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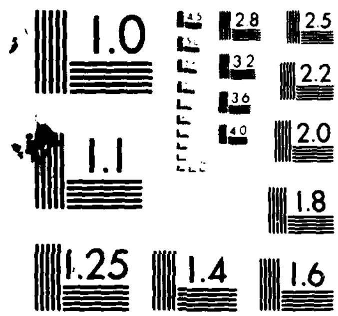

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NATIONAL BUREAU OF STANDARDS 1963 A

AFWAL-TR-81-2087
Part III

AN EXPLORATORY RESEARCH AND DEVELOPMENT PROGRAM LEADING TO SPECIFICATIONS FOR AVIATION TURBINE FUEL FROM WHOLE CRUDE SHALE OIL

PART III
Production of Specification JP-4 Jet Fuel From Geokinetics Shale Oil

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Sun Tech, Inc., A Subsidiary of SUN COMPANY
P.O. Box 1135
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October 1981

INTERIM REPORT FOR PERIOD 1 JANUARY 1980 - 1 APRIL 1980

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Paraho Shale Oil	Hydrocracking	Operating Costs
Geokinetics Shale Oil	Hydrorefining	Product Costs
JP-4 Jet Fuel	Jet Fuel Specifications	
JP-8 Jet Fuel	Processing Schemes	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

270 barrels of specification JP-4 jet fuel were produced by hydrorefining 890 barrels of raw Geokinetics shale oil under severe operating conditions in a continuous process development unit. On a once thru basis the yield of JP-4 off the hydrotreater was about 35 volume % of the feed. Preliminary estimates of plant investments and economics indicate that for the combination severe hydrorefining and hydrocracking, an 85 volume % yield can be attained based on total refinery energy input. Capital investments and manufacturing costs do not appear to be excessive for a shale oil refinery.

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FOREWORD

This interim report details the results of SUN TECH'S studies in Phase VI of this contract.

Production of Specification JP-4 Jet Fuel from Geokinetics Shale Oil was carried out under Contract F33615-78-C-2024, MOD P00004. The program is sponsored by the Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratory, Wright-Patterson AFB, Ohio, under Project 2480, Task 00 and work unit 01 with Ms. Eva Conley/AFWAL/POSF as the Project Engineer in charge.

Phase VI work reported herein was performed during the period of 1 January 1980 to 1 April 1980 under the direction of Dr. Abraham Schneider, Scientific Advisor, SUN TECH, INC. This report was released by the authors in October 1981.

SUN TECH'S program manager wishes to express his appreciation to Mr. Arthur Churchill and Dr. Herbert Lander for their help and guidance in bringing this project to a successful and on schedule conclusion, and to Ms. Eva Conley for her assistance in overcoming administrative problems associated with this project.

The authors wish to thank HYDROCARBON RESEARCH, INC., for their cooperation and efficiency in which they carried out the PDU conversion and work program to meet product supply schedules. The authors gratefully acknowledge the contributions of E. J. Janoski for his assistance in finding solutions to JFTOT test failures and C. Nowack of the Naval Materials Center-Trenton, New Jersey for his assistance in correcting the copper strip corrosion deficiencies of the off-spec material and for his assistance with the JFTOT tests.

This report is Part III of a planned number of parts of an exploratory research and development program leading to specifications for aviation turbine fuel from whole crude shale oil. Part I, Preliminary Process Analyŝes, evaluated three different technically feasible processing schemes proposed by SUN TECH, INC., for converting 100,000 BPCD of raw Paraho shale oil into military turbine fuels. Part II, Process Variable Analyses and Laboratory Sample Production, incorporated pilot plant process data in three design bases for manufacturing military fuels from raw Occidental shale oil. Other parts will follow as the different phases of the program are completed.

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LIST OF SYMBOLS AND ABBREVIATIONS

SYMBOLS

Bbl/SD	Barrels per Stream Day
Bbl/Ton	Barrels per Ton
BTU/lb	British Thermal Units per Pound
¢/Gal	Cents per Gallon
^{o}F	Degrees Fahrenheit
$/B	Dollars per Barrel
$/CD	Dollars per Calendar Day
H/C	Hydrocracking
H_2/Oil	Hydrogen to Oil Ratio
LT/SD	Long Tons per Stream Day
mm Hg	Millimeters of Mercury
# PSD	Pounds per Stream Day
SCF H_2/Bbl	Standard Cubic Feet Hydrogen per Barrel
SCF H_2/SD	Standard Cubic Feet Hydrogen per Stream Day
ST/SD	Short Tons per Stream Day
Vol. %	Volume percent
Wt. %	Weight percent

ABBREVIATIONS

API	American Petroleum Institute
ASTM	American Society of Testing and Materials
atm	Atmosphere
Bbl	Barrel

LIST OF SYMBOLS AND ABBREVIATIONS (Cont'd)

BPCD	Barrels per Calendar Day
BPSD	Barrels per Stream Day
BR	Boiling Range
BTU's	British Thermal Units
Cu	Copper
DCF	Discounted Cash Flow
EP	End Point
FOE	Fuel Oil Equivalent
H_2	Hydrogen Gas
HP Sep	High Pressure Separator
HRI	Hydrocarbon Research, Incorporated
H_2S	Hydrogen Sulfide Gas
H_2SO_4	Sulfuric Acid
IBP	Initial Boiling Point
JFTOT	Jet Fuel Thermal Oxidation Tester
LHSV	Liquid Hourly Space Velocity
LP Sep	Low Pressure Separator
N_2	Nitrogen
NA	Not Available
NH_3	Ammonia Gas
O_2	Oxygen Gas
PDU	Process Development Unit
pp	Partial Pressure

LIST OF SYMBOLS AND ABBREVIATIONS (Concluded)

ppm	Parts per Million by Weight
psia	Pounds per Square Inch Absolute Pressure
psig	Pounds per Square Inch Gage Pressure
P_T	Total Pressure
R-1	First Reactor
R-2	Second Reactor
RSO	Raw Shale Oil
RVP	Reid Vapor Pressure
S	Sulfur
SCF	Standard Cubic Feet
T	Temperature
TBP	True Boiling Point Distillation
TPO	Texaco Partial Oxidation Process
WWT Plant	Waste Water Treating Plant

SECTION I

SUMMARY

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

A three-month program was initiated on about 1 January 1980 by Hydrocarbon Research, Inc. under subcontract to and in conjunction with the Applied Research Division of Sun Tech, Inc. to produce 300 barrels of specification grade JP-4 jet fuel from Geokinetics *in situ* whole crude

shale oil. The process involved catalytic hydrorefining of the raw shale oil, with Shell 324 nickel molybdenum-on-alumina catalyst, under the relatively severe temperature of 825°F at 2800 psig total pressure and a liquid hourly space velocity of one. These severe conditions were needed to produce thermal cracking in order to meet the JP-4 20% maximum distillation temperature specification. Essentially complete removal of nitrogen occurred under these conditions and distillation of the hydrorefined product gave 30-40 vol. % yields of specification grade JP-4 jet fuel based on the raw shale oil charged to hydrorefining. HRI's equipment produced approximately 10 barrels per day of finished JP-4 jet fuel. Due to prior commitment of the PDU, HRI was obliged to suspend operations after 270 barrels of JP-4 had been produced. It is likely that the entire 300 barrels could have been produced if three additional days of running time had been available.

SECTION II

INTRODUCTION

Sun Tech's program to produce specification JP-4 jet fuel from raw Geokinetics shale oil had three objectives:

(1) To prepare 300 barrels of specification quality JP-4 from Geokinetics shale oil by the best means available;

(2) Preparation was to be as close as possible to contemplated commercial production; and

(3) Delivery of the jet fuel sample was to be made to meet the U.S. Air Force combustion testing program for synthetic fuels.

In Sun Tech's process design, a guard case is normally used to remove metals and saturate olefins. The raw shale oil feedstock would be heated to 600-625°F before entering the guard case, and the effluent would then be thermally stable and could be heated to the temperature desired before entering the main hydrotreating reactor. Due to time and equipment constraints, it was not possible to employ a separate guard case before the hydrotreating reactor.

SECTION III

PROGRAM DETAILS

Sun Tech has evaluated a number of different shale oils during the course of its work with the Aero Propulsion Laboratory. Table 1 presents inspections and analyses for Geokinetics and Paraho shale oils. Geokinetics shale oil is easier to process than Paraho shale oil based on boiling range, average molecular weight, nitrogen and sulfur contents.

Prior to the beginning of the operation in HRI's Process Development Unit (PDU), bench-scale continuous hydrorefining studies were carried out at HRI on Geokinetics shale oil using three different hydrorefining catalysts. Shell 324 nickel molybdenum-on-alumina catalyst gave the best performance for this application and was selected for use in the Process Development Unit.

As received from HRI, a JP-4 sample prepared by distillation of a product of bench-scale hydrorefining contained 39 ppm total nitrogen. The sample had a low Reid vapor pressure of 1.2 psia due to loss of butane during handling of the hydrorefined product. Gas analysis at HRI indicated that sufficient butanes are produced during hydrorefining to yield JP-4 with the specified Reid vapor pressure of 2 to 3 psia.

This JP-4 sample also failed the copper strip corrosion and JFTOT thermal stability tests. At Sun Tech, a procedure was developed for percolation of the JP-4 product through an acidic clay at commercially feasible dosages. The use of this procedure resulted in the sample passing the JFTOT test. The copper strip corrosion test was not affected by clay percolation. We believe that failure of this test was due to incomplete stripping of hydrogen sulfide from the reactor effluent, before they come into contact with air. The end result of this reaction with oxygen is the formation of elemental sulfur which dissolves in the fuel. JP-4 product analyses, both before and after clay percolation, are shown in Table 2.

HRI's PDU normally operated in the upflow ebulating bed mode. For this application, it was converted to a downflow fixed-bed unit. This conversion was completed in one month. Figure 1 is a schematic flow diagram of HRI's Process Development Unit for hydrorefining Geokinetics shale oil. Dewatered and filtered Geokinetics shale oil is combined with makeup hydrogen, heated, and fed to a fixed three-bed reactor. Hydrogen quench is provided between catalyst beds for temperature control. Gaseous and liquid products are separated at the high pressure separator. The recycle gas is scrubbed, compressed, and combined with makeup hydrogen for use in the reactor. The liquid effluent is distilled into a C_4-480°F JP-4 cut and a 480°F+ bottoms fraction. The JP-4 cut is passed through a stabilizer and a clay treater before being sent to product storage.

During the production run, one shutdown occurred approximately 2 weeks after start-up due to plugging in the fresh feed heater coil. Analysis of the deposits showed 65% ash (45 wt. % iron and 6 wt. % arsenic). By the end of the run (nearly 3 weeks later), the pressure drop had increased again over the heater coil and the reactor requiring a reduction in feed rate. It is our opinion that these plugging problems are attributable to the operation of the heater outlet at 700°F with the raw shale oil feedstock. If a separate guard case was available to saturate olefins and remove iron and arsenic, these problems would have been eliminated.

Two shipments of JP-4 jet fuel amounting to 270 barrels met all specifications. JP-4 product analyses for the two shipments are shown in Table 3. 1700 gallons of JP-4 produced initially in the PDU failed the copper strip corrosion test. The addition of 5 ppm benzotriazole corrected this deficiency. During steady state operation of the PDU, this problem vanished. Note that 1% of external butane had to be added to meet Reid Vapor Pressure requirements, since light ends recovery facilities were not available. Table 4 presents inspections and analyses of the Geokinetics shale oil feedstock and the 480°F+ bottoms fraction. The bottoms contained 4 ppm total nitrogen and 16.3 wt. % aromatics. We have seen samples of the 480°F+ bottoms from the PDU operation containing as much as 109 ppm total nitrogen and 22 wt. % aromatics. The variations in characteristics of the bottoms are probably attributable to aging of the hydrorefining catalyst system and ultimately to the absence of a separate guard case.

Figure 2 is Sun Tech's simplified flow diagram of a conventional raw shale oil hydrorefining and distillation operation. Provisions are made for separate guard cases as well as a vacuum still to produce a 1000°F+ bottoms fraction. This 1000°F+ bottoms fraction would be present in hydrotreated Paraho shale oil from Sun Tech's Phase I study,[1] but would not be present when processing Geokinetics shale oil. Generally bottoms fractions of this sort are excluded from a subsequent hydrocracking step. Table 5 compares operating conditions and product characteristics estimated in Sun Tech's Phase I Base Case Study with the actual operating conditions and product characteristics actually found in hydrorefining Geokinetics shale oil at HRI. The chemical consumption of hydrogen in the Paraho base case was projected to be significantly larger than that actually observed in the Geokinetics case. This results from the greater non-hydrocarbon content of the raw Paraho shale oil and its higher average molecular weight.

For comparison, a schematic flow diagram of Sun Tech's Phase I Base Case is shown in Figure 3. The Base Case includes a relatively severe hydrorefining of raw Paraho shale oil followed by an acid wash of the total liquid hydrorefined product. The 850°F+ distillation bottoms is sent to the Texaco Partial Oxidation (TPO) plant in order to produce a portion of the hydrogen required in the hydrorefining reactor. Hydrocracking is not used in this case.

Figure 4 is a schematic flow diagram of the hydrorefining of raw Geokinetics shale oil as practiced at HRI, showing the direct production of specification JP-4 jet fuel as a "straight-run" fraction and a 480°F+ waxy bottoms material. Hydrocracking of the 480°F+ waxy bottoms would be significantly cheaper than conventional hydrocracking, if the waxy bottoms feed to the hydrocracking operation can be routinely produced to contain less than 10 ppm total nitrogen. This low level of nitrogen is needed in order to avoid poisoning the acid sites of the R-2 hydrocracking catalyst. Figure 5 presents a schematic flow diagram for a two-reactor (R-1 hydrotreater, R-2 hydrocracker), single stage hydrocracker with extinction recycle of the fractionator bottoms. This type of operation is required for processing feedstock containing more than 10 ppm total nitrogen into high yields of JP-4 jet fuel. If the feedstock contains less than 10 ppm total nitrogen, the hydrotreating reactor might not be necessary. Figure 6 depicts a single reactor (R-2 hydrocracker), single stage hydrocracking operation with extinction recycle of the fractionator bottoms. High yields of JP-4 jet fuel can be produced.

Table 6 examines three alternate cases for producing JP-4 jet fuel from whole crude shale oil:

<u>Base Case (Paraho)</u>

The first, Sun Tech's Phase I Base Case for hydrorefining, acid washing and distillation produces 26.8 volume % "straight-run"

JP-4 jet fuel from raw Paraho shale oil, based on total energy input to the refinery. Refinery fuel, electricity, and steam were converted to an FOE basis, with raw shale oil taken at 6×10^6 net BTU's per barrel.

High Severity Alternate (Geokinetics)

The second case is the Sun Tech-HRI process for severe hydrorefining and distillation to produce "straight-run" JP-4 jet fuel from raw Geokinetics shale oil. Based on total energy input to the refinery, a 34.1 volume % yield of JP-4 jet fuel is obtained.

High Severity Alternate with Hydrocracking (Geokinetics)

The third case incorporates the Sun Tech process for hydrorefining, distillation, and hydrocracking to produce high yields of JP-4 jet fuel from raw Geokinetics shale oil. Here an 87.8 volume % JP-4 jet fuel yield is obtained.

SECTION IV

ECONOMIC EVALUATION

Guidelines for developing Phase I economics are given in Table 7. A September 1978 cost base is used for this work. Crude shale oil is valued at $16/Bbl and all product fuels are equally valued at $21/Bbl. These prices were used for calculating interest charges for working capital. Plant capacities and investments for the three specified cases are presented in Table 8. The main hydrotreater and the Texaco Partial Oxidation plant account for the majority of the processing facility cost. Total capital costs range from $527.9 million for the Sun Tech-HRI process for severe hydrorefining and distillation to produce "straight-run" JP-4 jet fuel to $691.2 million for the third case incorporating a gas oil hydrocracker to maximize the yield of JP-4 jet fuel from raw Geokinetics shale oil. Comparing Sun Tech's Phase I Base Case with the Sun Tech-HRI case for producing "straight-run" JP-4 jet fuel, it is seen that the major reason for the smaller total capital cost for the latter case is the associated smaller investment in hydrogen producing and distillation facilities.

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

A preliminary cost comparison for manufacturing JP-4 jet fuel from whole crude shale oil is given in Table 9. Mainly because of the utilities purchased for the hydrocracking step, total daily operating expenses for the case to maximize JP-4 jet fuel are significantly larger than those of the other two cases. Hydrocracking is very energy intensive.

Adjusted crude cost in dollars per barrel is defined as:

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

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

$$\frac{\text{vol. shale oil in (process feed + fuel + utilities converted to FOE)}}{\text{vol. products out}}$$

would relate this fraction to the thermal efficiency of the process and would further increase the adjusted crude cost. Total product costs including the adjusted crude costs are $0.63/gallon of product for the Phase I Base Case; $0.58/gallon of product for the high severity Geokinetics alternate; and $0.64/gallon of product for the high severity Geokinetics alternate with hydrocracking.

The Sun Tech-HRI process for producing JP-4 jet fuel from raw Geokinetics shale oil turns out to have the cheapest cost per barrel of total fuel products. The Phase I Base Case for producing JP-4 jet fuel by hydrorefining Paraho whole crude shale oil and the case involving maximum yields of JP-4 jet fuel from raw Geokinetics shale oil by hydrocracking have essentially the same cost per barrel of total fuel products. It is noteworthy that the higher capital and manufacturing costs in the latter case are offset by the sizeable increase in daily volume of total liquid products. This increase in volume results from the overall reduction in average molecular weight and the increase in hydrogen content in the total liquid products during the hydrocracking operation. Hydrocracking to maximize JP-4 jet fuel yields is advantageous in increasing total liquid product volumes. Hydrogen can be generated more cheaply from C_1-C_3 gases from hydrocracking than from the Texaco Partial Oxidation of heavy liquids. This advantage may be magnified in the manufacture of JP-8 (and JP-5) instead of JP-4 jet fuel since with the kerosene types of jet fuel perhaps all of the hydrogen could be generated from C_1-C_4 hydrocarbons plus the light naphtha formed during hydrocracking.

The costs in Table 9 are based on September 1978 costs and on $16 per barrel raw shale oil. Assuming June 1980 labor and investment costs and $25 per barrel of raw shale oil, an additional $12.60/barrel or $0.30/gallon must be added to each case for the total fuel product costs at the bottom of the table. It should be noted that these preliminary economics did not have the benefit of optimizing the overall processing schemes or product slates.

SECTION V

CONCLUSIONS

1. 270 barrels of specification JP-4 turbine fuel was produced by severly hydrotreating Geokinetics shale oil. Reid Vapor Pressure of the JP-4 fraction (I-480^{o}F) ran about 1.4 psia. 1% n-butane was added to meet specification RVP (2.0 min. - 3.0 max.). Some butane was lost in the PDU operation which normally would be recovered in a commercial operation.

2. A total of 890 barrels of shale oil was processed thru HRI's Process Development Unit. JP-4 yield averaged about 35 vol.% of charge. During the run, one shutdown occurred about 2 weeks after start-up due to plugging in the fresh feed heater coil. Analysis of the deposits showed 65% ash (45 wt% iron and 6 wt% arsenic). By the end of the run (nearly 3 weeks later), pressure drop had increased again over the heater coil and the reactor requiring a reduction in feed rate. These plugging problems are attributable to the operation of the heater outlet at 700^{o}F in the absence of a separate guard case. If a separate guard case was available, these problems would have been eliminated.

3. Problems meeting both JFTOT and Copper Strip Corrosion Tests were encountered with the initial JP-4 production in both the Bench Scale and PDU runs. Clay treating corrected thermal stability (JFTOT) problems. Copper strip corrosion problems with the product from the Bench Scale Unit were attributed to trace quantities of H_2S remaining in the liquid product. 1700 gallons of JP-4 produced initially in the PDU failed the Copper Corrosion Test. The addition of 5 ppm benzotriazole corrected this deficiency. During steady state operation of the PDU, these problems vanished.

4. Preliminary process design bases were prepared for developing rough plant investments and economics (Geokinetics Shale Oil) for comparison with the Phase I Base Case (Paraho Shale Oil). A September 1978 cost base and a $16 per barrel price for raw shale oil was used.[1]

   Sun Tech's Phase I Base Case for hydrorefining, acid washing and distillation produces 26.8 volume % JP-4 jet fuel based on total refinery input (crude, fuel and utilities converted to an FOE basis). Total capital investment was $582 million and a total product cost of $0.63 per gallon was attained.

   Sun Tech-HRI process for severe hydrorefining and distillation of Geokinetics shale oil yields 34.1 volume % "straight-run" JP-4 jet fuel at a total product cost of $0.58 per gallon. Total capital investment was $527.9 million.

Sun Tech's process for hydrorefining, distillation, and hydrocracking of Geokinetics shale oil yields 87.8 volume % JP-4 jet fuel at a toal product cost of $0.64 per gallon. Total capital investment was $691.2 million.

5. Capital investment and manufacturing costs do not appear to be excessive for a shale oil refinery.

SECTION VI

RECOMMENDATIONS

It is recommended that:

1. A catalyst life study be initiated for severe operation of the raw shale oil hydrotreater to more accurately estimate catalyst life expectancy.

2. The temperature of the raw shale oil feedstock leaving the heater be held to 600-625°F max. and enter a guard case to saturate olefins and remove arsenic and iron before entering the main hydrotreating reactor.

3. Hydrocracking studies be initiated in the pilot plant to firm up yield and product quality estimates.

4. The merits of including a hydrocracker in the processing scheme be fully investigated. Inclusion of a hydrocracker would permit milder operating conditions in the raw shale oil hydrotreater. A full slate of distillate fuels would be possible with a hydrocracker (JP-8, #2 Diesel Fuel, and Marine Diesel Fuel).

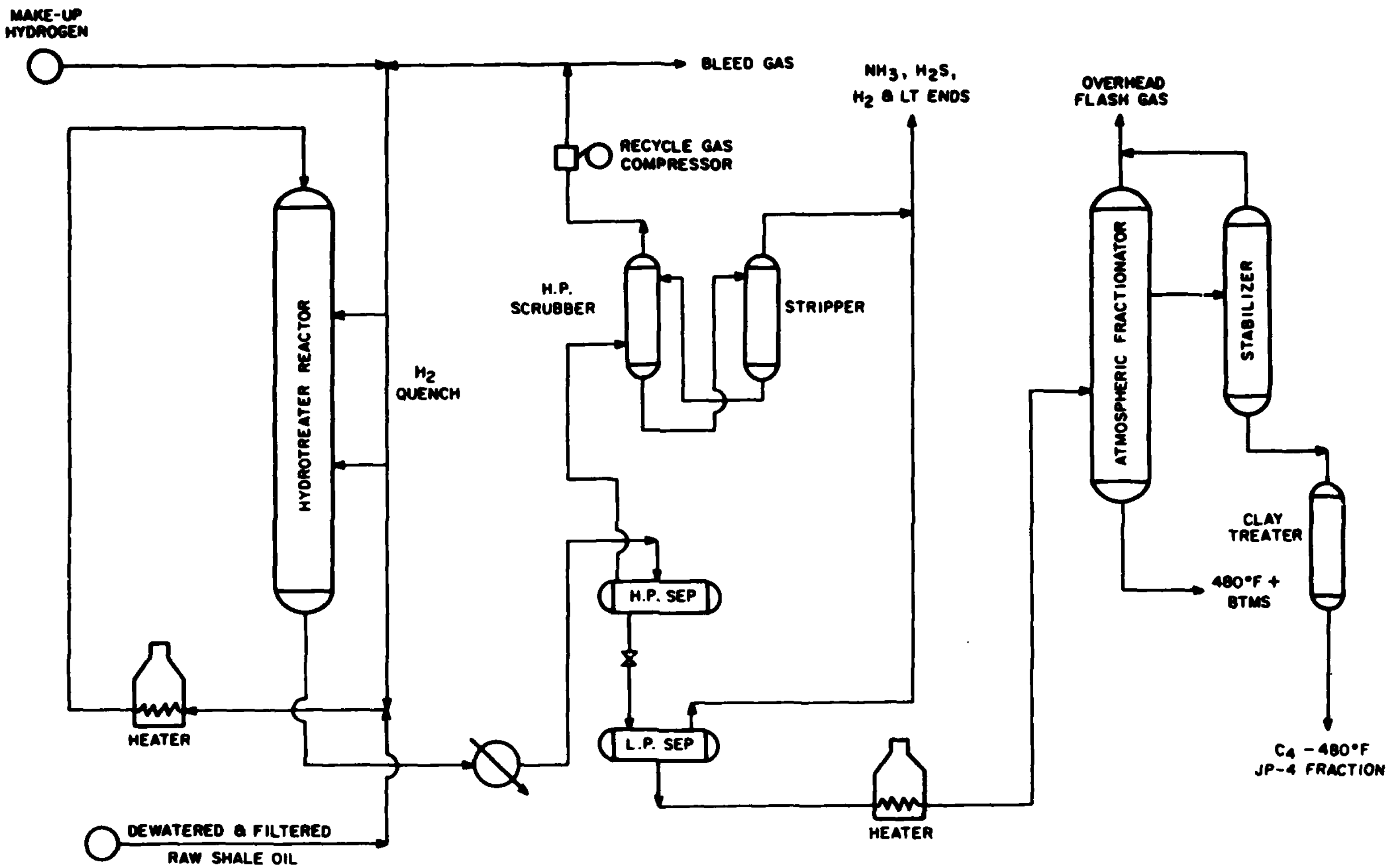
5. Catalytic cracking data be obtained to confirm yields. Inspections and analysis of the 480°F+ bottoms indicated that this material would be an excellent FCC feed for manufacturing gasoline and #2 fuel oil.

6. The 480°F+ bottoms be considered as a potential feedstock for lube oils and other fuels. This fraction is waxy and would likely need additional processing to make acceptable products heavier than JP-4 jet fuel.

7. The applicability of processing other shale oils using high severity hydrorefining be investigated. Paraho and Occidental shale oils contain more nitrogen, sulfur, and arsenic than Geokinetics. Greater reactor severity would be required to equal the hydrotreated product quality obtained with the Geokinetics feed. Hence, catalyst life would be shorter. For the hydrotreater/hydrocracker or FCC processing routes, data are needed to evaluate trade-offs.

REFERENCES

1. H. E. Reif, J. P. Schwedock, and A. Schneider, "An Exploratory Research and Development Program Leading to Specifications for Aviation Turbine Fuels from Whole Crude Shale Oil, Phase I - Part I AFWAL-TR-81-2087 - Preliminary Process Analyses", Report prepared for the Department of Defense U.S. Air Force by Sun Tech, Inc., under contract No. F33615-78-C-2024, 1981.



NOTES:

H.P. SEP: HIGH PRESSURE SEPARATOR

L.P. SEP: LOW PRESSURE SEPARATOR

Figure 1

SCHEMATIC FLOW DIAGRAM OF HRI'S PDU FOR HYDROTREATING GEOKINETICS SHALE OIL

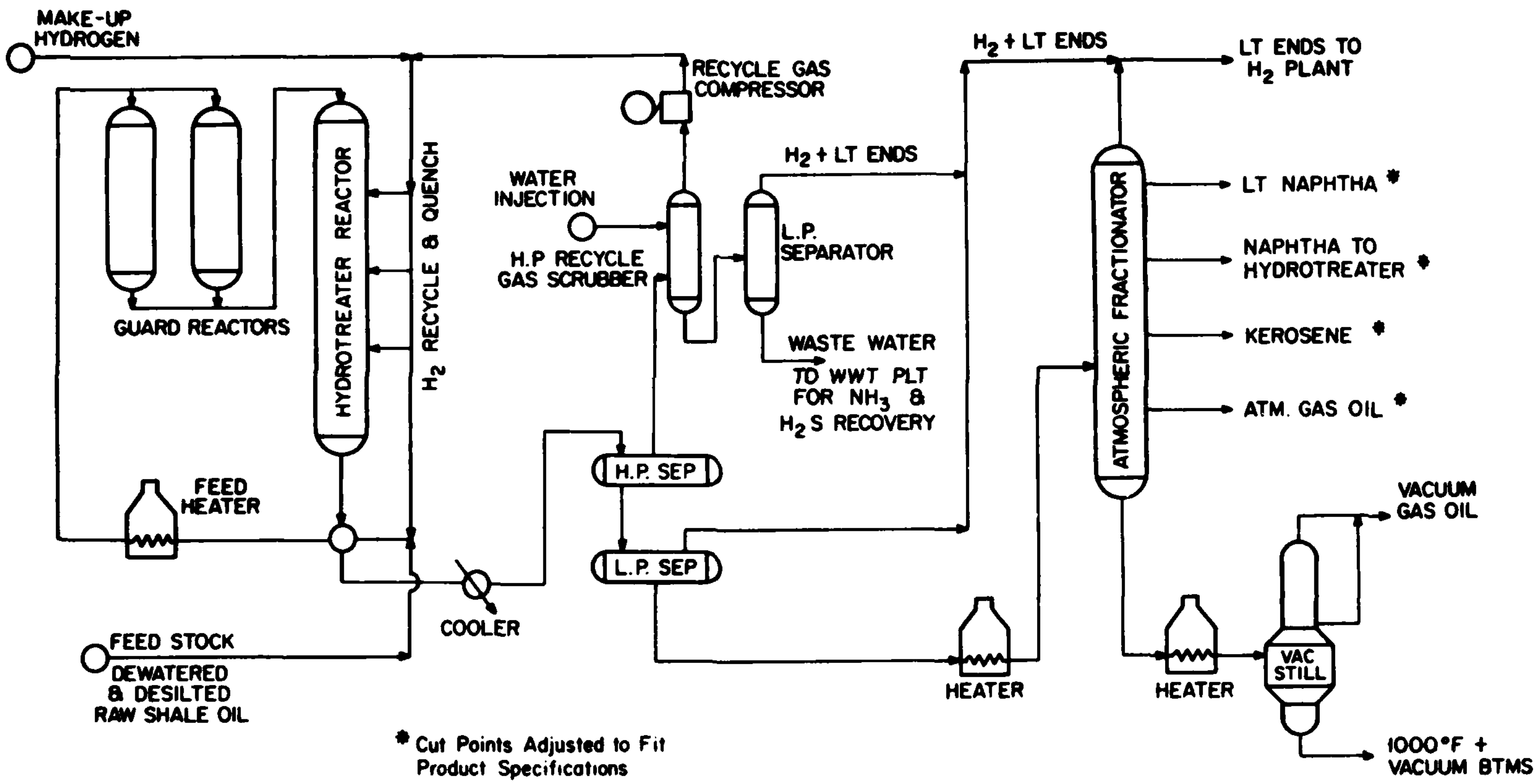
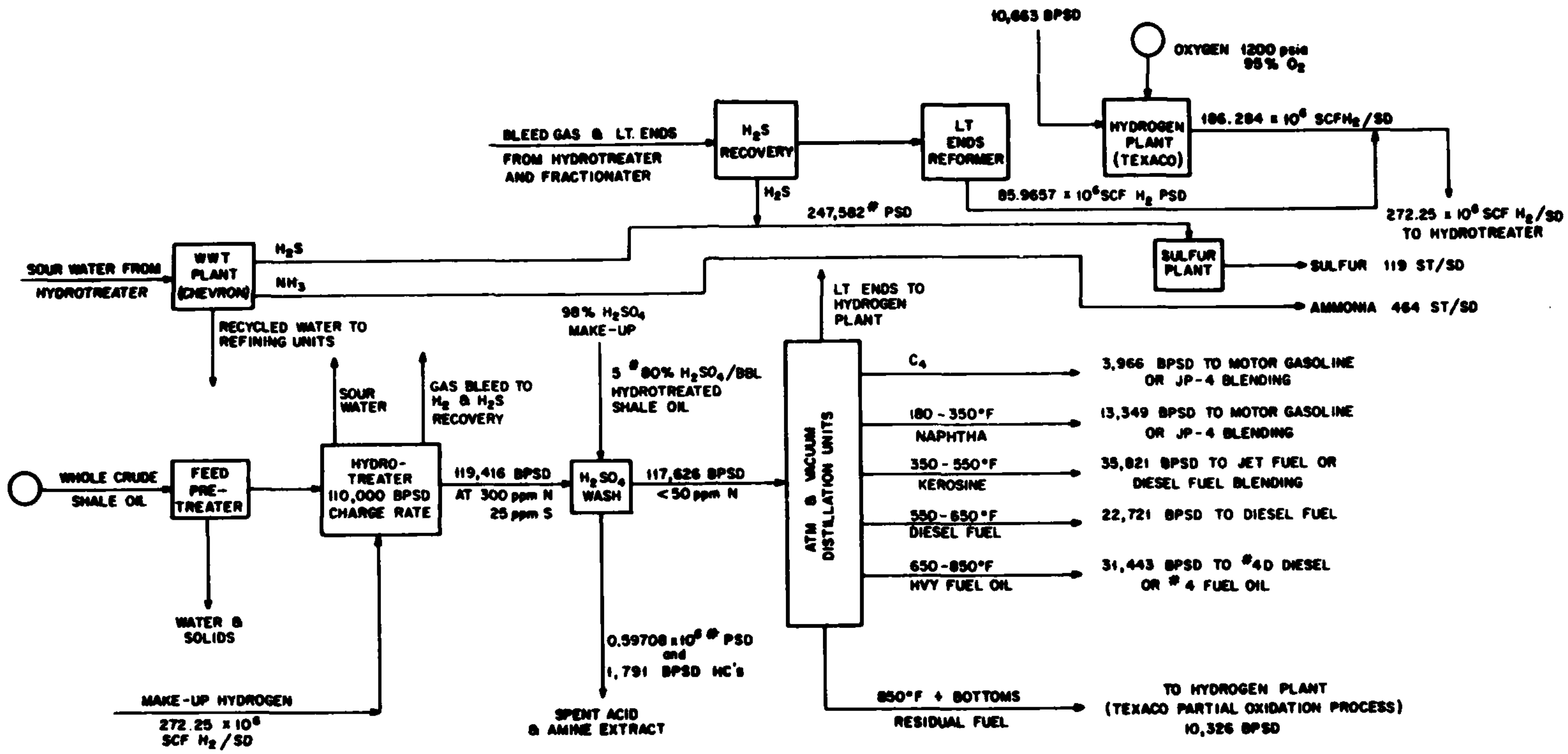


Fig. 2 SIMPLIFIED FLOW DIAGRAM OF RAW SHALE OIL HYDROTREATER AND DISTILLATION PLANTS



NOTE: ALL FRACTIONS ARE ON TBP BASIS.

BASIS: RAW PARAHO SHALE OIL OF CHARGE RATE 110,000 BPSD TO HYDROTREATER OR 100,000 BPCD.

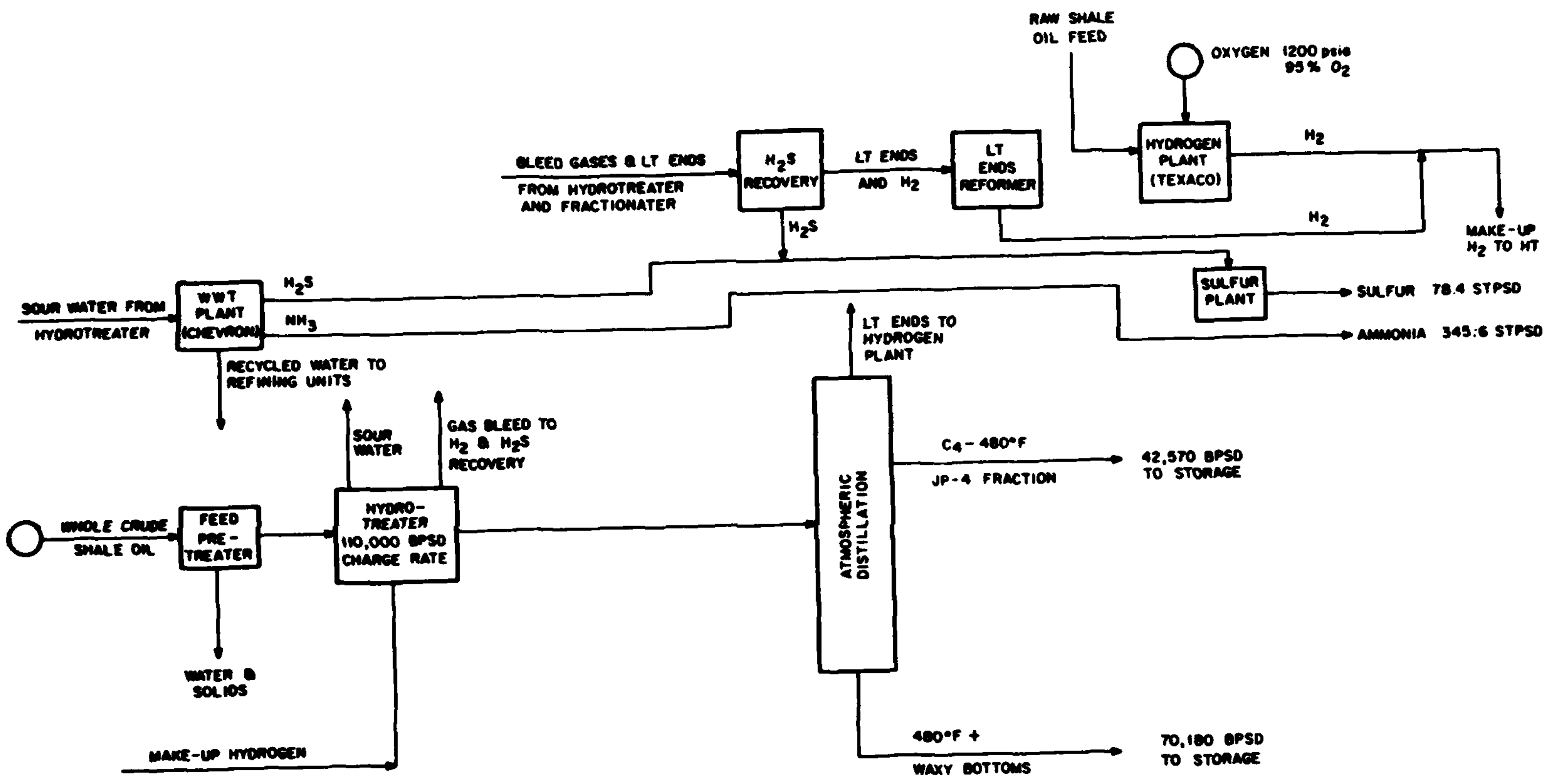
BPSD: BARRELS PER STREAM DAY
BPCD: BARRELS PER CALENDAR DAY
SCF H_2/SD: STANDARD CUBIC FEET HYDROGEN PER STREAM DAY
PSD: POUND PER STREAM DAY
ST/SD: SHORT TONS PER STREAM DAY

SCHEMATIC FLOW DIAGRAM - BASE CASE

HYDROTREATING, ACID WASHING AND DISTILLATION FOR TRANSPORTATION FUELS

Fig. 3 REFINING RAW PARAHO SHALE OIL

2-28-79
T.G. McD./JCC

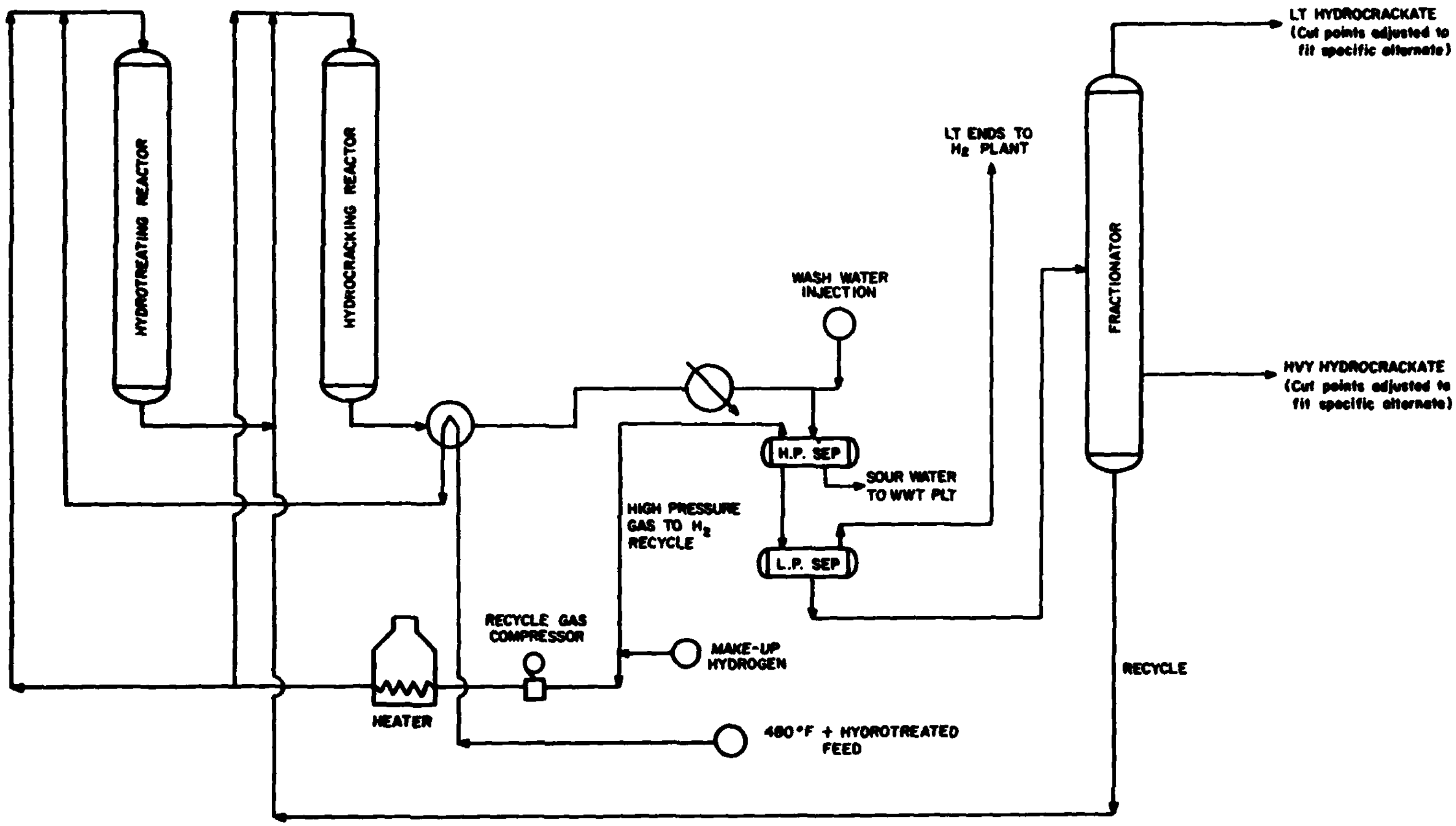


NOTE: ALL FRACTIONS ARE ON TBP BASIS.

BPSD: BARRELS PER STREAM DAY
STPSD: SHORT TONS PER STREAM DAY

SCHEMATIC FLOW DIAGRAM

Fig. 4 REFINING GEOKINETICS SHALE OIL VIA HYDROTREATING



NOTES:

H.P. SEP: HIGH PRESSURE SEPARATOR

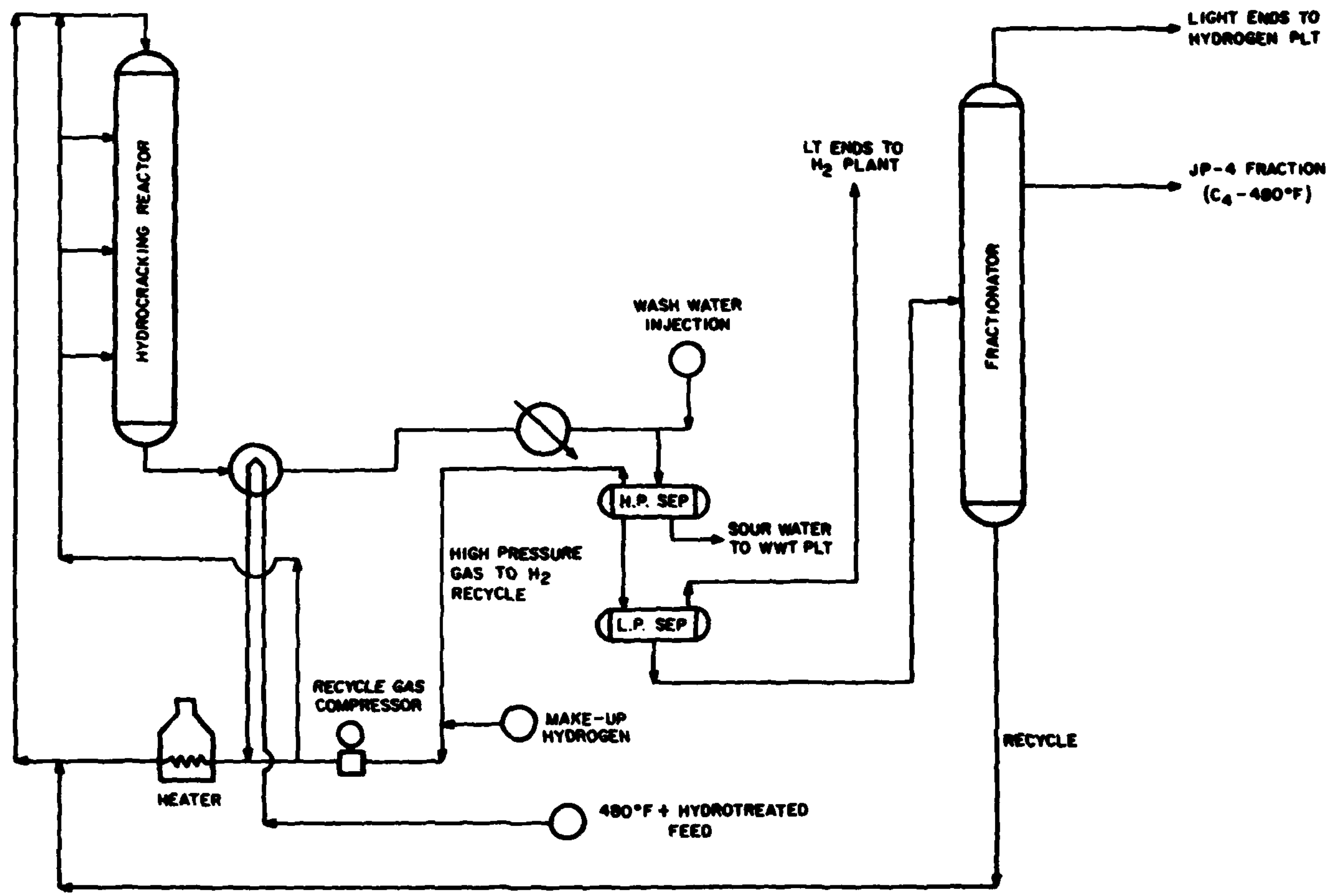
L.P. SEP: LOW PRESSURE SEPARATOR

WWT PLANT: WASTE WATER TREATING PLT.

Figure 5

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

HER/JCC
5/29/79



NOTES:

H.P. SEP: HIGH PRESSURE SEPARATOR

L.P. SEP: LOW PRESSURE SEPARATOR

WWT PLANT: WASTE WATER TREATING PLT

Figure 6

SCHEMATIC FLOW DIAGRAM OF SINGLE REACTOR HYDRO-CRACKER WITH EXTINCTION RECYCLE FOR MANUFACTURING TURBINE FUELS FROM SEVERELY HYDROTREATED SHALE OIL

TABLE 1

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

INSPECTION DATA	PARAHO	GEOKINETICS
API @ 60°F	20.6	26.8
Distillation, ASTM D1160 corrected to 1 Atm., °F		
IBP/5	133/456	345/437
10/30	508/687	469/566
50	798	655
70/90	918/1057	785/880
EP	1065 @ 95%	975 @ 95.5%
Ramsbottom Carbon Residue, Wt., %	1.4	
ASH, Wt. % (ASTM D486)	0.03	0.03
Average Molecular Weight	326	280
Chemical Composition, Wt. %		
Carbon	83.83	84.48
Hydrogen	11.72	11.69
Sulfur	0.75	0.48
Total Nitrogen	2.13	1.66
Oxygen	1.31	1.75
Arsenic	34 ppm	20 ppm
Iron	90 ppm	60 ppm

TABLE 2

BENCH SCALE UNIT

JP-4 PRODUCT ANALYSIS(1)

	JP-4 SPECIFICATION	AS RECEIVED	CLAY TREATED(2)
API @ 60 °F	45-57	49.9	49.9
Distillation, ASTM D-86			
IBP, °F	Report	163	
10	Report	245	
20	293 Max.	284	
50	374 Max.	359	
90	473 Max.	430	
E.P.	518 Max.	470	
Residue, v.%	1.5 Max.	1.0	
Loss, v.%	1.5 Max.	1.0	
Sulfur, wt%	0.40 Max.	0.0124	0.0122
Nitrogen, ppm	NA	39	3
Olefins, v.%	5.0 Max.	3.5	2.1
Aromatics, v.%	25.0 Max.	9.3	8.2
Freeze Pt., °F	-72 Max.	-74	
Cu Strip Corrosion, Max.	1B	2C	
RVP, psia, Min-Max	2-3	1.2	
Heating Value			
Net BTU/lb. Min.	18,300	18,700	
JFTOT			
ΔP, mm Hg, Max.	25	250	0
Deposit Code, Max.	3	4	0

(1) NiMo Catalyst, LHSV = 1.0, T = 825°F, P_T = 2600 psig, H_2/Oil = 4000 SCF H_2/BBL. Feed.

(2) Clay Dosage = 250 BBL./TON

TABLE 3

JP-4 PRODUCT ANALYSES

	JP-4 SPECIFICATION	FIRST SHIPMENT	SECOND SHIPMENT
API @ 60°F	45-57	50.2[(1)]	49.8
Distillation, ASTM D-86			
IBP, °F	Report	129	140
10	Report	246	246
20	293 Max.	285	282
50	374 Max.	357	355
90	473 Max.	442	432
E.P.	518 Max.	506	494
Residue, v.%	1.5 Max.	1.0	1.0
Loss, v.%	1.5 Max.	1.0	1.0
Sulfur, wt%	0.40 Max.	0.0006	0.0016
Mercaptans, wt%	0.001 Max.	-	<2 ppm
Nitrogen, ppm	NA	3 ppm	<1 ppm
Olefins, v.%	5.0 Max.	1.6	2.0
Aromatics, v.%	25.0 Max.	7.3	10.4
Freeze Pt., °F	-72 Max.	-76[(1)]	-76
Cu Strip Corrosion, Max.	1B	1B	1A
RVP, psia, Min-Max	2-3	2.6	2.3[(1)]
Heating Value			
Net BTU/lb. Min.	18,300	18,736	18,696
JFTOT			
ΔP, mm Hg, Max.	25	0	0
Deposit Code, Max.	3	0	0

(1) HRI Analysis

TABLE 4

INSPECTIONS AND ANALYSES OF GEOKINETICS FEED AND BOTTOMS PRODUCT

	GEOKINETICS FEEDSTOCK	480°F+ BOTTOMS FROM HYDROTREATING
API Gravity @ 60°F	26.8	37.7
Distillation, °F (ASTM D1160)		
IBP	345	465
5 v.%	437	482
10	469	500
20	520	530
50	655	600
70	785	665
90	880	765
EP/V.%	975/95.5	820/95.0
Aromatics, wt.%	73.0	16.3
Sulfur, wt.%	0.48	4 ppm
Nitrogen, wt.%	1.66	4 ppm
Arsenic, ppm	20	<1

TABLE 5

ESTIMATED OPERATING CONDITIONS FOR WHOLE SHALE OIL HYDROTREATER

Charge Rate: 110,000 BPSD (100,000 BPCD)
Operating Factor: 0.91
Catalyst: NiMo on Alumina
Catalyst Life: 6 months

REACTOR OPERATING CONDITIONS

CASE	PHASE I BASE (1)	GEOKINETICS ALTERNATE
LHSV, V/Hr/V	0.4	1.0
Avg. Catalyst Temp., °F	760	825
Pressure, Total psia	1,880	2,800
H_2PP	1,600	2,600
Recycle Gas Rate, SCF/B	4,100	6,000
Hydrogen Consumption, SCF/B		
Chemical	2,250	1.700
Dissolved	150	250
Bleed	75	200
Total to Hydrotreater	2,475	2,150
PRODUCT		
Total Nitrogen, ppm	300	3
Sulfur, ppm	25	100
C_4+ Yield, Vol.% Feed	108.56	102.5
JP-4 Fraction	29.3	38.7
Bottoms	79.3	63.8
	108.6	102.5

(1) Paraho Shale Oil

TABLE 6

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

BASIS: 110,000 BPSD Feed Rate	PARAHO BASE	GEOKINETICS W/H_2 ONLY	GEOKINETIC W/H_2 & H/C
Total Hydrogen, SCFX10^6	272.25	221.38	316.32
Net Products, BPSD (TBP Cuts)			
JP-4 Fraction	32,268	42,570	120,651
Other Fuels (480°F+)	75,032(1)	70,180	0
TOTAL	107,300	112,750	120,651
Other Products, STP/SD			
Ammonia	464	346	346
Sulfur	119	78	78
Liquid Fuel Products Yields			
Total Products as Vol% Feed	97.6	102.5	109.7
JP-4 Vol % Feed	29.3	37.8	109.7
Total Refinery Crude Input (Crude and Fuel), BPSD	119,167	120,609	128,039
Total Refinery Input (Crude, Fuel and Utilities Converted to FOE BPSD)	120,393	124,948	137,433
Total Products as Vol.% Refinery Input	89.1	90.2	87.8
JP-4	26.8	34.1	87.8

(1) 450-850°F Fraction

TABLE 7

BASIS FOR DEVELOPING PHASE I ECONOMICS

GENERAL

1. Capital and operating cost estimates for each refining scheme based on: a) In-house data. b) Literature sources.
2. Processing schemes were not optimized in this phase.
3. No allowances for transporting raw shale oil to refinery or finished products from refinery.

PLANT COSTS

Location:	Mid West
Type:	Grass Roots (adjacent to existing refinery)
Cost Base:	September 1978
Feed:	Whole raw shale oil (Paraho)
Tankage:	30 days storage capacity for raw shale oil and products
Crude Rate:	100,000 BPCD
Utilities:	Available at plant site at costs specified: Electricity Steam Fuel Cooling Water

CAPITAL RECOVERY

Equity Financing: 100%

Debt Financing: 10% annual interest rate

Return on Investment:	15% discounted cash flow after taxes.
Plant Life:	16 years with zero salvage value
Depreciation:	13 years sum of years digits
Federal Plus State Tax Rate:	50%
Investment Tax Credit:	10% of capital investment
Working Capital:	30 days inventory of crude @ $16/Bbl and 30 days product @ $21/Bbl

TABLE 7 (Cont'd)

BASIS FOR DEVELOPING PHASE I ECONOMICS

OPERATING COSTS

Direct Labor

Operators:	$9.50/hr.	wtd. avg. $8.80/hr.
Helpers:	$8.50/hr.	
Supervision:	25% of labor costs	

NOTE: 4.2 shift positions plus 10% relief required for continuous operation.

Overhead:	100% direct labor (fringe benefits, overhead, general and administrative and control laboratory costs)
Maintenance, Local Taxes, and Insurance:	4.5% estimated erected plant costs
Start-Up Costs:	5% estimated erected plant costs
Crude Shale Oil:	$16.00 per Bbl. at plant site
Product Values:	All fuels equal ($21.00/Bbl. for calculating working capital) By-Products - Ammonia - $120/short ton Sulfur - $ 53/long ton

UTILITIES

Fuel:	$16.00 per Bbl (Raw Shale Oil Equivalent)
Electricity:	3.5¢ per kw hour
Cooling Water:	3¢ per 1,000 gallons
Saturated Steam:	600 psig @ $3.90/1,000 lbs. 250 psig @ $3.30/1,000 lbs. 50 psig @ $2.50/1,000 lbs.
Catalyst and Chemicals:	At cost
Royalties:	Running basis

TABLE 8

PRELIMINARY ESTIMATES OF PLANT INVESTMENTS (JP-4)

September 1978

Case	Phase I Base		High Severity Alt. Base		High Severity Alt. Max. JP-4	
	Capacity	$ x 10^6	Capacity	$ x 10^6	Capacity	$ x 10^6
H_2 (Partial Ox) MMSCF/D	186	107.4	101	79.1	135	91.3
H_2 (Steam Ref) MMSCF/D	86	28.8	120	35.2	182	45.1
Sulfur Recovery, ST/SD	119	11.5	78	10.0	78	10.0
Waste Water Treating $STNH_3$/SD	464	22.3	346	19.3	346	19.3
Main Hydrotreater and H_2 Recovery MB/SD	110	160.0	110	160.0	110	160.0
Atm. and Vac. Distn, MB/SD	118	36.8				
Main Atm. Distn. MB/SD			118	26.4	118	26.4
Hydrocracker, MB/SD					70	89.1
Acid Wash, MB/SD	120	0.5				
SUB TOTAL		367.3		330.0		441.2
Tankage, MM Bbls.	6.9	49.4	6.9	49.4	7.2	51.5
TOTAL ONSITES		416.7		379.4		492.7
Offsites (45% Onsites - Tankage)		165.3		148.5		198.5
TOTAL CAPITAL COST		582.0		527.9		691.2

TABLE 9

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

BASIS: 100,000 BPCD Crude to Hydrotreater

TOTAL PLANT INVESTMENT, $ x 10	PHASE I BASE	HIGH SEVERITY ALTERNATE	HIGH SEVERITY ALT W/HC
Plant	582.0	527.9	691.2
Catalysts	9.9	5.5	10.8
Working Capital	112.1	113.9	119.6
TOTAL	704.0	647.3	821.6
MANUFACTURING COSTS - $/CD			
Direct Labor	8,976	8,184	10,296
Purchased Power & Cooling Water	177,400	176,330	318,202
Catalyst, Chemicals & Royalties	87,960	34,873	57,054
Overhead @ 100% Direct Labor	8,976	8,184	10,296
Maint., Local Taxes & Insurance	51,374	46,775	60,744
Subtotal	334,686	274,346	456,592
Less NH_3 & S (Credit)	(55,823)	(41,521)	(41,521)
Direct Costs	278,863	232,825	415,071
Per Bbl Liquid Product	$2.86	$2.27	$3.78
TOTAL LIQUID FUELS, BPCD	97,643	102,602	109,792
JP-4 YIELD, BPCD	29,364	38,739	109,792
TOTAL MANUFACTURING COSTS, $/Bbl Product(1)	8.58	7.22	9.79
ADJUSTED CRUDE COST, $/Bbl Product(2)	17.77	17.12	16.98
TOTAL PRODUCT COST			
$/Bbl	26.35	24.34	26.77
¢/Gal	63	58	64

(1) Total Manufacturing Costs computed on the basis shown in Table 7 for Developing Phase I Preliminary Economics.

(2) Includes fuel @ $16.00 per barrel (Raw Shale Oil Equivalent)

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