illustrated in Figure 18 as determined by high-resolution NMR. The carbon aromaticities range from a fraction of 0.0495 in sample UOP 164 to 0.1865 in sample SUN 152P.

The concentrations of specific aromatic compound classes in the samples were determined by mass spectrometry. The naphthalene concentration·is greater in the JP-8 samples - 0.5 to 1.3% compared to less than 0.8% for the JP-4 samples, primarily because more naphthalenes fall in the boiling range of JP-8 than that of JP-4 (see Figure 19).

The concentration of indans and tetralins (3.6 to 10.6 wt%) was much higher in the JP-8 and JP-5 samples than in the JP-4 samples. More indan and tetralin compounds fall in the boiling range of JP-8 and JP-5 than in that of JP-4.

The concentration of single ring aromatics is 5.2 to 18.2 weight percent. The differences in single ring aromatic content are due to two main reasons: (1) some of the single ring aromatics may have been blended into the JP-4 cut or (2) in some cases, some of the indan and tetralin compounds were cracked to form single ring compounds.

The structure of the single ring aromatics was investigated by high-resolution NMR. This method determined that the average aromatic ring had an average of 2.7 to 3.9% hydrogens attached to it (Figure 20).

The paraffin content of the fuel was determined by mass spectrometry and high-resolution gas chromotography; it ranged between 72.4 and 90.2 weight percent. The SUN 152P sample had the lowest normal paraffin concentration at 10.0% and the SOH 62 sample at 29.5%, had the highest. The lower concentration of normal paraffins in most samples was due to hydrocracking.

The branched paraffins concentration ranged from a low of 14.2% for the Sohio 62 sample to a high of 37.7% for the UOP 164 sample, illustrating relative amounts of hydrocracking with the Sohio sample undergoing the smallest amount.

The cycloparaffin concentration for the JP-8 and JP-5 samples ranged from 31.0% for Amoco 159 to 45.0% for SUN 156.

A third type of fuel produced in Phase III was diesel fuel. Though not a jet fuel, these fuels are of interest for they represent the highest boiling fuel that can be used easily in a gas turbine engine.

Table 12 lists the shale-derived diesel fuel samples and the shale crude sources.

Figure 21 illustrates the weight percent hydrogen for the diesel samples. Numerical data are presented in Table 13. The hydrogen contents of the diesel samples range from 13.6 weight percent for the two Ashland samples to 13.9 weight percent for the UOP and SUN samples.

The hydrogen content of these fuels is influenced by the relative amount of low carbon number compounds. The UOP 161 and SUN 153P samples have significant amounts of the fuel boiling below normal undecane (C-11) causing relatively high hydrogen content, whereas the Ash 143 and Ash 144 samples maintain a high hydrogen content by spanning a narrow boiling range of only 11 to 20 carbon numbers (see Figure 22 and Table 14).

A significant difference in the diesel fuels is the aromatic content of the samples. Figure 23 illustrates the carbon aromaticity by high-resolution NMR. Sample Ash 144 has a carbon aromaticity of 0.0438, whereas the rest of the samples have an aromaticity of approximately 0.11. The NMR data for sample Ash 144 appear inconsistent with the weight percent hydrogen and the MS data. These results will be redetermined.

The concentrations of specific aromatics were determined by mass spectrometry (MS). The aromatics by MS range between 15.4 to 24.4 percent by weight. Naphthalene contents for these samples range between 1.7% for SUN 153 and 2.6% for ASH 143. Indans and tetralins concentrations range from 5.7% for UOP 161 to 13.4% for ASH 144. Single ring aromatic concentrations range between 7.7% for ASH 143 and 10.7 weight percent for SUN 153 (see Figure 24).

The structure of the single ring aromatics was investigated by high-resolution NMR. This method determined that the average aromatic ring had an average of 2.3 to 3.8 hydrogens attached to it (Figure 25).

The paraffin concentration of these fuels ranged from 75.6 to 84.6 percent by weight. The normal paraffin concentrations ranged between 17.9 and 23.4 percent. Branched paraffin concentration ranged from 17.9 to 28.4 percent. Cycloparaffin concentration ranged from 28.7 to 38.5 percent by weight.

The information attained from this study yielded the following conclusions: (1) many of the fuels produced in Phase III meet all the fuel specifications; (2) all JP-4 samples produced in Phase III exhibited improved fuel properties over those produced by Shale I. These improvements included a reduction in aromatic content, a reduction in normal paraffins, an increase in cycloparaffins, and an increase in boiling range which increased the yield.

An area of future investigation suggested by this study is an investigation of the effect of disulfide compounds on fuel performance and material compatibility. This study found possibly significant concentrations of disulfide compounds in two fuel samples.

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# TABLE 1. SOURCE OF SHALE DERIVED FUEL SAMPLES

SOURCE OF SHALE DERIVED FUEL SAMPLES

| PROCESSING PROGRAM | CRUDE SOURCE | CONTRACTOR |
|---|---|---|
| ● 1975 | | |
| SHALE I | PARAHO I | GARY WESTERN |
| ● 1978 | | |
| SHALE II | PARAHO II | SOHIO TOLEDO |
| ● 1979 - 1981 | | |
| PROCESS METHODS | PARAHO II/OXY 6 | ASHLAND |
| PROCESS METHODS | PARAHO II/OXY 6 | SUNTECH |
| PROCESS METHODS | PARAHO II/OXY 6 | UOP |
| ● 1979 - 1981 | | |
| CATALYST DEVELOPMENT | OCCIDENTAL 6 | AMOCO |
| ● 1980 | | |
| SHALE III | GEOKINETICS | HRI-SUNTECH |

## TABLE 2. ANALYTICAL METHODS FOR SHALE-DERIVED FUELS

ANALYTICAL METHODS FOR SHALE-DERIVED FUELS

| METHOD | FUEL PROPERTY | UNITS |
|---|---|---|
| WIDE-LINE NUCLEAR MAGNETIC RESONANCE (NMR)(D3701) | HYDROGEN CONTENT | WT% |
| LAMP FLAME (D1322) | SMOKE POINT | MM FLAME |
| MASS SPECTROMETRY(D2789 MODIFIED) | HYDROCARBON TYPES | WT% |
| HIGH-RESOLUTION GAS CHROMATOGRAPHY | n-ALKANE CONTENT | AREA% |
| FLUORESCENT INDICATOR ADSORPTION (FIA)(D1319) | AROMATICS AND OLEFINS | VOL% |
| HIGH-RESOLUTION GAS CHROMATOGRAPHY | BOILING RANGE BY CARBON # | AREA% |
| X-RAY SPECTROGRAPH (D2622) | SULFUR CONTENT | WT% |
| HIGH-RESOLUTION PROTON NMR AND C-13 NMR | AROMATIC CARBON & HYDROGEN | ATOM FRACT |
|  | HYDROCARBON TYPES | MOLE% |

TABLE 3. ANALYSES BY HIGH RESOLUTION NMR

## ANALYSES BY HIGH RESOLUTION NMR

- CALCULATED DIRECTLY FROM RAW DATA
    - FRACTION AROMATIC CARBON (CAR/CTOTAL) BY C13 NMR
    - FRACTION AROMATIC HYDROGEN (HAR/HTOTAL) BY H NMR
    - HYDROGEN/CARBON AROMATICS RATIO (HAR/CAR) BY H NMR, C13 NMR, WT % H

- CALCULATED FROM RAW DATA WITH ASSUMPTONS
    - NUMBER OF HYDROGENS ON AVERAGE AROMATIC RING (6 X HAR/CAR)
    - MOLE PERCENT NAPHTHALENES CALCULATED FROM H NMR
    - MOLE PERCENT ALKYL BENZENES CALCULATED FROM H NMR
    - MOLE PERCENT TOTAL AROMATICS CALCULATED FROM H NMR
    - MOLE PERCENT PARAFFINS CALCULATED FROM H NMR

## TABLE 4. COMPARISON OF ANALYTICAL METHODS

MASS SPECTROMETRY (MS) - MOLECULAR IONS AND FRAGMENTS - WEIGHT PERCENT
- NAPHTHALENES, INDANS & TETRALINS, SINGLE-RING AROMATICS, PARAFFINS, CYCLOPARAFFINS
- BOILING RANGE LIMITATIONS ON METHOD

FLUORESCENT INDICATOR ADSORPTION (FIA) - COMPOUND POLARITY - VOLUME PERCENT
- AROMATICS, OLEFINS, AND SATURATES
- BOILING RANGE LIMITATIONS ON METHOD

NUCLEAR MAGNETIC RESONANCE (NMR) - MOLECULAR ENVIRONMENT OF C & H ATOMS - ATOM RATIO
- AROMATIC HYDROGENS/TOTAL HYDROGENS
- AROMATIC CARBONS/TOTAL CARBONS
- AROMATIC HYDROGEN/AROMATIC CARBONS
- CALCULATED MOLE% HYDROCARBON TYPE
- NOT SUBJECT TO BOILING RANGE LIMITATIONS

## TABLE 5. JP4 PHASE III SAMPLE INFORMATION

| | | |
|---|---|---|
| ● ASHLAND | | |
| VN-81-141 | "JP4" | OCCIDENTAL CRUDE |
| ● SUNTECH | | |
| VN-81-150 | "X190-76" | PARAHO CRUDE |
| VN-81-155 | "X190-123" | OCCIDENTAL CRUDE |
| ● UOP | | |
| VN-81-149 | "3794-153" | OCCIDENTAL CRUDE |
| ● AMOCO | | |
| VN-81-158 | "JP4" | OCCIDENTAL CRUDE |
| ● HRI | | |
| VN-80-61 | "JP4" | GEOKINETICS CRUDE |
| ● GWR | | |
| VN-77-11 | "JP4" | PARAHO CRUDE |

TABLE 6. FUNDAMENTAL FUEL FEATURES WHICH REDUCE HYDROGEN CONTENT

FUNDAMENTAL FUEL FEATURES
WHICH REDUCE HYDROGEN CONTENT
DOUBLE BONDS - SINGLE-RING AROMATICS
$C_6H_6$ (BENZENE)-------- 7.7 WT% H
$C_{16}H_{26}$(DECYLBENZENE)-- 11.9 WT% H
-SATURATES (PARAFFINS)
$C_4H_{10}$ (BUTANE)--------- 17.2 WT% H
$C_{16}H_{34}$(HEXADECANE)---- 15.0 WT% H
SATURATED RINGS
-MONOCYCLOPARAFFINS--- 14.37 WT% H
INCREASED BOILING RANGE (FOR PARAFFINIC FUEL)
-SATURATES 17.2(C-4) TO 15.0(C-16)
%H DECREASES WITH INCREASED BP
-AROMATICS 7.7(C-8) TO 11.9(C-16)
%H INCREASES WITH INCREASED BP

# TABLE 7. JP4 PHASE III DATA SUMMARY

| CHEMICAL COMPOUND CLASSES (%) | ASH 141 | SUN 155 | UOP 149 | AMOCO 158 | SUN 150P | HRI 61 | GWR 77-11P |
|---|---|---|---|---|---|---|---|
| NORMAL PARAFFINS GC (AREA) | 13.41 | 13.52 | 13.08 | 14.14 | 14.21 | 23.80 | 41.00 |
| BRANCHED PARAFFINS MS/GC (WT) | 27.59 | 37.78 | 35.52 | 30.76 | 34.19 | 19.40 | 23.20 |
| CYCLIC PARAFFINS MS (WT) | 45.40 | 42.40 | 42.20 | 35.90 | 41.20 | 44.40 | 22.90 |
| TOTAL PARAFFINS MS (WT) | 86.40 | 93.70 | 90.80 | 80.80 | 89.60 | 87.60 | 87.10 |
| TOTAL PARAFFINS NMR (MOLE) | 88.24 | 93.70 | 93.70 | 83.48 | 92.63 | 89.69 | 86.70 |
| TOTAL PARAFFINS FIA (VOL) | 86.50 | 93.70 | 89.10 | 80.30 | 90.20 | 87.00 | 86.80 |
| NAPHTHALENES MS (WT) | .60 | .30 | .30 | .50 | .80 | .10 | 0.00 |
| NAPHTHALENES NMR (MOLE) | .91 | .33 | .49 | .62 | .18 | .80 | 1.47 |
| INDANS AND TETRALINS MS (WT) | 2.40 | 1.30 | 3.70 | 6.10 | 2.80 | 4.20 | 1.70 |
| ALKYL BENZENES MS (WT) | 10.60 | 4.70 | 5.20 | 12.60 | 6.80 | 8.10 | 11.20 |
| ALKYL BENZENES NMR (MOLE) | 9.83 | 5.17 | 5.67 | 15.73 | 6.99 | 9.49 | 11.80 |
| TOTAL AROMATICS MS (WT) | 13.60 | 6.30 | 9.20 | 19.20 | 10.40 | 12.40 | 12.90 |
| TOTAL AROMATICS NMR (MOLE) | 10.74 | 5.50 | 6.16 | 16.35 | 7.16 | 10.10 | 13.20 |
| TOTAL AROMATICS FIA (VOL) | 12.70 | 5.80 | 9.20 | 18.80 | 9.10 | 12.00 | 11.70 |
| OLEFINS FIA (VOL) | .80 | .50 | 1.70 | .90 | .70 | 1.00 | 1.50 |
| OLEFINS NMR (MOLE) | 1.01 | .81 | .14 | .17 | .21 | .21 | .05 |
| OTHER PROPERTIES | | | | | | | |
| FRACT. AROMATIC CARBON (ATOM) | .1031 | .0575 | .0564 | .1359 | .0817 | .0799 | .1073 |
| FRACT. AROM. HYDROGEN (ATOM) | .0308 | .0165 | .0158 | .0411 | .0218 | .0243 | .0340 |
| HYDROGEN CONTENT (WT %) | 14.09 | 14.66 | 14.49 | 13.98 | 14.46 | 14.32 | 14.49 |
| SMOKE POINT (MM) | 26.00 | 28.00 | 28.00 | 21.00 | 27.00 | 27.00 | 32.50 |
| TOTAL SULFUR (WT %) | 0.00 | 0.00 | .08 | 0.00 | .01 | .03 | .02 |
| H/C AROMATICS NMR (ATOM) | .5838 | .5873 | .5655 | .5857 | 5374 | .6500 | .6418 |
| NO. HYDROGENS ON AROM RING | 3.50 | 3.52 | 3.39 | 3.51 | 3.22 | 3.90 | 3.85 |
| | ASH JP4 | SUN X190 -123 | UOP 3794 -153 | AMOCO JP4 | SUN X190 -76 | HRI JP4 | GWR JP4 |

## TABLE 8. JP4 PHASE III BOILING RANGE BY HIGH RESOLUTION GC

| CARBON NUMBER GROUP | % OF FUEL BOILING IN GROUP BY HR-GC | | | | | | |
|---|---|---|---|---|---|---|---|
| FUEL | ASH 141 | SUN 155 | UOP 149 | AMO 158 | SUN 150P | HRI 61 | GWR 11P |
| 3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 4 | 1.2 | 1.0 | 0.0 | 0.0 | 0.0 | 0.8 | 0.2 |
| 5 | 2.2 | 2.0 | 0.5 | 0.9 | 2.3 | 1.2 | 0.9 |
| 6 | 3.9 | 3.3 | 2.8 | 3.4 | 9.2 | 2.5 | 1.6 |
| 7 | 6.5 | 15.6 | 6.9 | 7.3 | 15.4 | 4.7 | 12.1 |
| 8 | 20.6 | 21.3 | 10.6 | 11.6 | 18.5 | 10.0 | 20.0 |
| 9 | 12.9 | 13.9 | 10.9 | 13.3 | 15.1 | 13.2 | 21.1 |
| 10 | 11.9 | 9.7 | 10.1 | 11.9 | 8.7 | 14.9 | 18.7 |
| 11 | 12.3 | 8.1 | 10.0 | 10.5 | 8.1 | 17.5 | 16.1 |
| 12 | 10.3 | 7.9 | 10.7 | 10.8 | 8.1 | 15.9 | 7.9 |
| 13 | 7.8 | 9.3 | 11.8 | 11.8 | 8.1 | 12.5 | 1.3 |
| 14 | 5.0 | 6.9 | 11.0 | 8.8 | 5.1 | 4.8 | 0.1 |
| 15 | 3.6 | 1.2 | 10.9 | 6.7 | 0.9 | 1.7 | 0.0 |
| 16 | 1.5 | 0.0 | 3.4 | 2.4 | 0.1 | 0.2 | 0.0 |
| 17 | 0.0 | 0.0 | 0.0 | 0.4 | 0.1 | 0.1 | 0.0 |
| 18 | 0.0 | 0.0 | 0.0 | 0.1 | 0.1 | 0.1 | 0.0 |
| 19 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 |
| 20 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 21 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 22 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 23 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 24 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 25 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

# TABLE 9. JP5 and JP8 PHASE III SAMPLE INFORMATION

| | | | |
|---|---|---|---|
| ● ASHLAND | | | |
| VN-81-145 | "JP8" | | OCCIDENTAL CRUDE |
| ● SUNTECH | | | |
| VN-81-151 | "X190-77" | JP5 | PARAHO CRUDE |
| VN-81-152 | "X190-78" | JP8 | PARAHO CRUDE |
| VN-81-156 | "X190-224" | JP8 | OCCIDENTAL CRUDE |
| VN-81-157 | "X190-225" | JP5 | OCCIDENTAL CRUDE |
| ● UOP | | | |
| VN-81-164 | "3794-157C" | JP8 | OCCIDENTAL CRUDE |
| ● AMOCO | | | |
| VN-81-159 | "JP8" | | OCCIDENTAL CRUDE |
| ● SOHIO | | | |
| VN-80-62 | "JP8" | | PARAHO |

## TABLE 10. JP5 and JP8 PHASE III DATA SUMMARY

| CHEMICAL COMPOUND CLASSES (%) | ASH 145 | SUN 156 | UOP 164 | AMOCO 159 | SUN 152P | SUN 157-5 | SUN 151P-5 | SOHIO 62P |
|---|---|---|---|---|---|---|---|---|
| NORMAL PARAFFINS GC (AREA) | 12.38 | 14.82 | 12.87 | 16.52 | 9.95 | 18.06 | 13.53 | 29.50 |
| BRANCHED PARAFFINS MS/GC (WT) | 24.12 | 27.18 | 37.73 | 29.78 | 24.25 | 23.14 | 21.57 | 14.20 |
| CYCLIC PARAFFINS MS (WT) | 42.80 | 45.00 | 39.60 | 31.00 | 38.20 | 41.80 | 38.20 | 33.20 |
| TOTAL PARAFFINS MS (WT) | 79.30 | 87.00 | 90.20 | 77.30 | 72.40 | 83.00 | 73.30 | 23.00 |
| TOTAL PARAFFINS NMR (MOLE) | 85.45 | 94.12 | 93.60 | 81.67 | 80.96 | 87.42 | 83.97 | 82.50 |
| TOTAL PARAFFINS FIA (VOL) | 75.90 | 87.70 | 88.70 | 77.70 | 73.50 | 82.80 | 75.20 | 76.20 |
| NAPHTHALENES MS (WT) | .80 | .50 | 1.00 | 1.30 | 1.20 | 1.00 | 1.30 | 1.00 |
| NAPHTHALENES NMR (MOLE) | .09 | .11 | .20 | .82 | 1.18 | .37 | .16 | .70 |
| INDANS AND TETRALINS MS (WT) | 7.20 | 4.30 | 3.60 | 7.00 | 8.20 | 6.90 | 9.40 | 10.60 |
| ALKYL BENZENES MS (WT) | 12.50 | 8.20 | 5.20 | 14.40 | 18.20 | 9.10 | 16.00 | 11.40 |
| ALKYL BENZENES NMR (MOLE) | 14.21 | 5.21 | 6.06 | 17.35 | 17.63 | 11.31 | 15.47 | 16.00 |
| TOTAL AROMATICS MS (WT) | 20.50 | 13.00 | 9.80 | 22.70 | 27.60 | 17.60 | 26.70 | 87.00 |
| TOTAL AROMATICS NMR (MOLE) | 14.30 | 5.32 | 6.26 | 18.16 | 18.00 | 11.68 | 15.64 | 17.50 |
| TOTAL AROMATICS FIA (VOL) | 22.80 | 11.40 | 10.20 | 21.40 | 25.10 | 16.00 | 23.90 | 22.20 |
| OLEFINS FIA (VOL) | 1.30 | .90 | 1.10 | .90 | 1.40 | 1.20 | .90 | 1.60 |
| OLEFINS NMR (MOLE) | .26 | .56 | .14 | .17 | .23 | .90 | .40 | 0.00 |
| OTHER PROPERTIES | | | | | | | | |
| FRACT. AROMATIC CARBON (ATOM) | .1167 | .0734 | .0495 | .1434 | .1865 | .0861 | .1317 | .1300 |
| FRACT. AROM. HYDROGEN (ATOM) | .0275 | .0178 | .0137 | .0361 | .0450 | .0226 | .0349 | .0400 |
| HYDROGEN CONTENT (WT %) | 13.76 | 14.23 | 14.41 | 13.84 | 13.62 | 14.06 | 13.59 | 13.89 |
| SMOKE POINT (MM) | 19.00 | 25.00 | 26.00 | 21.00 | 18.00 | 22.00 | 17.00 | 20.40 |
| TOTAL SULFUR (WT %) | .04 | 0.00 | .05 | .02 | .01 | 0.00 | .01 | 0.00 |
| H/C AROMATICS NMR (ATOM) | .4479 | .4794 | .5552 | .4818 | .4533 | .5117 | .4965 | .6500 |
| NO. HYDROGENS ON AROM RING | 2.69 | 2.88 | 3.33 | 2.89 | 2.72 | 3.07 | 2.98 | 3.90 |
| REFINERS CODE NUMBERS | ASH JP8 | SUN X190 -224 | UOP 3794 -157C | AMOCO JP8 | SUN X190 -78 | SUN X190 -225 | SUN X190 -77 | SOHIO JP8 |

# TABLE 11. JP5 AND JP8 PHASE III BOILING RANGE BY HIGH RESOLUTION GC

| CARBON NUMBER GROUP | % OF FUEL BOILING IN GROUP BY HR-GC | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| FUEL | ASH 145 | SUN 156 | UOP 164 | AMO 159 | SUN 152P | SUN 157-5 | SUN 151P5 | SOH 62P |
| 3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 6 | 0.0 | 0.0 | 0.0 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 |
| 7 | 0.0 | 0.0 | 0.2 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| 8 | 0.8 | 1.4 | 6.6 | 1.0 | 2.1 | 0.2 | 0.2 | 0.0 |
| 9 | 9.8 | 10.5 | 9.5 | 6.7 | 13.1 | 4.7 | 4.0 | 0.5 |
| 10 | 13.2 | 15.2 | 9.6 | 12.3 | 18.5 | 10.8 | 12.9 | 18.2 |
| 11 | 16.3 | 17.3 | 10.0 | 12.6 | 14.7 | 14.6 | 16.2 | 28.8 |
| 12 | 15.3 | 18.0 | 11.0 | 13.7 | 15.1 | 17.1 | 20.9 | 24.1 |
| 13 | 13.4 | 21.2 | 13.2 | 14.6 | 17.0 | 24.3 | 25.4 | 18.7 |
| 14 | 10.7 | 12.6 | 11.8 | 11.1 | 14.8 | 19.3 | 17.1 | 8.0 |
| 15 | 9.1 | 4.0 | 11.7 | 9.0 | 4.6 | 8.8 | 3.0 | 1.8 |
| 16 | 5.9 | 0.0 | 10.7 | 6.5 | 0.0 | 0.2 | 0.0 | 0.2 |
| 17 | 3.9 | 0.0 | 5.5 | 6.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| 18 | 1.5 | 0.0 | 0.0 | 5.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 19 | 0.0 | 0.0 | 0.0 | 1.4 | 0.0 | 0.0 | 0.0 | 0.0 |
| 20 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 21 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 22 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 23 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 24 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 25 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

TABLE 12. DIESEL FUELS PHASE III SAMPLE INFORMATION

| | | |
|---|---|---|
| • ASHLAND | | |
| VN-81-143 | "DF-2" | OCCIDENTAL CRUDE |
| VN-81-144 | "DF-2" | OCCIDENTAL CRUDE |
| • SUNTECH | | |
| VN-81-153 | "X190-79" | PARAHO CRUDE |
| • UOP | | |
| VN-81-161 | "3794-152" | OCCIDENTAL CRUDE |

## TABLE 13. DIESEL FUELS PHASE III DATA SUMMARY

| CHEMICAL COMPOUND CLASSES (%) | ASH 143 | ASH 144 | UOP 161 | SUN 153P |
|---|---|---|---|---|
| NORMAL PARAFFINS GC (AREA) | 20.82 | 22.66 | 23.38 | 17.86 |
| BRANCHED PARAFFINS MS/GC (WT) | 28.38 | 24.24 | 23.38 | 17.86 |
| CYCLIC PARAFFINS MS (WT) | 30.20 | 28.70 | 38.50 | 36.70 |
| TOTAL PARAFFINS MS (WT) | 79.40 | 75.60 | 84.60 | 81.50 |
| TOTAL PARAFFINS NMR (MOLE) | 88.13 | 92.86 | 91.08 | 88.88 |
| TOTAL PARAFFINS FIA (VOL) | 68.40 | 62.50 | 74.80 | 76.00 |
| NAPHTHALENES MS (WT) | 2.60 | 2.30 | 2.00 | 1.70 |
| NAPHTHALENES NMR (MOLE) | 1.70 | .45 | .62 | .77 |
| INDANS AND TETRALINS MS (WT) | 10.30 | 13.40 | 5.70 | 6.10 |
| ALKYL BENZENES MS (WT) | 7.70 | 8.70 | 7.70 | 10.70 |
| ALKYL BENZENES NMR (MOLE) | 10.05 | 6.13 | 8.14 | 10.09 |
| TOTAL AROMATICS MS (WT) | 20.60 | 24.40 | 15.40 | 18.50 |
| TOTAL AROMATICS NMR (MOLE) | 11.75 | 6.58 | 8.76 | 10.85 |
| TOTAL AROMATICS FIA (VOL) | 29.50 | 35.80 | 23.90 | 22.20 |
| OLEFINS FIA (VOL) | 2.10 | 1.70 | 1.30 | 1.80 |
| OLEFINS NMR (MOLE) | .11 | .57 | .16 | .27 |
| OTHER PROPERTIES | | | | |
| FRACT. AROMATIC CARBON (ATOM) | .1219 | .0438 | .1059 | .1191 |
| FRACT. AROM. HYDROGEN (ATOM) | .0320 | .0146 | .0209 | .0277 |
| HYDROGEN CONTENT (WT %) | 13.62 | 13.57 | 13.92 | 13.85 |
| SMOKE POINT (MM) | 18.00 | 16.00 | 22.00 | 21.00 |
| TOTAL SULFUR (WT %) | 0.00 | 0.00 | .01 | 0.00 |
| H/C AROMATICS NMR (ATOM) | .4932 | .6242 | .3803 | .4455 |
| NO. HYDROGENS ON AROM RING | 2.96 | 3.75 | 2.28 | 2.67 |
| REFINERS CODE NUMBER | ASH DF2 5 GAL CAN | ASH DF2 55 GAL DRUM | UOP 3794 -152 | SUN X190 -79 |

# TABLE 14. DIESEL FUELS PHASE III BOILING RANGE BY HIGH RESOLUTION GC

| CARBON NUMBER GROUP | % OF FUEL BOILING IN GROUP BY HR-GC | | | |
|---|---|---|---|---|
| FUEL | ASH 143 | ASH 144 | UOP 161 | SUN 153P |
| 3 | 0.0 | 0.0 | 0.0 | 0.0 |
| 4 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5 | 0.0 | 0.0 | 0.1 | 0.0 |
| 6 | 0.0 | 0.0 | 0.0 | 0.0 |
| 7 | 0.0 | 0.0 | 0.0 | 0.0 |
| 8 | 0.1 | 0.0 | 1.7 | 0.0 |
| 9 | 0.0 | 0.0 | 3.9 | 1.8 |
| 10 | 0.0 | 0.0 | 4.4 | 7.5 |
| 11 | 0.0 | 0.0 | 5.0 | 8.1 |
| 12 | 10.5 | 2.4 | 6.1 | 8.0 |
| 13 | 12.8 | 19.1 | 9.2 | 8.7 |
| 14 | 8.7 | 18.3 | 9.6 | 9.0 |
| 15 | 6.4 | 20.0 | 9.5 | 9.6 |
| 16 | 7.9 | 14.5 | 8.4 | 10.3 |
| 17 | 24.3 | 14.1 | 9.5 | 12.2 |
| 18 | 2.6 | 10.5 | 9.9 | 12.0 |
| 19 | 2.8 | 0.8 | 8.4 | 9.8 |
| 20 | 0.0 | 0.0 | 5.3 | 3.1 |
| 21 | 0.0 | 0.0 | 4.4 | 0.0 |
| 22 | 0.0 | 0.0 | 2.2 | 0.0 |
| 23 | 0.0 | 0.0 | 1.7 | 0.0 |
| 24 | 0.0 | 0.0 | 0.8 | 0.0 |
| 25 | 0.0 | 0.0 | 0.0 | 0.0 |

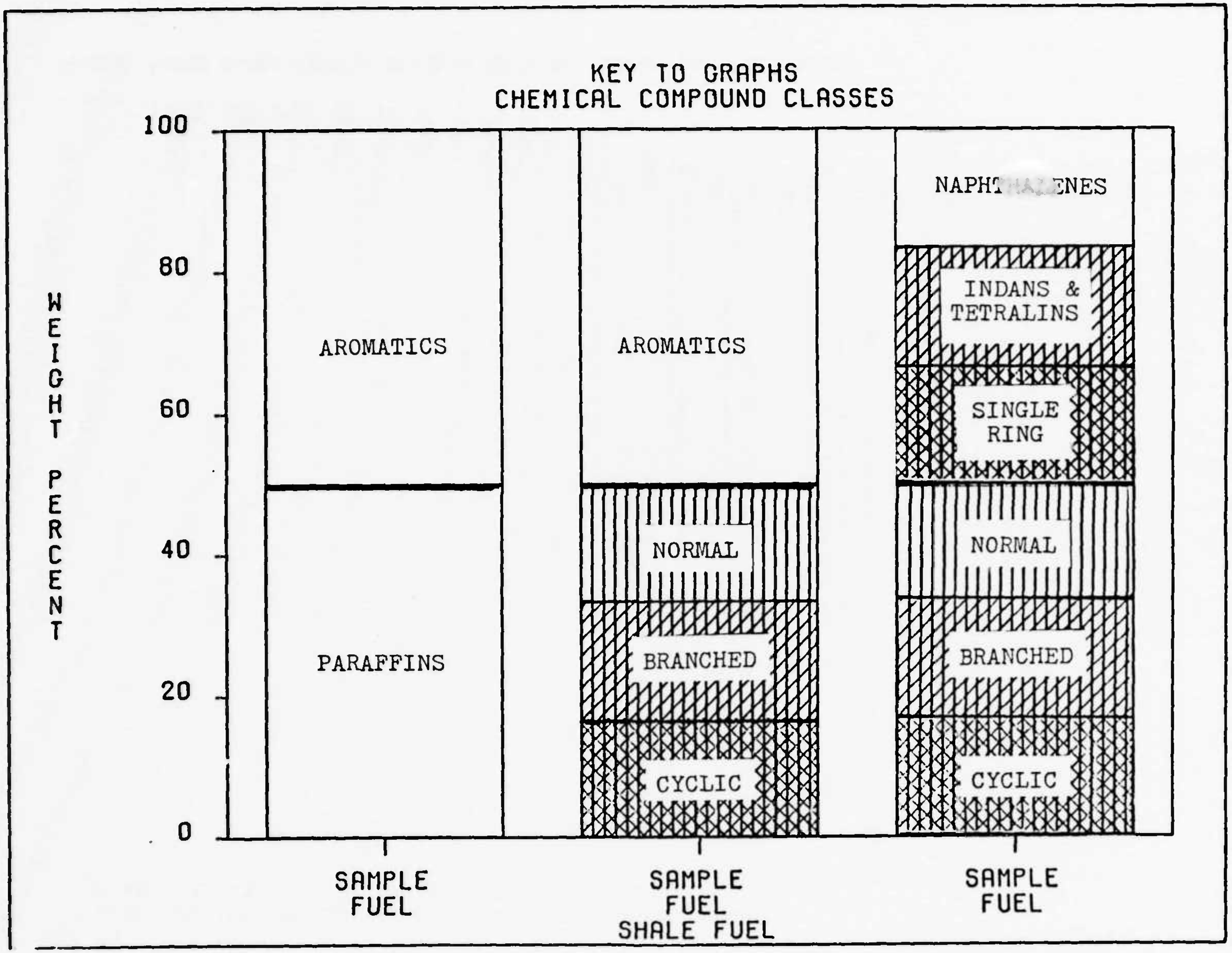


Figure 1. Key to graphs, chemical compound classes.

HIGH-RESOLUTION CAPILLARY COLUMN GAS CHROMATOGRAPHY
NORMAL ALKANES IN SHALE-DERIVED DIESEL FUEL

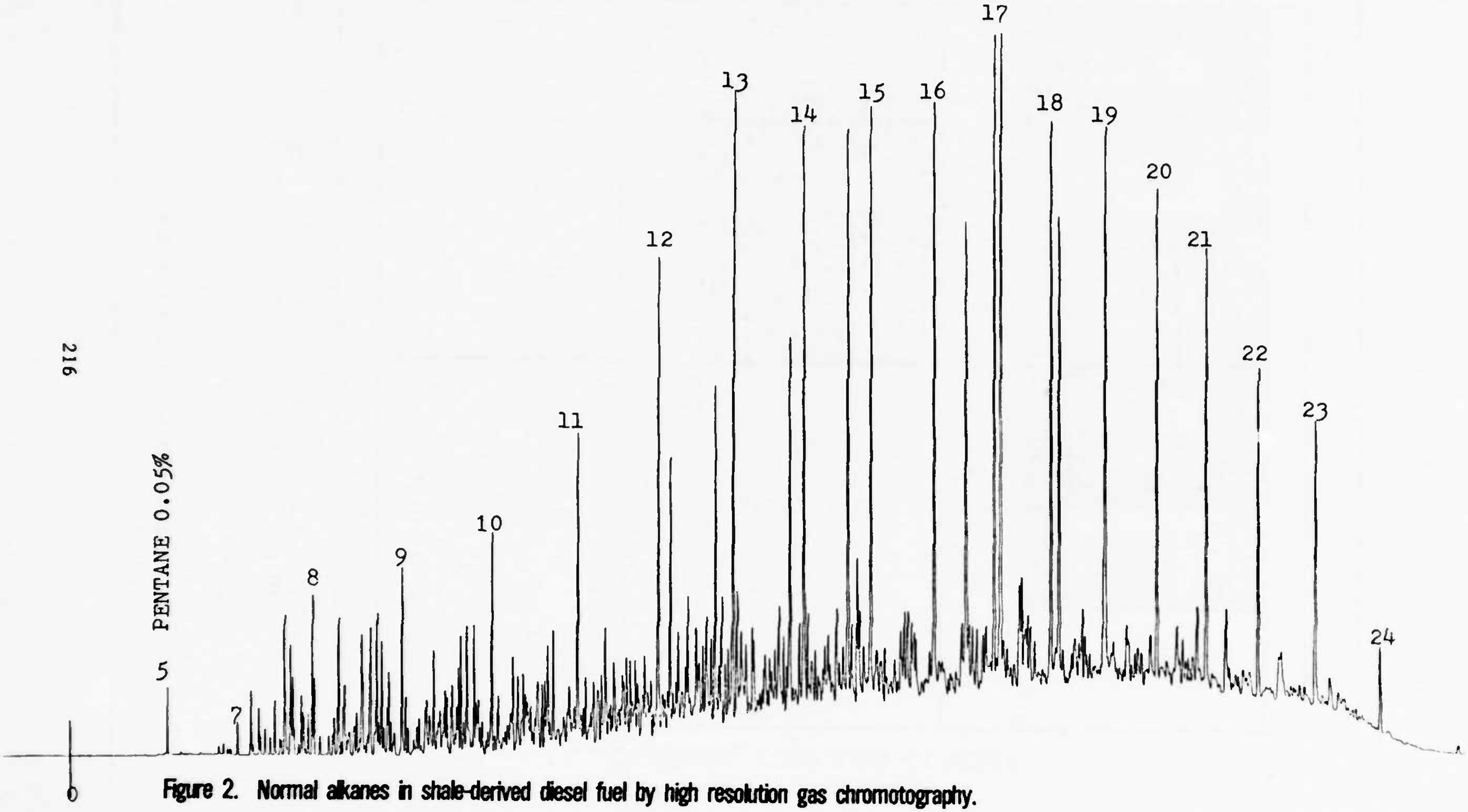


Figure 2. Normal alkanes in shale-derived diesel fuel by high resolution gas chromatography.

HIGH-RESOLUTION CAPILLARY COLUMN GAS CHROMATOGRAPHY
FUEL BOILING RANGE REPORTED AS THE INTEGRAL (AREA %) OF
THE GC PEAKS GROUPED BY CARBON NUMBER.
SHALE-DERIVED JP-4

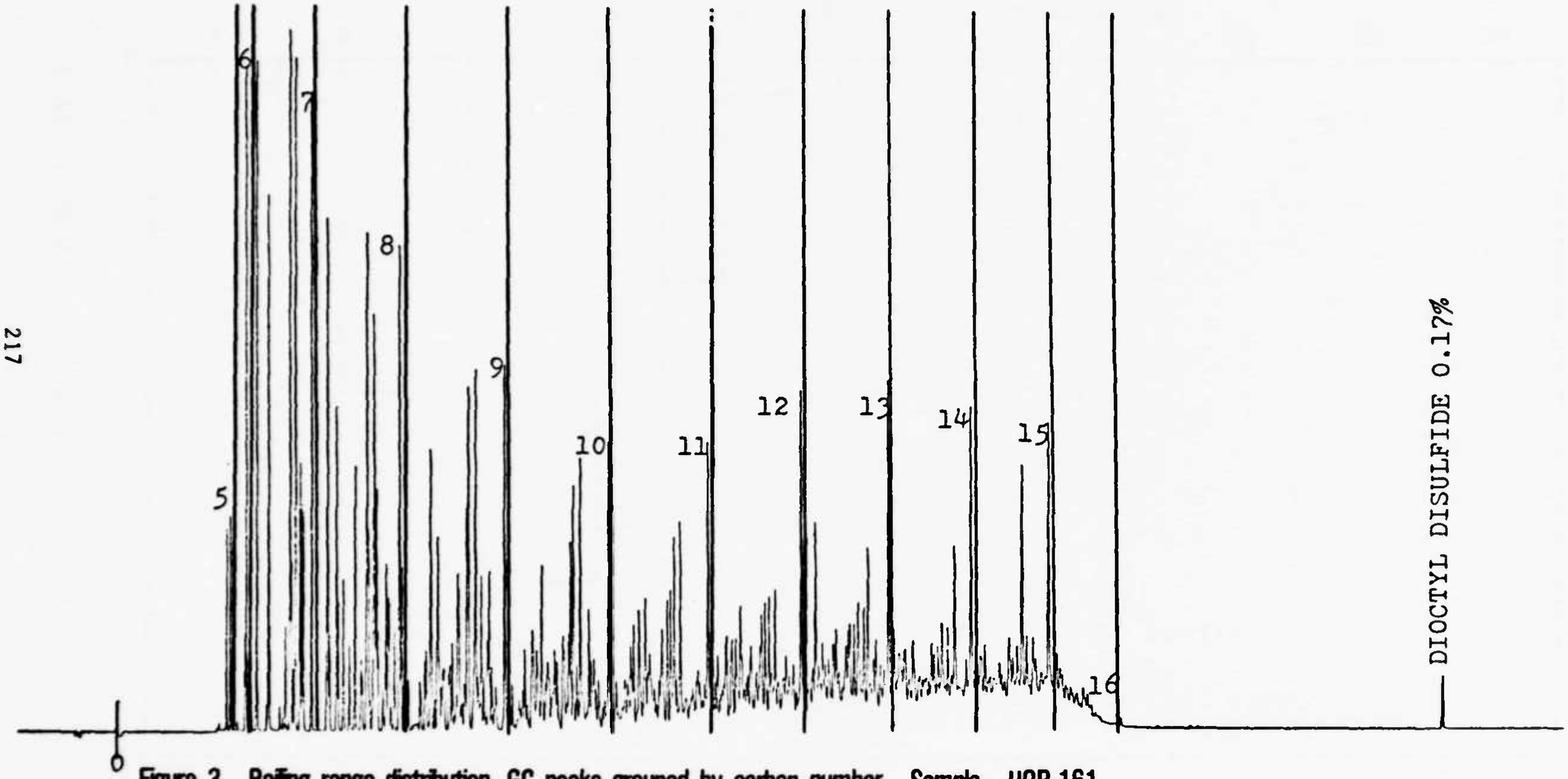


Figure 3. Boiling range distribution, GC peaks grouped by carbon number. Sample. UOP-161

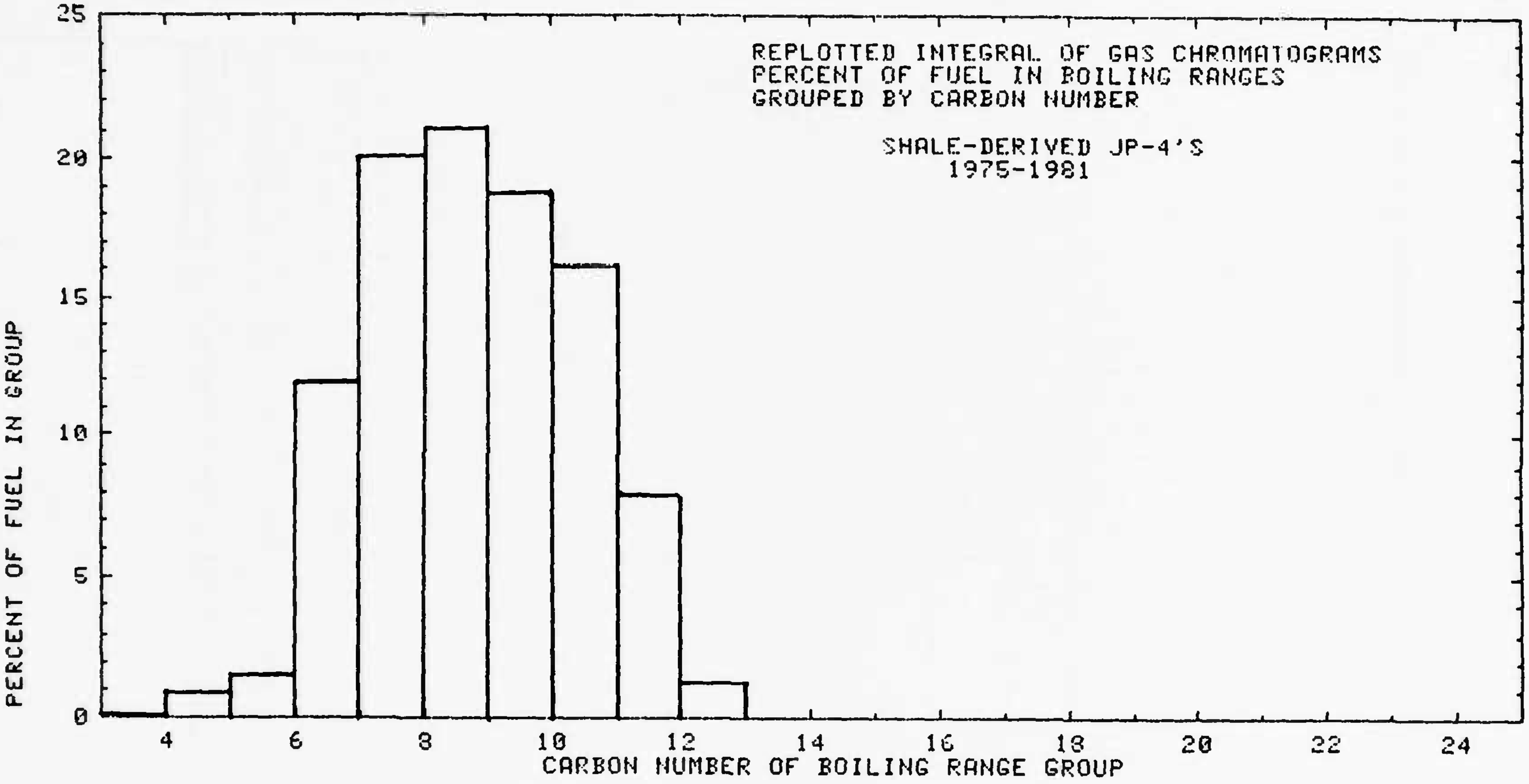


Figure 4. Histogram: Percent of fuel in boiling ranges grouped by carbon number. Sample GWR-11

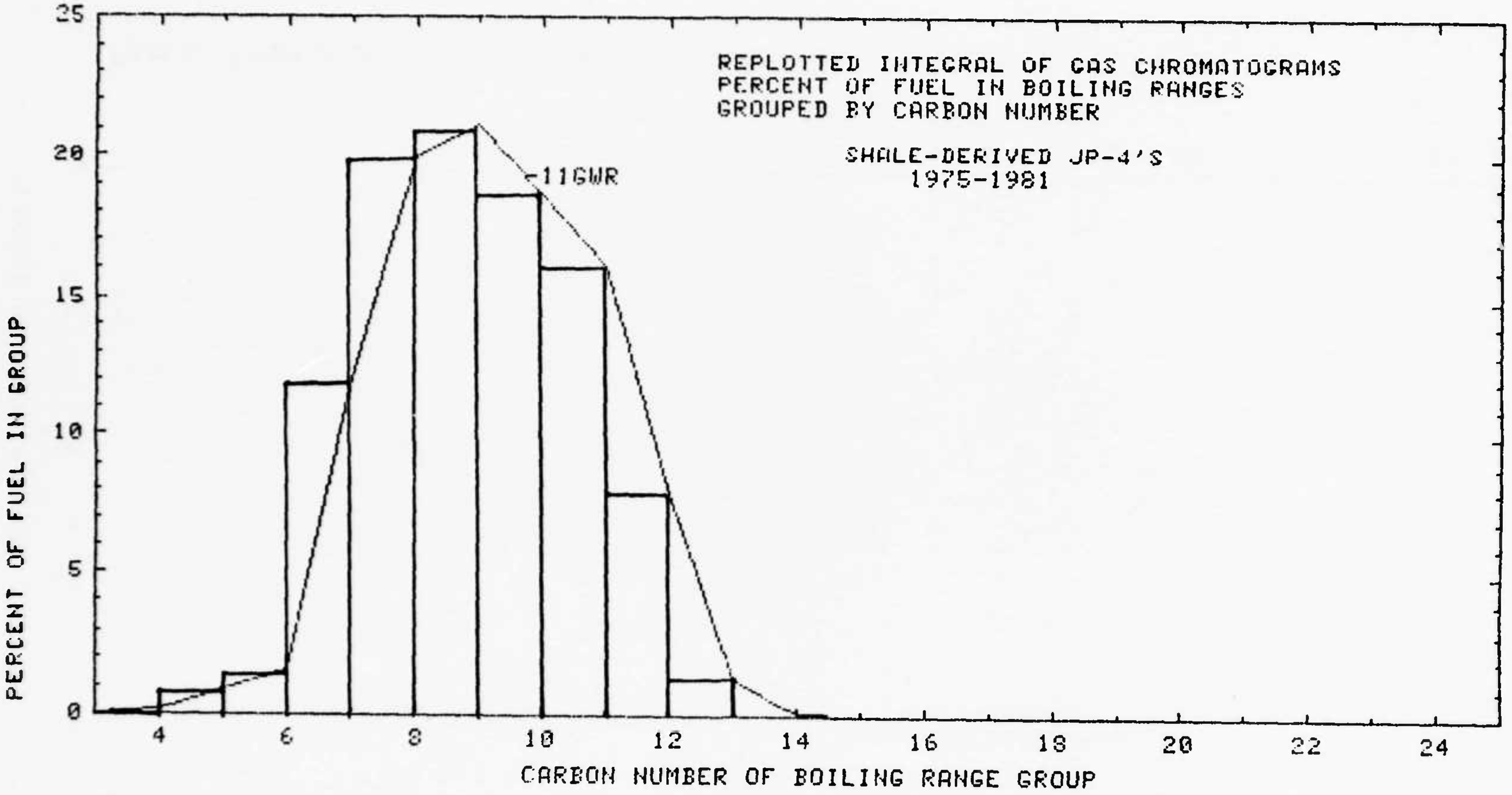


**Figure 5. Linegraph:** Percent of fuel in boiling ranges grouped by carbon number. Sample GWR-11

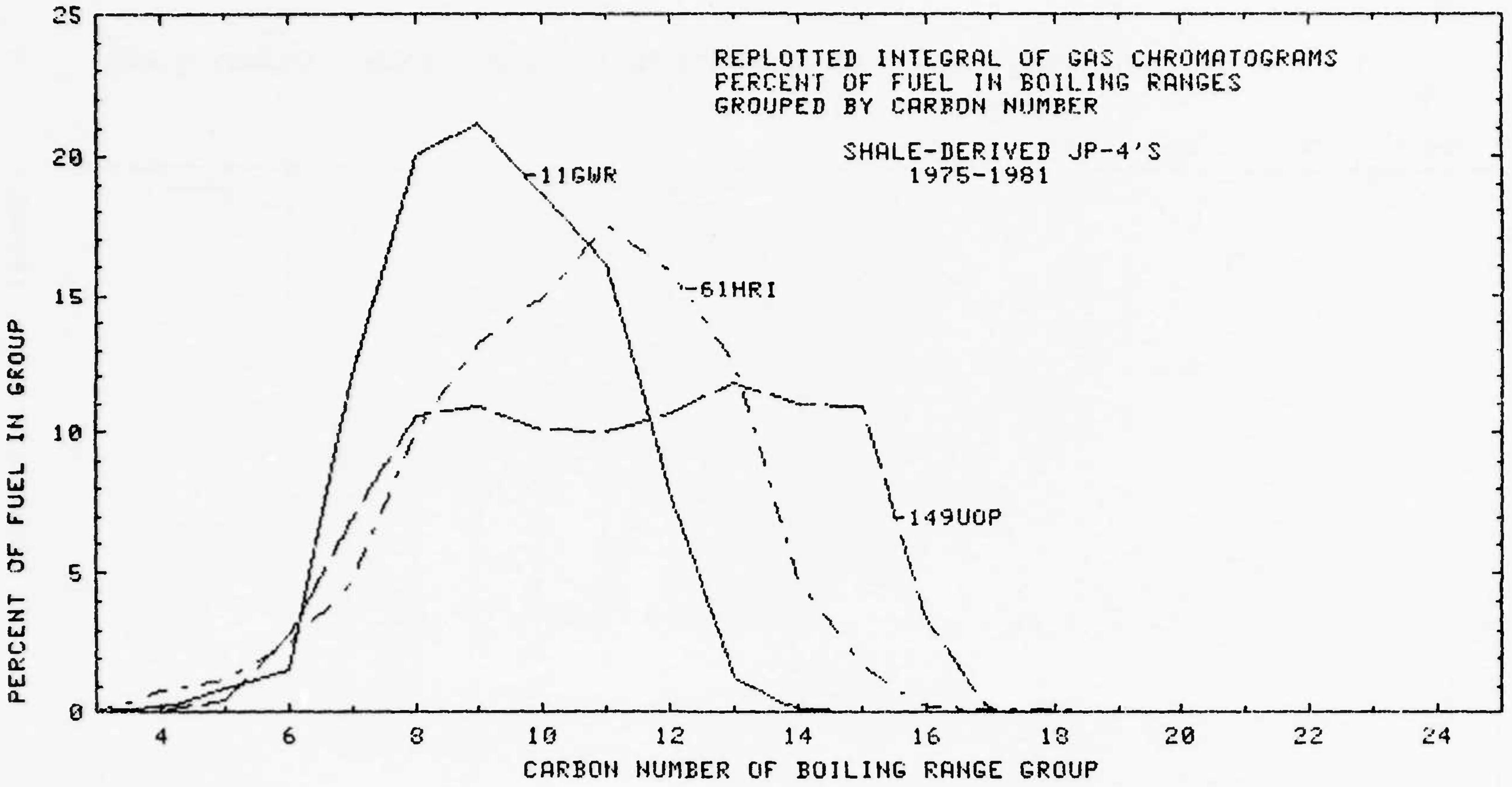
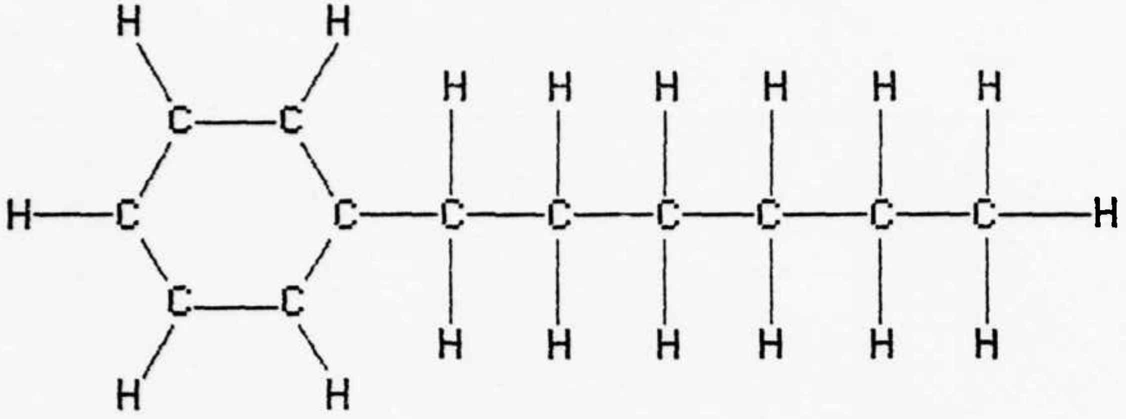


Figure 6. Percent of fuel in boiling ranges grouped by carbon number. Shale-derived JP-4's 1975-1981

# COMPARISON OF ANALYTICAL METHODS



$C_6H_5-$ FW=77 $C_6H_{13}-$ FW=85

HEXYLBENZENE ($C_{12}H_{18}$) FW=162 11.1 WT % HYDROGEN

| ANALYTICAL METHOD | EXPECTED ANALYTICAL RESULT: CONTRIBUTION WHEN HEXYLBENZENE IS ADDED TO A FUEL. |
|---|---|
| WIDE-LINE NMR | HYDROGEN CONTENT = 11.1 WT PERCENT: EFFECT PROPORTIONAL |
| FLUORESCENT INDICATOR ADSORPTION | AROMATICS 100% BY VOLUME |
| MASS SPECTROMETRY | AROMATICS 48 WT% (77/162) TO 100 WT% |
| PROTON NUCLEAR MAGNETIC RESONANCE | 28 % ATOMIC RATIO (5 AROMATIC H / 18 TOTAL H) |
| CARBON-13 NUCLEAR MAGNETIC RESONANCE | 50 % ATOMIC RATIO (6 AROMATIC C / 12 TOTAL C) |
| GAS TURBINE ENGINE | ?? |

NMR - NOT WRONG - JUST DIFFERENT - FRACTION AROMATIC CARBON FROM C-13 NMR CORRELATES WELL WITH SOME ENGINE DATA.

Figure 7. Comparison of analytical methods - hexyl benzene.

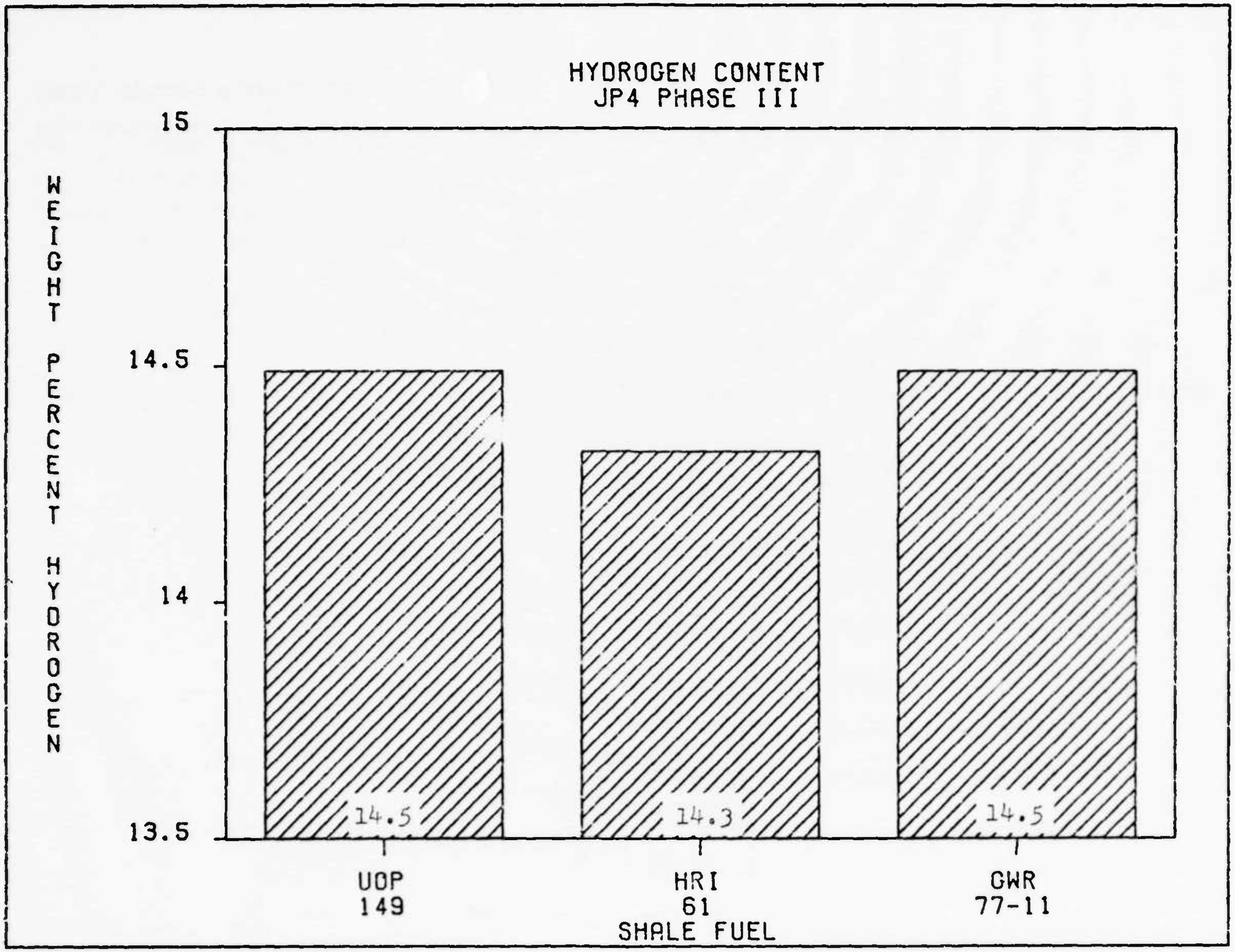


Figure 8. Hydrogen content, JP4 Phase III.

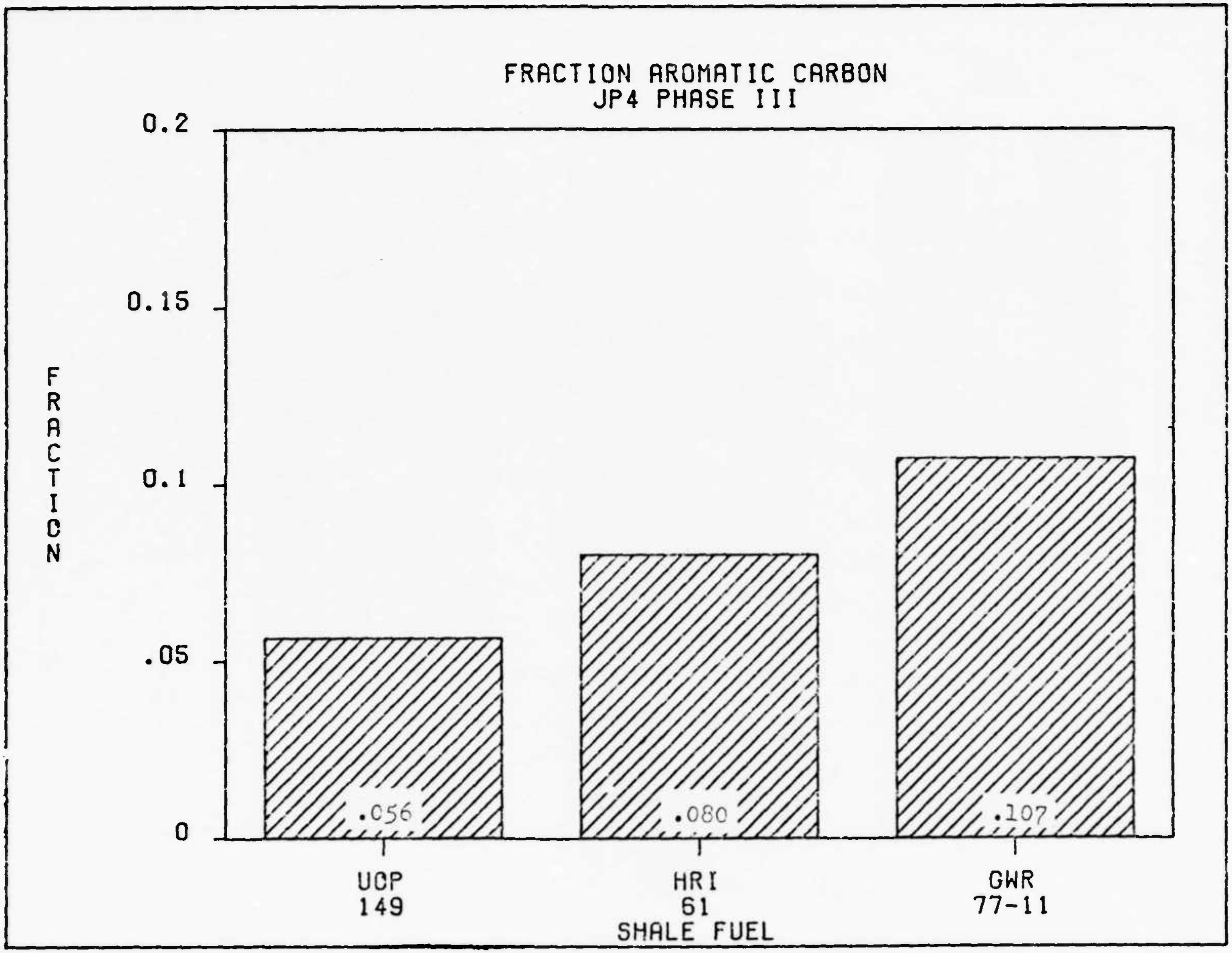


Figure 9. Fraction aromatic carbon, JP4 Phase III.

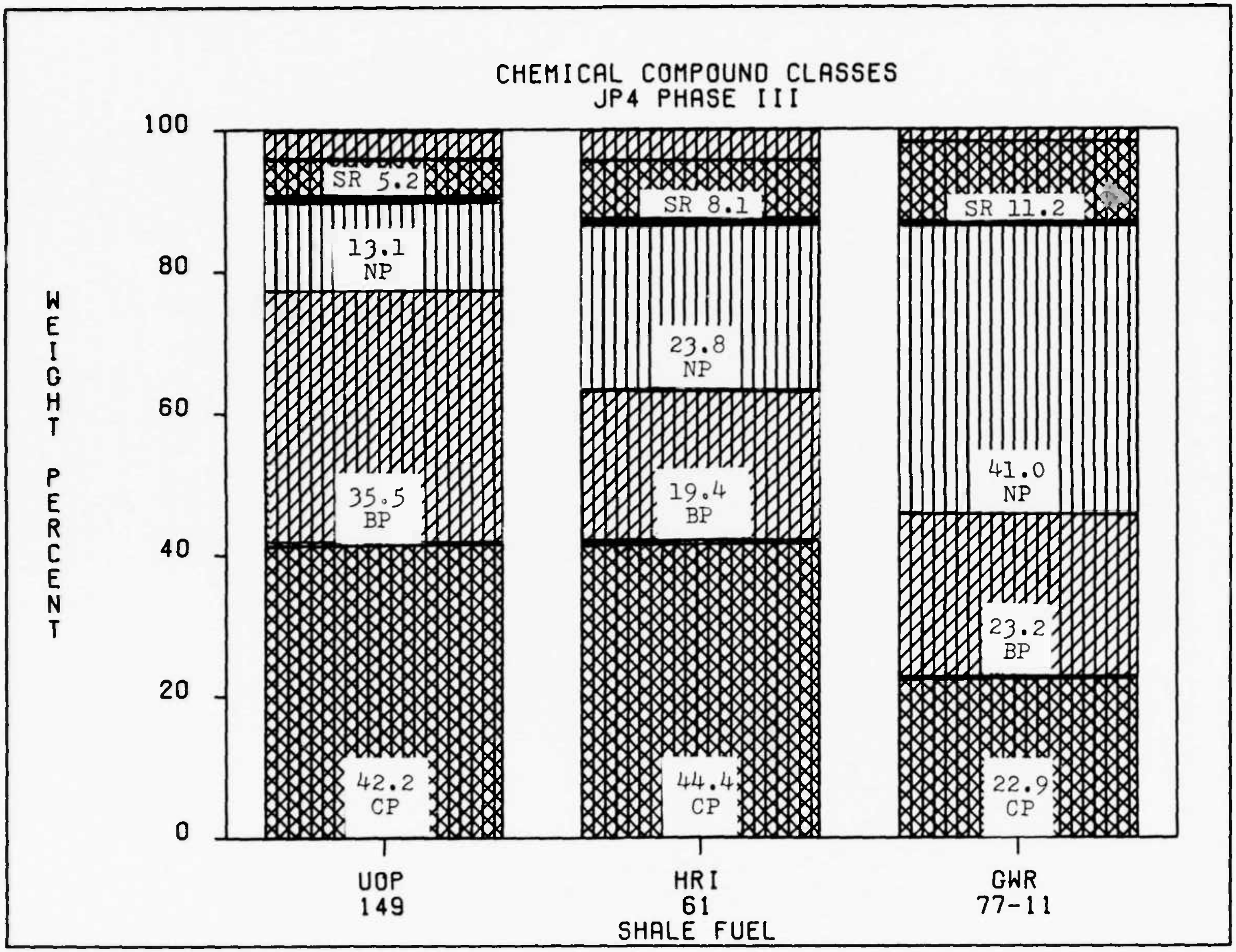


Figure 10. Chemical compound classes, JP4 Phase III.

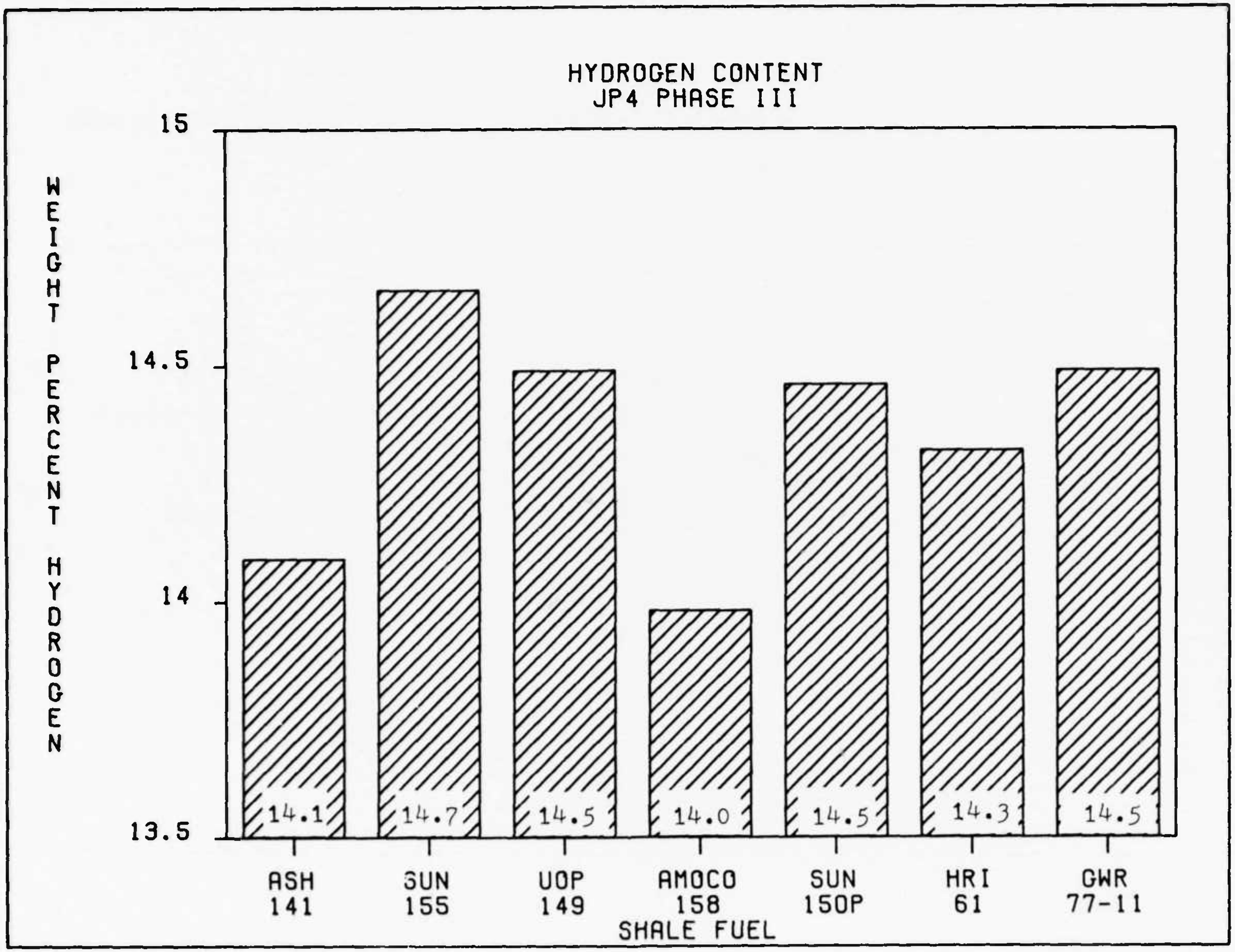


Figure 11. Hydrogen content, JP4 Phase III.

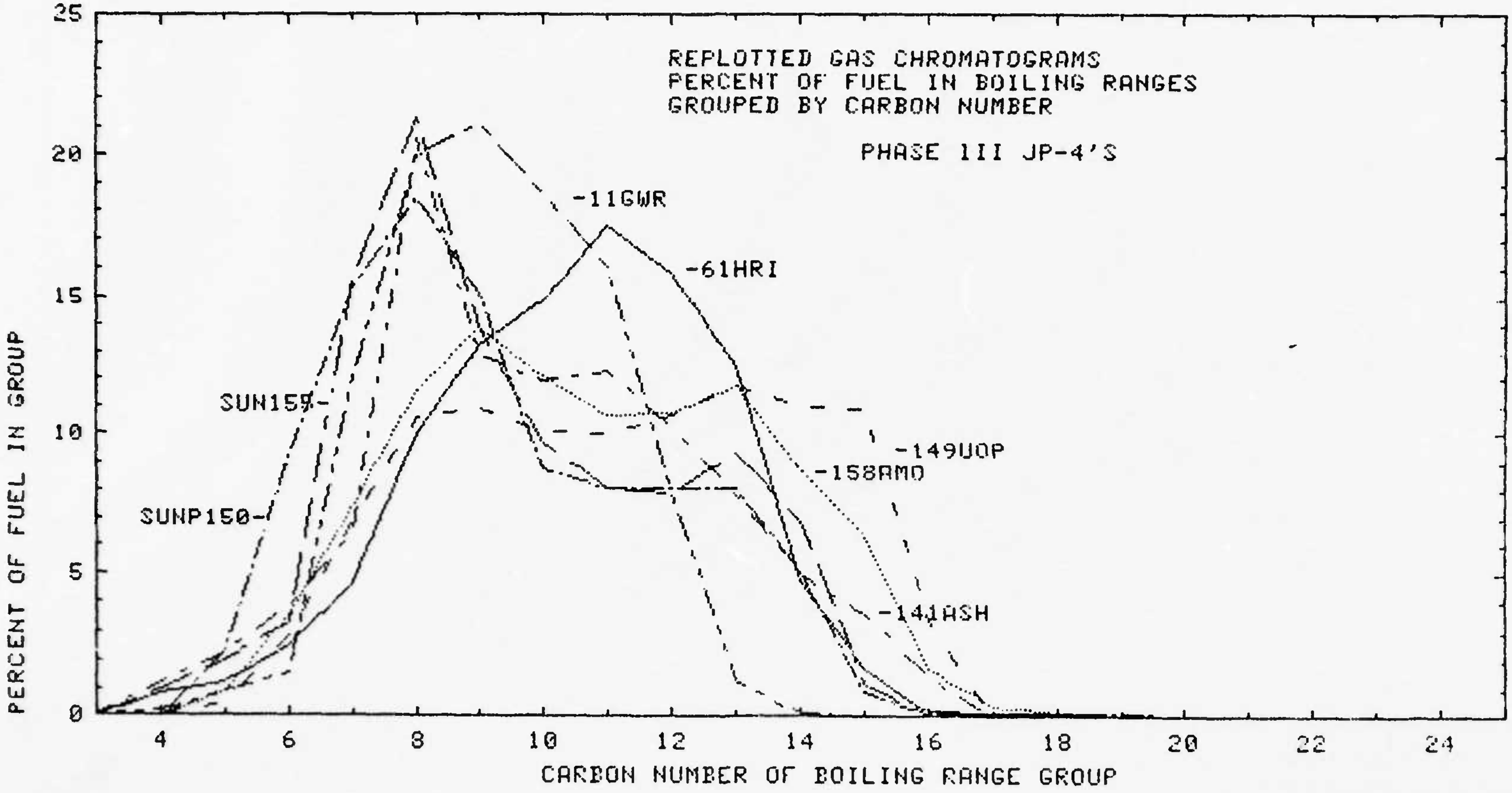


Figure 12. Boiling range distribution grouped by carbon number, JP4 Phase III.

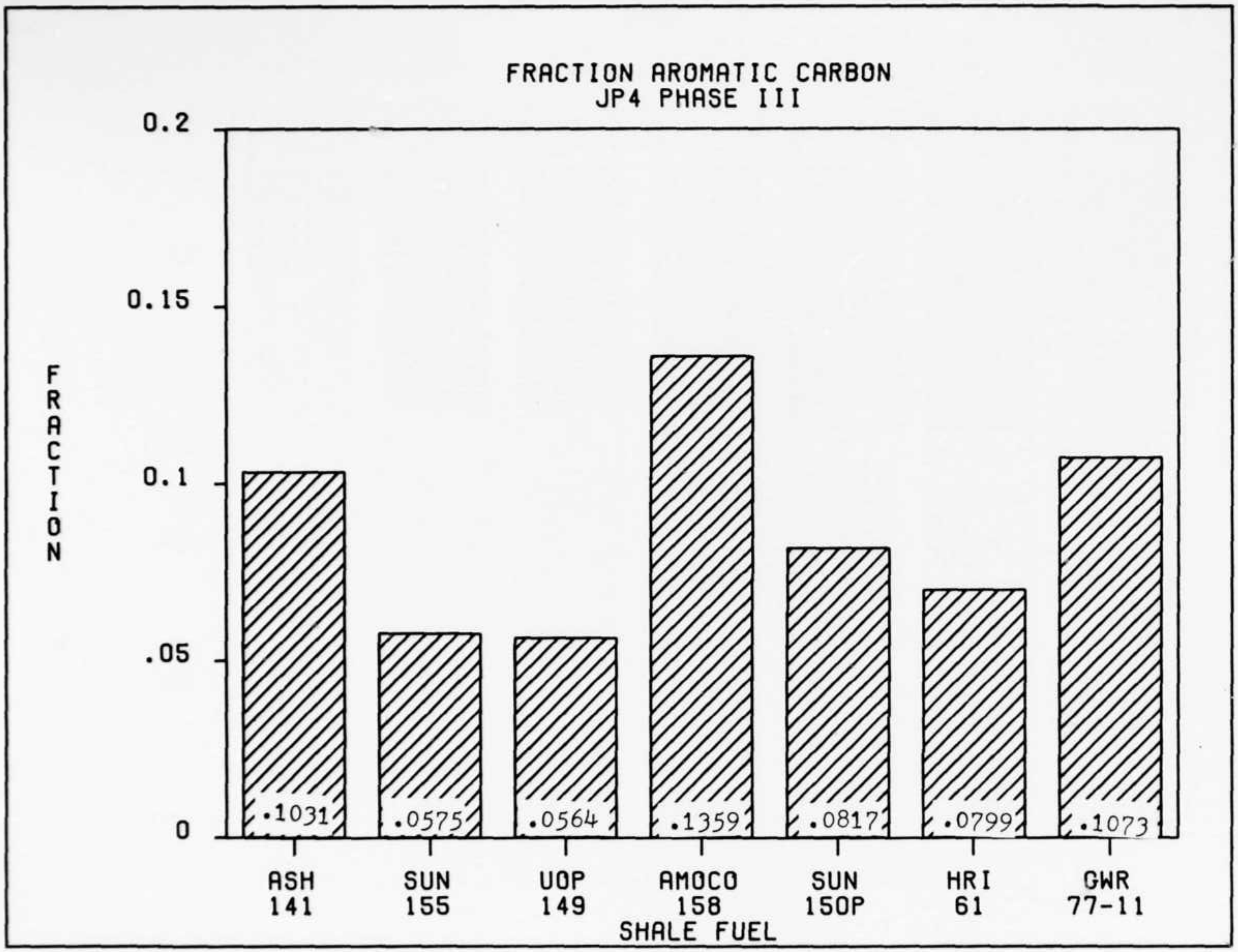


Figure 13. Fraction aromatic carbon, JP4 Phase III.

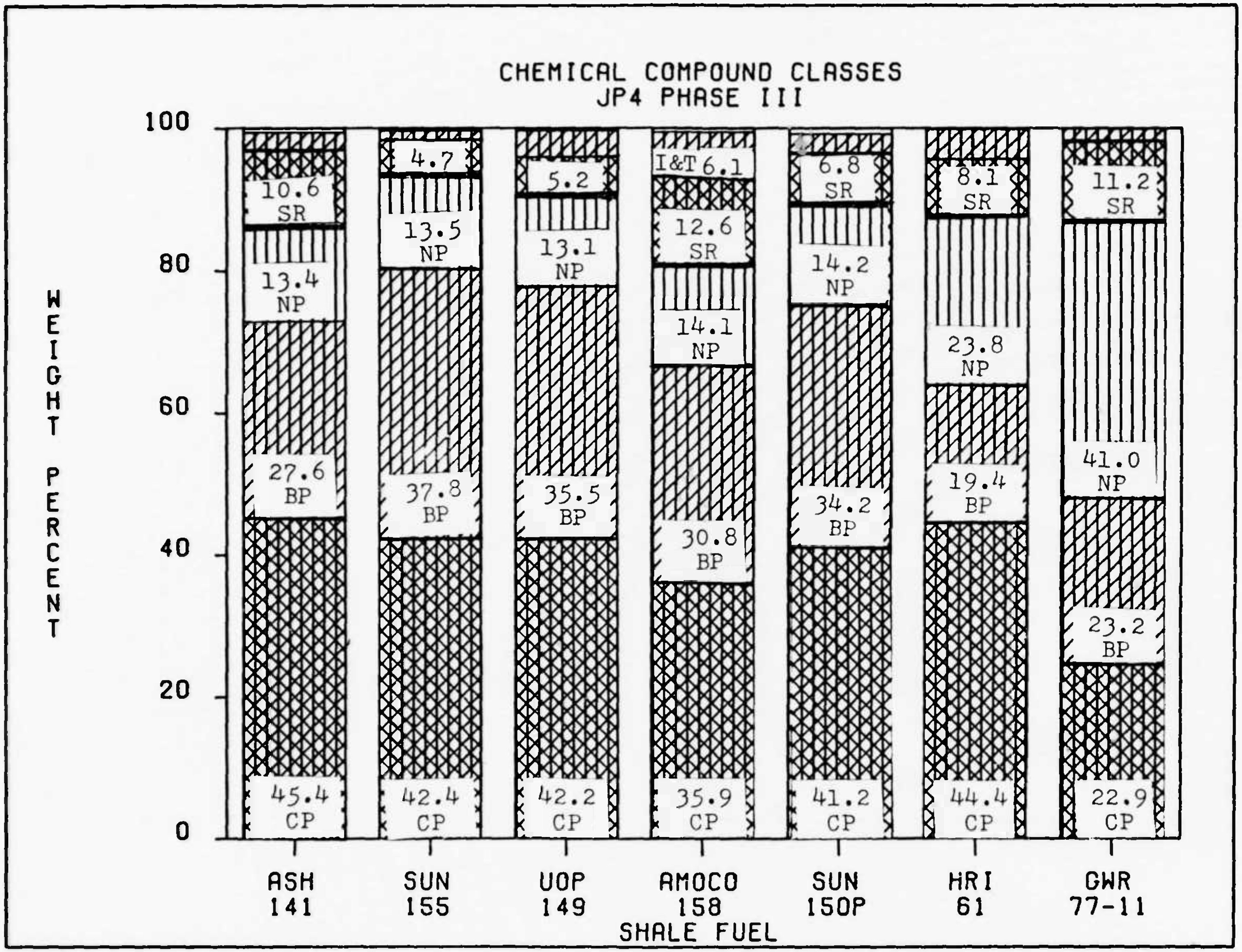


Figure 14. Chemical Compound Classes, JP4 Phase III.

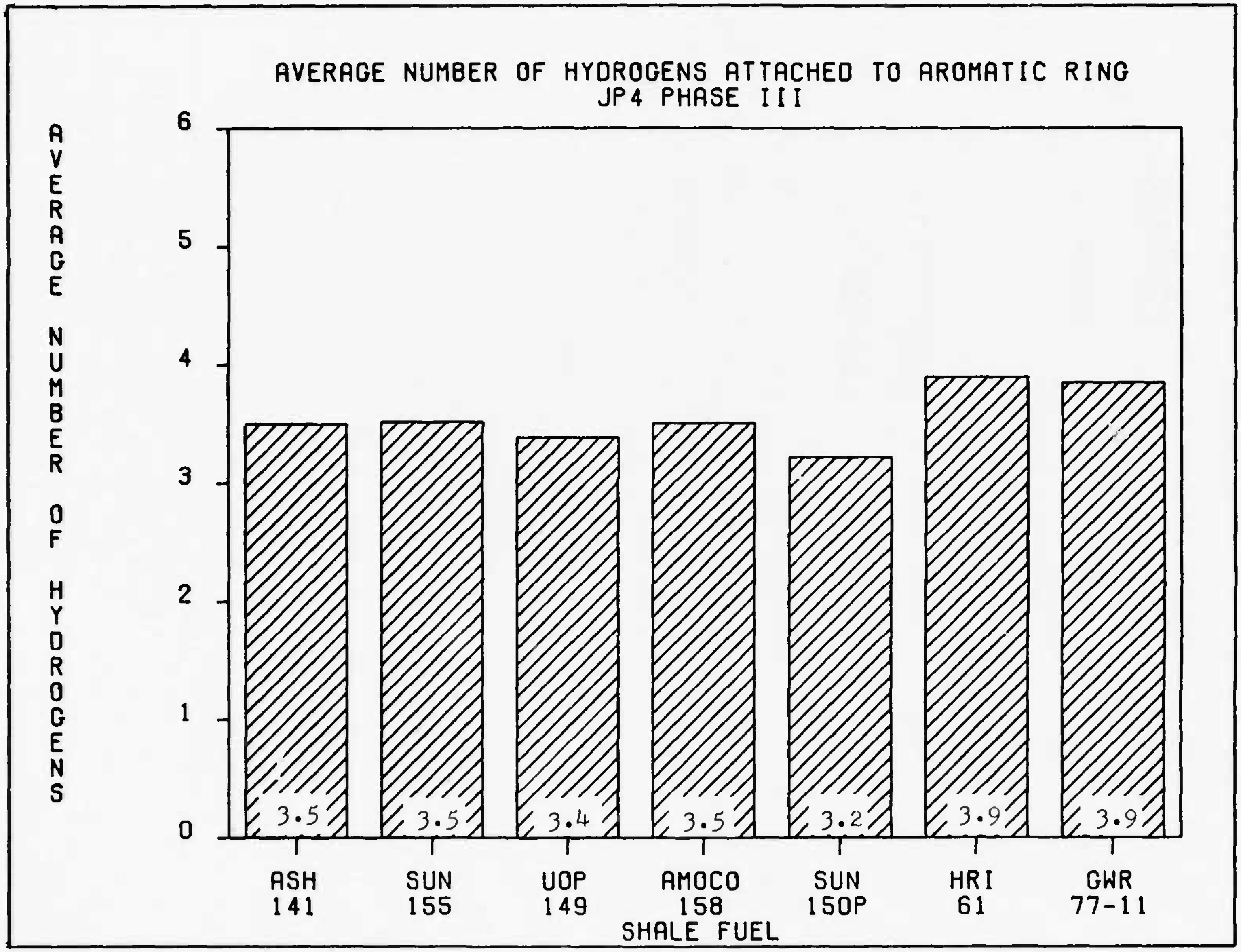


Figure 15. Average number of hydrogens attached to aromatic ring, JP4 Phase III.

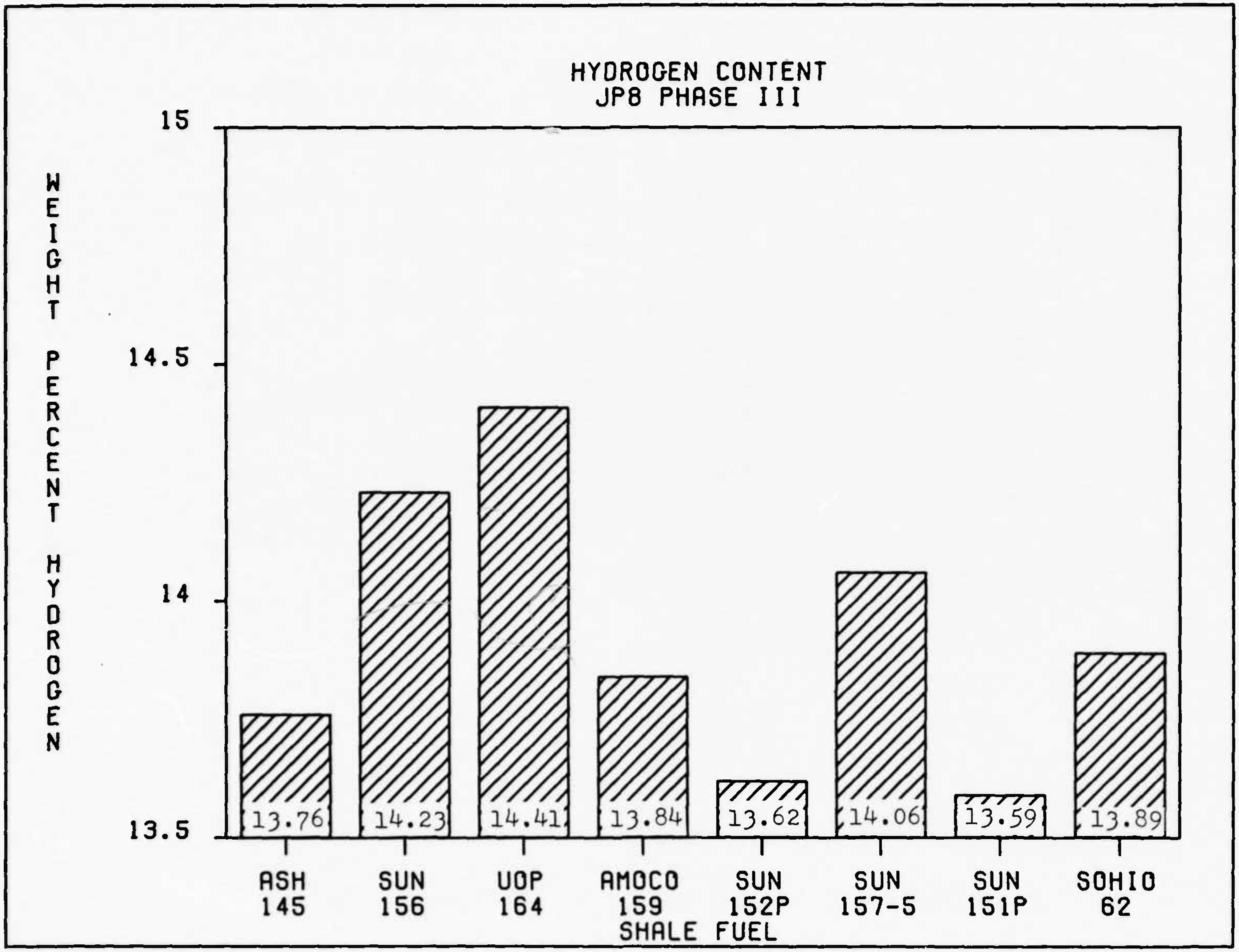


Figure 16. Hydrogen Content, JP5 and JP8 Phase III.

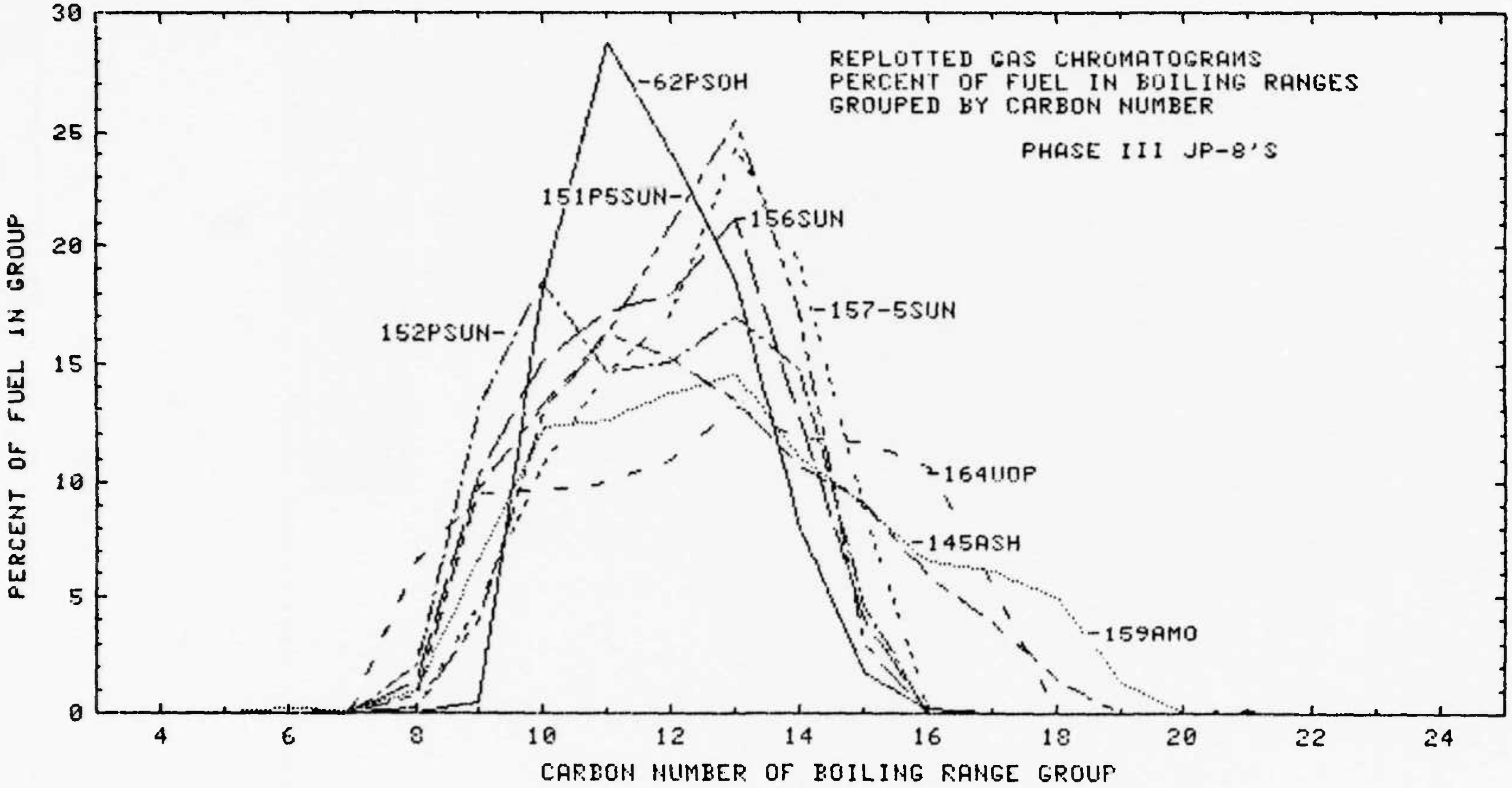


Figure 17. Boiling range distribution grouped by carbon number, JP5 and JP8 Phase III.

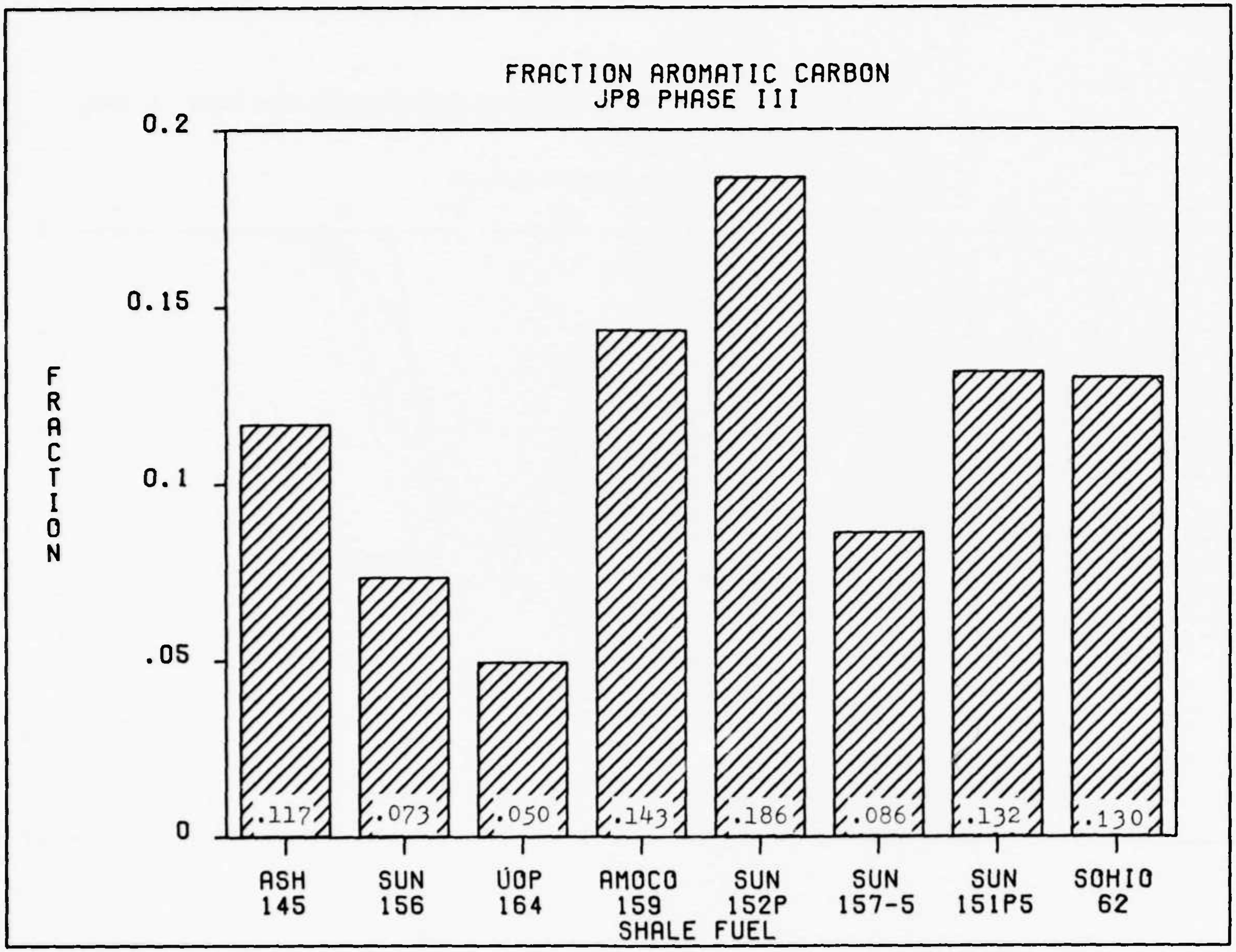


Figure 18. Fraction aromatic carbon, JP5 and JP8 Phase III.

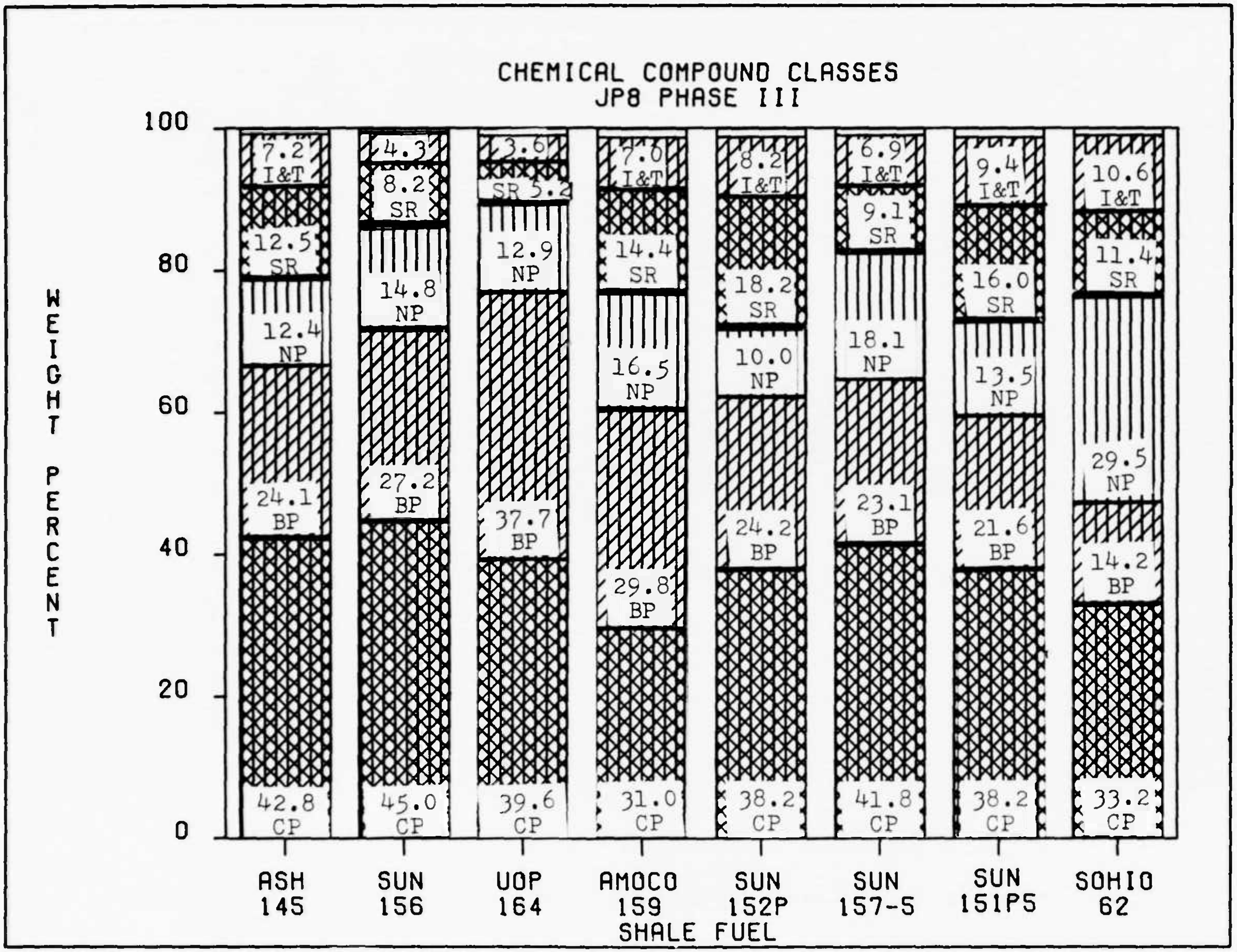


Figure 19. Chemical compound classes, JP5 and JP8 Phase III.

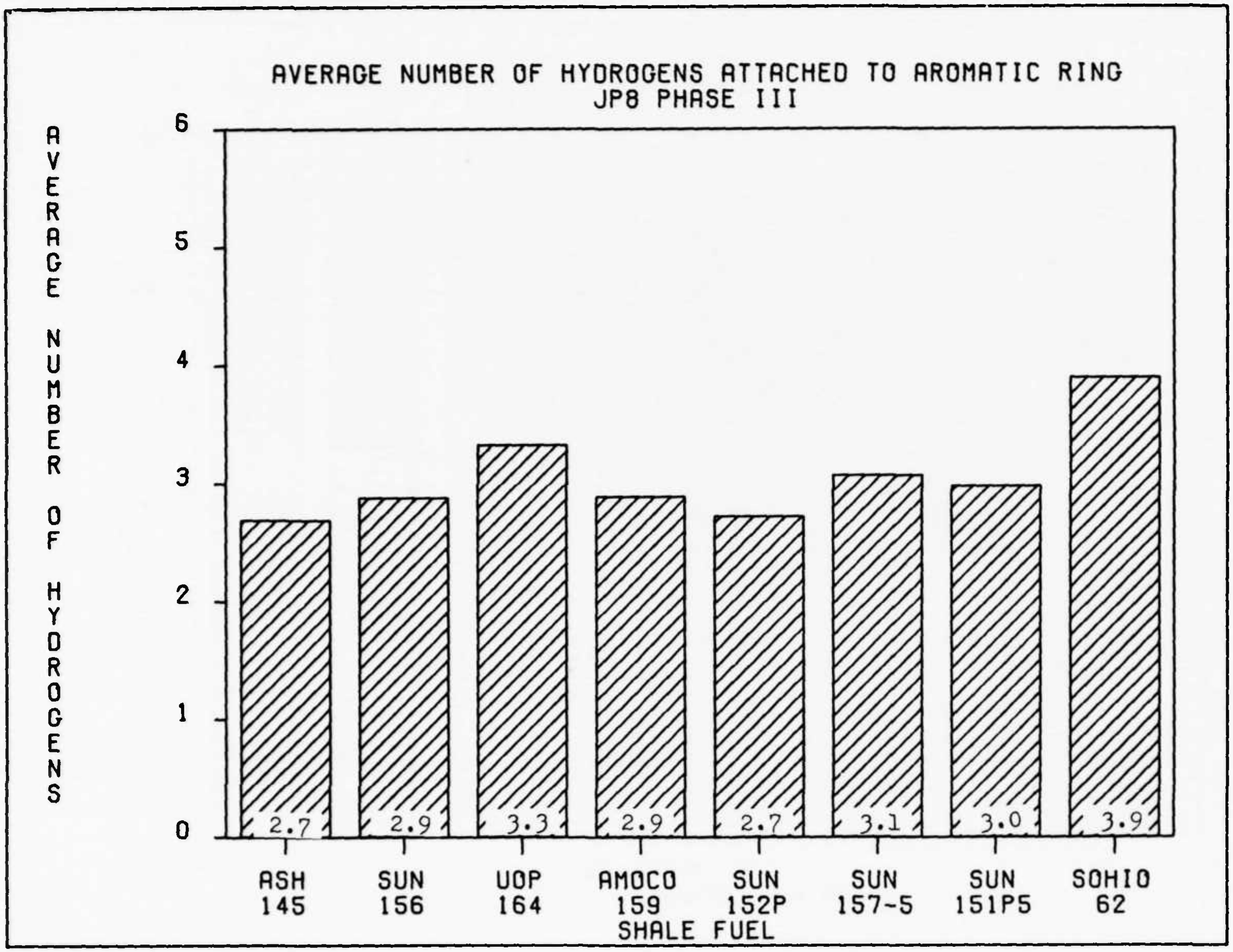


Figure 20. Average number of hydrogens attached to aromatic ring, JP5 and JP8 Phase III.

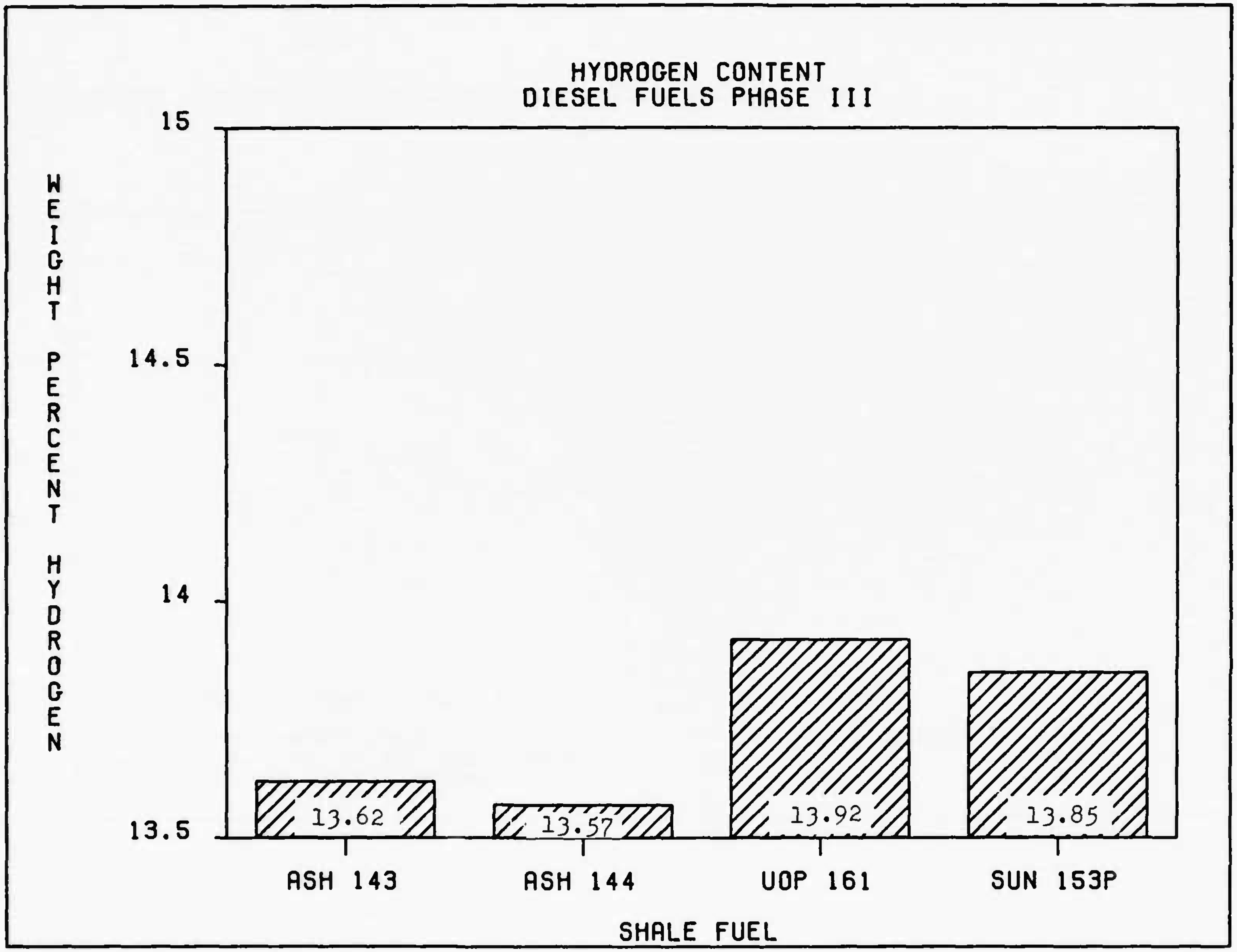


Figure 21. Hydrogen content, Diesel Fuels Phase III.

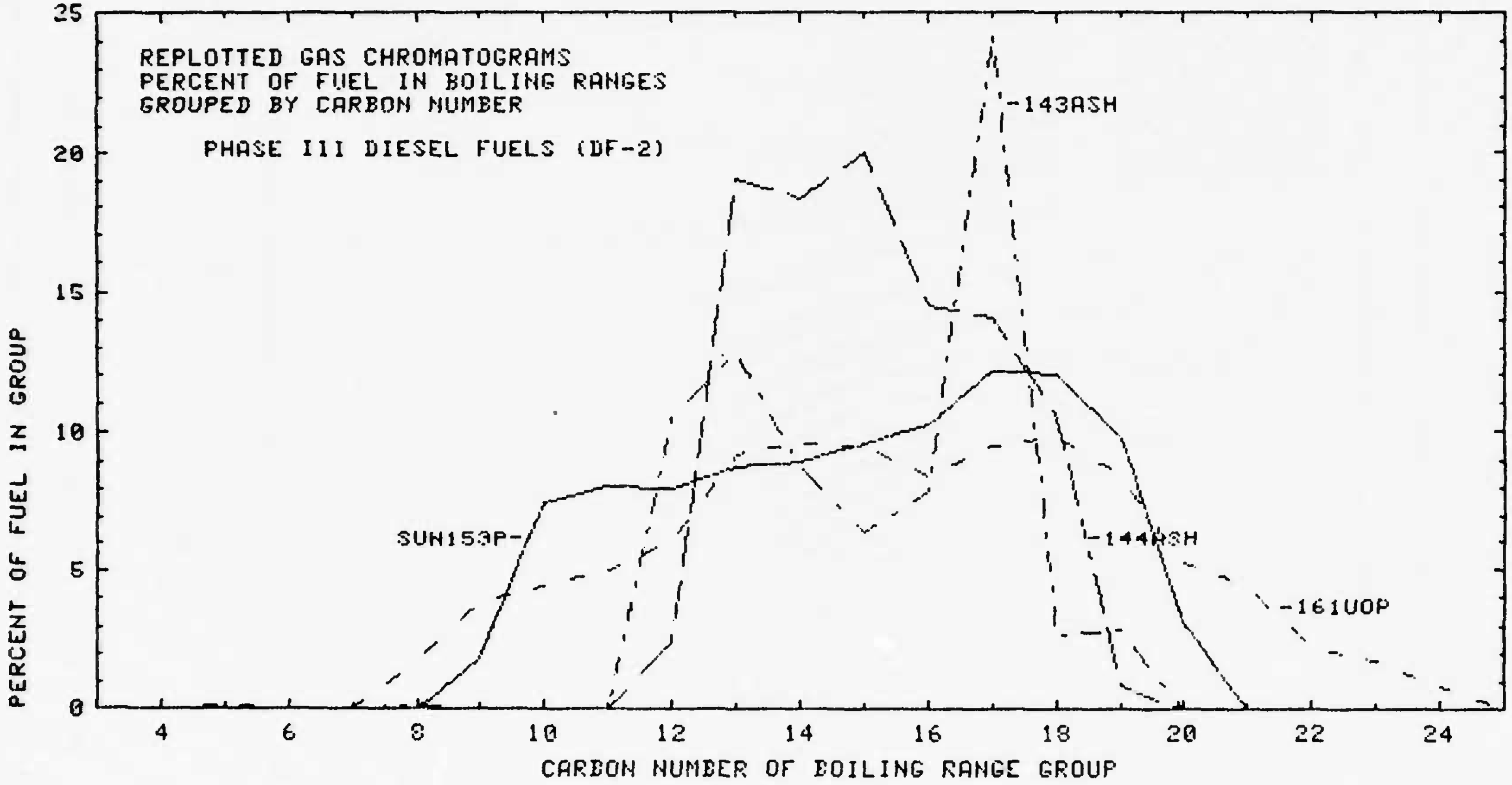


Figure 22. Boiling range distribution grouped by carbon number, Diesel Fuels Phase III.

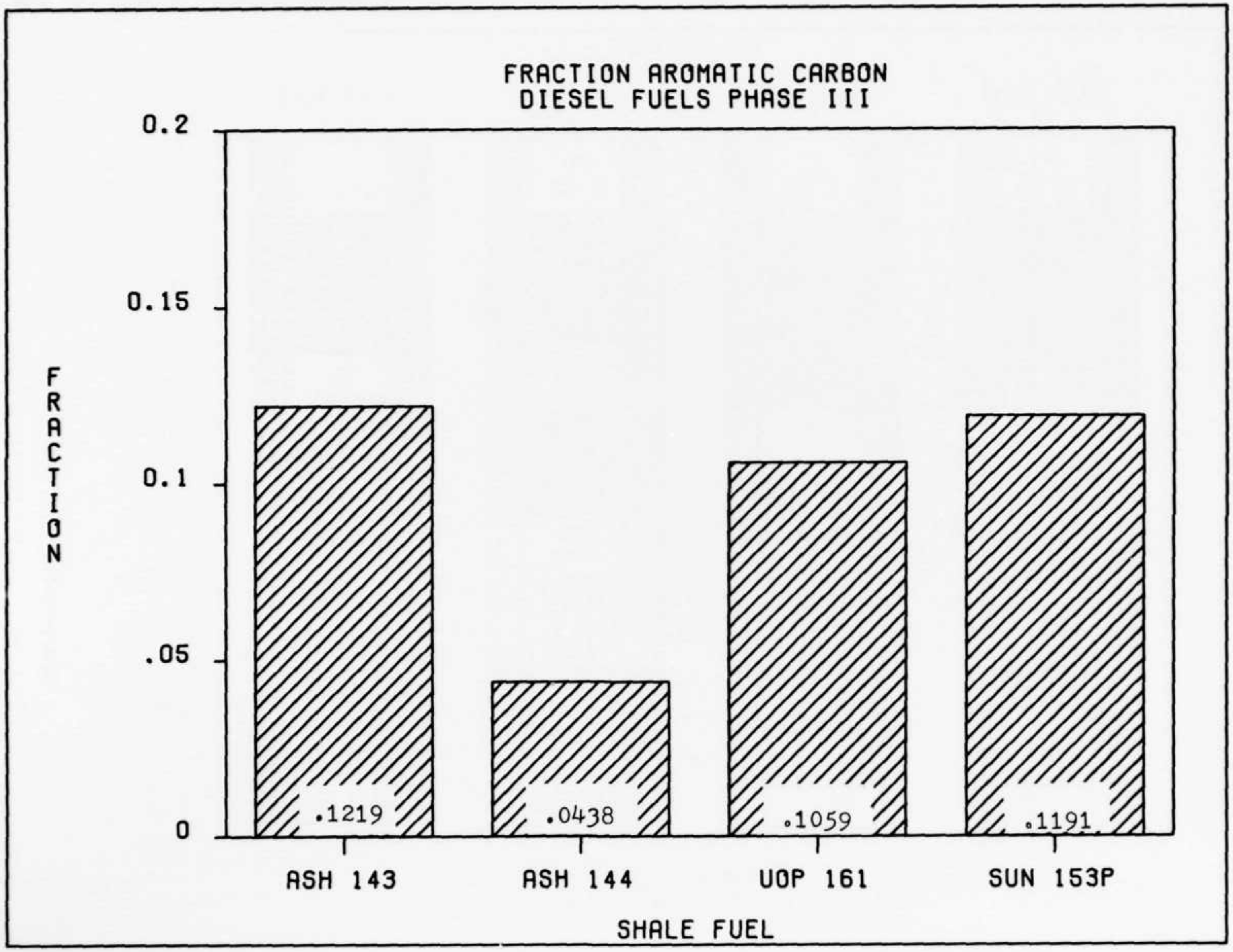


Figure 23. Fraction aromatic carbon, Diesel Fuels Phase III.

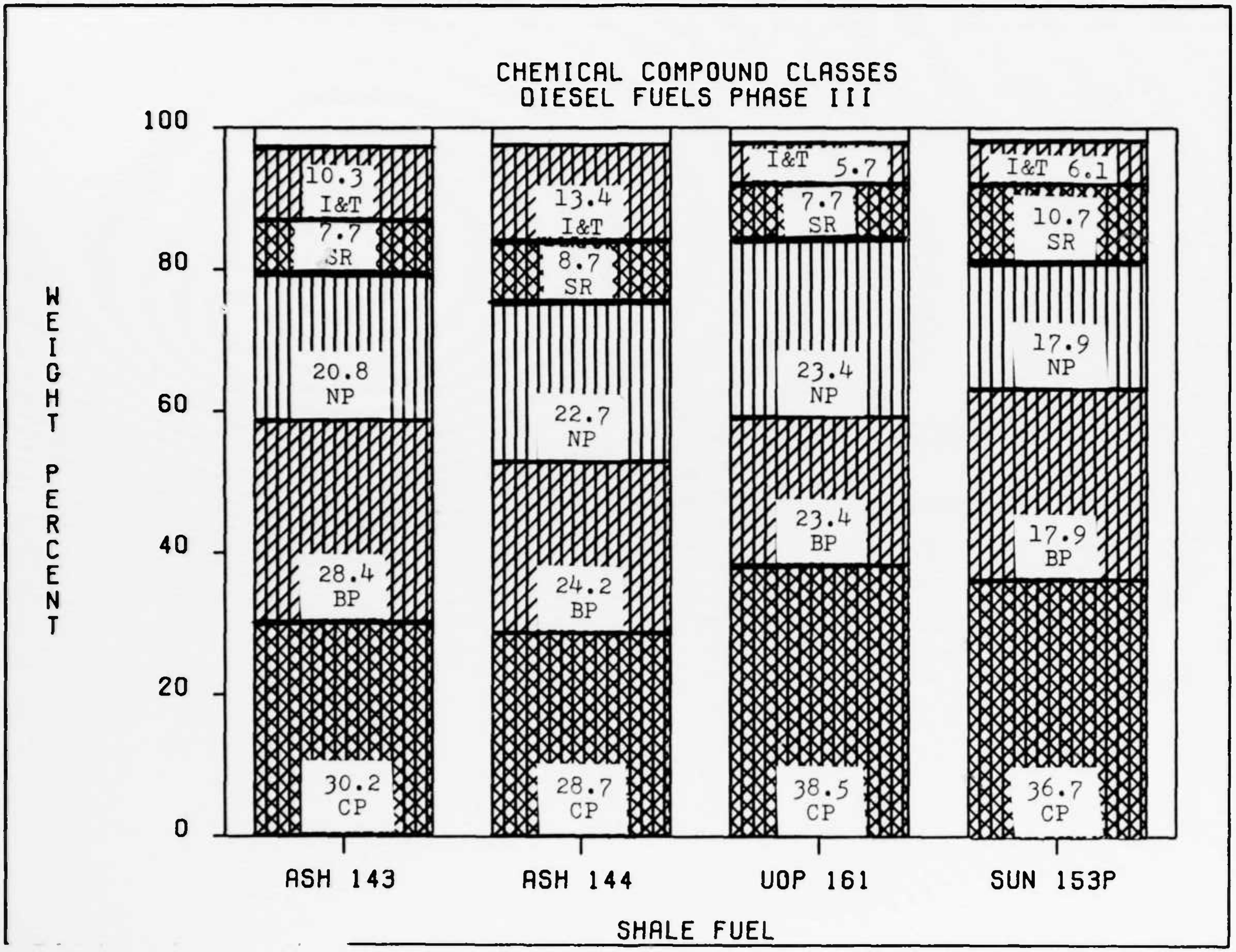


Figure 24. Chemical compound classes, Diesel Fuels Phase III.

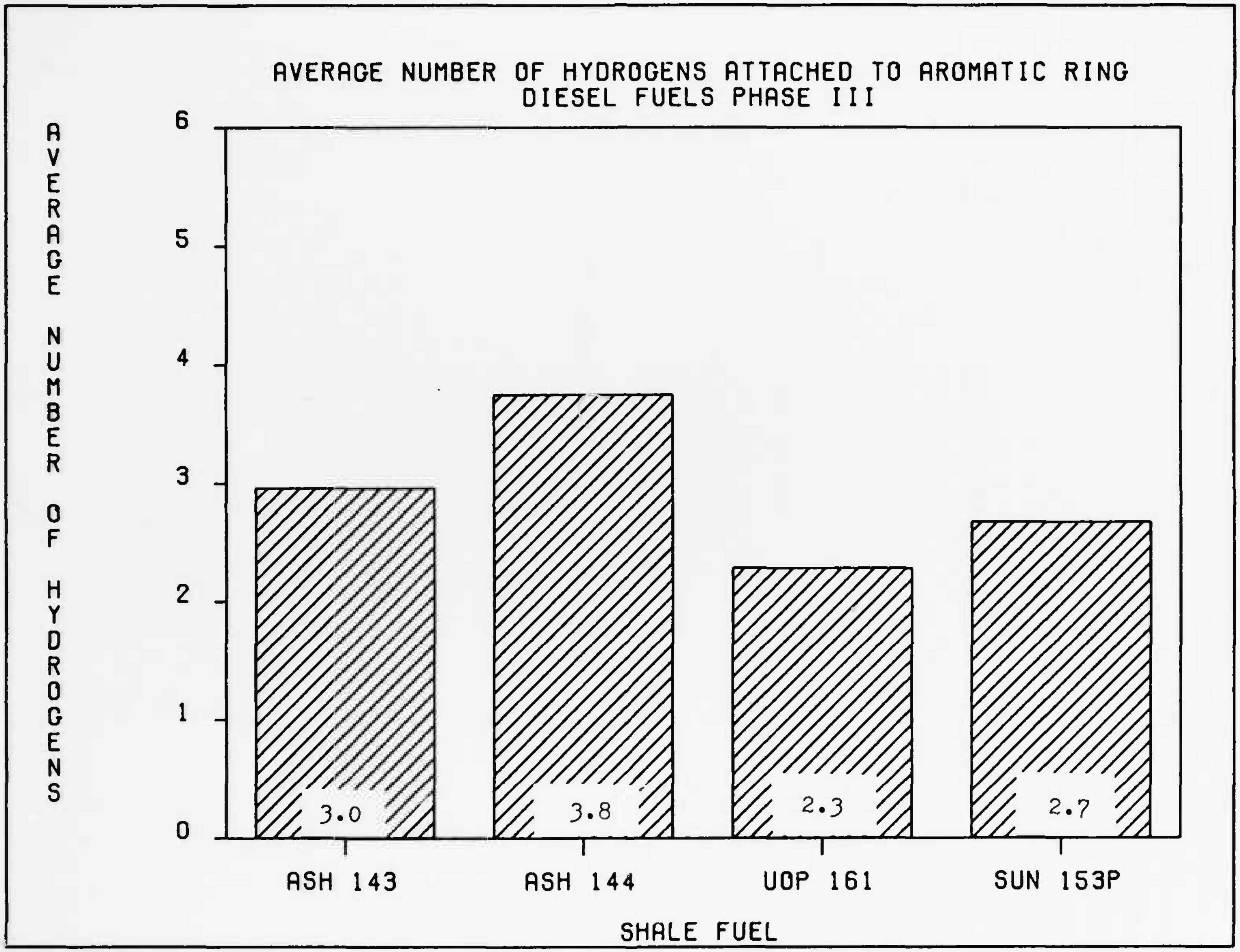


**Figure 25.** Average number of hydrogens attached to aromatic ring, Diesel Fuels Phase III.

# IX

# LIST OF ATTENDEES

ATTENDING THE

JET FUEL FROM SHALE OIL - 1981 TECHNOLOGY REVIEW

HOLIDAY INN - DAYTON MALL

MIAMISBURG, OHIO

17 - 18 NOVEMBER 1981

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