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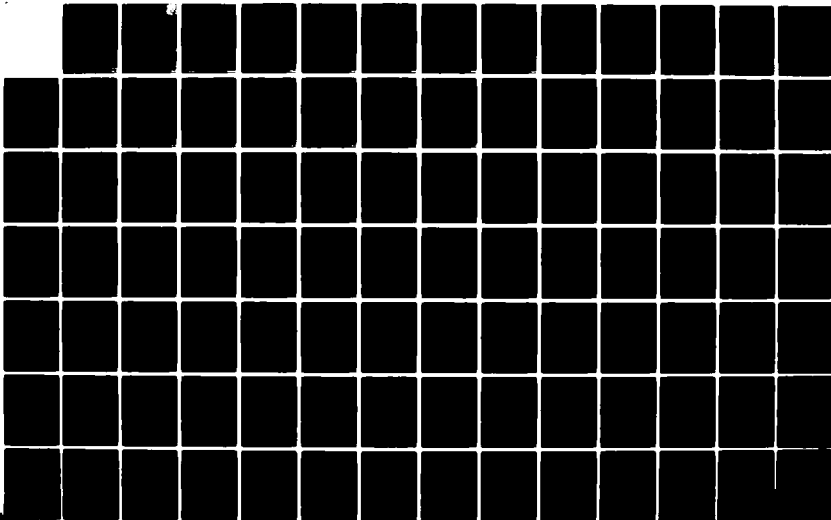
REFINING OF MILITARY JET FUELS FROM SHALE OIL PART IV
PROCESS COMPUTER MODELING STUDIES(U) ASHLAND PETROLEUM
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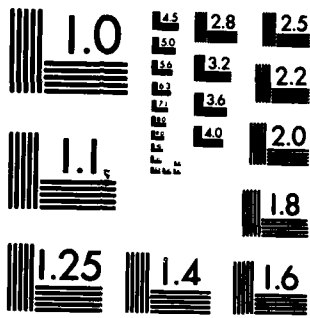
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AFWAL-TR-81-2056
Part IV

REFINING OF MILITARY JET FUELS FROM SHALE OIL

Part IV
Process Computer Modeling Studies

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ASHLAND RESEARCH AND DEVELOPMENT
ASHLAND, KENTUCKY 41101

AUGUST 1982

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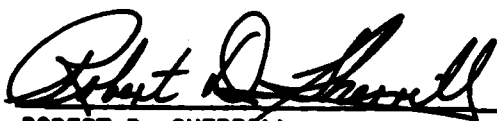
This technical report has been reviewed and is approved for publication.



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
An overall optimization study involving computer modeling of shale upgrading was performed in Phase IV. This study utilized the analytical and experimental data from Phases I, II, and III of the program. Computer modeling of the process was used to define an economic optimum configuration. The economic and yield trade-offs of producing either JP-4 or JP-8 aviation turbine fuels as the primary products were evaluated, along with a detailed analysis.		

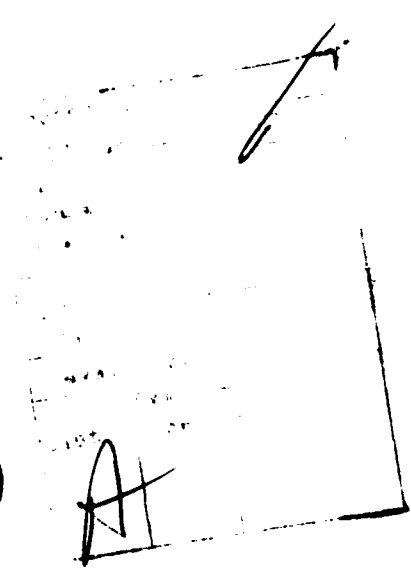
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FOREWORD

This project was sponsored by the U.S. Air Force Wright Aeronautical Laboratories (AFWAL), Air Force Systems Command, under contract No. F33615-78-C-2080. The work herein was performed during the period of June 1, 1981 to September 30, 1981 under Program Elements 62203F and 63215F, Work Units 30480504 and 24800004, respectively. Part IV describes the effort of Ashland Petroleum Company Research and Development personnel and Planning and Analysis personnel in the computer modeling optimization study of the overall EXTRACTACRACKING process.

While the many persons who contributed to the successful completion of this contract phase are too numerous to list by name, the authors wish to acknowledge the contributions of the following individuals: Dr. William P. Hettinger, Jr., Vice-President and Director of Research; Mr. W. A. Sutton, Program Manager; Mr. Lee Henton, Research Engineer; and Mrs. Carolyn Honaker, Correspondence Word Processor. The helpful suggestions of the Air Force Contract Monitor, Mrs. Charlotte Eigel, were greatly appreciated and were of benefit in the conclusion of this phase.

Prior reports under this contract may be found under AFWAL-TR-81-2056, Parts I, II (Volumes I, II, and III) and III.

TABLE OF CONTENTS

SECTION		PAGE
I	INTRODUCTION.....	1
	THE EXTRACTACRACKING PROCESS.....	5
II	PROCESS MODULE EVALUATION.....	9
	CRUDE OIL CHARACTERISTICS.....	9
	CRUDE SHALE OIL HYDROTREATER.....	11
	FLUID CATALYTIC CRACKING.....	18
	EXTRACTION.....	22
	GUARDCASE HYDROTREATING.....	27
	FREEZE POINT MODIFICATION.....	29
	AROMATIC SATURATION.....	32
	CONCLUSIONS.....	34
III	EXTRACTACRACKING - COMPUTER MODEL.....	37
	GOALS.....	37
	SYSTEM USED.....	38
	INPUT DATA.....	38
	CONSTRAINTS.....	46
IV	MODEL RESULTS.....	48
	OCCIDENTAL SHALE OIL.....	48

TABLE OF CONTENTS (CONT'D)

SECTION	PAGE
BASE CASE.....	48
SENSITIVITIES: (1) LEVEL OF TURBINE FUEL PRODUCTION.....	57
SENSITIVITIES: (2) AROMATICS CONTENT OF TURBINE FUELS.....	58
SENSITIVITIES: (3) FUEL GAS SALES ALLOWED.....	62
SENSITIVITIES: (4) ALKYLATION/ POLYMERIZATION.....	64
SENSITIVITIES: (5) FEEDSTOCK COST.....	64
SUMMARY - OCCIDENTAL ANALYSIS.....	67
PARAHO SHALE OIL.....	72
BASE CASE.....	72
SENSITIVITY: INCREMENTAL TURBINE FUEL PRODUCTION.....	77
SUMMARY - PARAHO SHALE OIL.....	77
V CONCLUSIONS AND QUESTIONS.....	79

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1.	THE EXTRACTACRACKING PROCESS.....	6
2.	HYDROTREATER AGING COMPARISON.....	16
3.	COMPARISON OF FCC LIQUID PRODUCT YIELDS.....	20
4.	COMPARISON OF FCC RESULTS BETWEEN PHASES.....	21
5.	DESULFURIZATION DURING FLUID CRACKING.....	23
6.	DENITROGENATION COMPARISON - FCC.....	24
7.	COMPARISON OF PHASE II AND III EXTRACTION RESPONSE.....	26
8.	BASE CASE PRODUCT VALUES AS A FUNCTION OF DCF RATE - OCCIDENTAL SHALE OIL.....	56
9.	INCREMENTAL PRODUCTION COST OF ADDITIONAL TURBINE FUEL.....	59
10.	VALUE OF OCCIDENTAL OIL AT PRESENT MARKET PRICES.....	69
11.	PRODUCT VALUES AS A FUNCTION OF DCF RATE.....	76
12.	INCREMENTAL TURBINE FUEL COST.....	78

LIST OF TABLES

TABLE		PAGE
1.	MILITARY JET FUELS FROM SHALE OIL.....	3
2.	MILITARY JET FUEL FROM SHALE OIL PHASES.....	5
3.	EXTRACTACRACKING'S ANSWER TO SHALE OIL REFINING PROBLEMS.....	8
4.	RANGE OF FEEDSTOCK PROPERTIES - OCCIDENTAL SHALE OIL.....	10
5.	DESIGN BASIS FEEDSTOCK PROPERTIES - OCCIDENTAL SHALE OIL.....	12
6.	COMPARISON OF PHASE II AND III DATA.....	14
7.	COMPARISON OF GUARDCASE RESULTS.....	28
8.	COMPARISON OF PRIMARY DATA REFORMING SECTIONS....	30
9.	DATA SUMMARY AND COMPARISON FOR AROMATIC SATURATION UNITS.....	33
10.	SCALE-UP AND DATA ANALYSIS SUMMARY.....	35
11.	PSEUDOCOMPONENT DEFINITION.....	39
12.	PHASE IV ANALYSIS BASES.....	41
13.	INVESTMENT AND RETURN BASES - PHASE IV.....	42
14.	PLANT OPERATING BASES - PHASE IV.....	43
15.	OPERATING COST BASES - PHASE IV.....	44
16.	PRODUCT VALUE BASES - PHASE IV.....	45

LIST OF TABLES (CONT'D)

TABLE	PAGE
17. PRODUCT CONSTRAINTS.....	47
18. CASE STUDIES EVALUATED.....	49
19. BASE CASE PLANT RESULTS - OCCIDENTAL SHALE OIL.....	51
20. OPTIMIZATION RESULTS - OCCIDENTAL SHALE OIL BASE CASE.....	52
21. OCCIDENTAL SHALE OIL - BASE PRODUCT SLATE.....	54
22. OVERALL PRODUCT COST SHEET.....	55
23. IMPACT OF TURBINE FUEL AROMATIC SPECIFICATION ON PLANT OPTIMUM.....	61
24. OCCIDENTAL SHALE OIL OVERALL PRODUCT COST SHEET - BASE CASE - FUEL GAS SALES ALLOWED.....	63
25. OCCIDENTAL SHALE OIL - PRODUCT SLATE - ADDITION OF ALKYLATION/POLYMERIZATION CAPACITY.....	65
26. OCCIDENTAL SHALE OIL - PRODUCT COST COMPONENTS - ADDITION OF ALKYLATION/ POLYMERIZATION CAPACITY.....	66
27. OCCIDENTAL SHALE OIL - REFINERY VALUES AND PRODUCT SLATE - FEEDSTOCK VALUE CALCULATION.....	68
28. BASE CASE RESULTS COMPARISON.....	73
29. BASE PRODUCT SLATE.....	74
30. OVERALL PRODUCT COST SHEET.....	75

ABBREVIATIONS

AFWAL	Air Force Wright Aeronautical Laboratories
°API	API Gravity
ASTM	American Society for Testing Materials
bb1	Barrel, 42 U.S. Gallons
BPCD	Barrels per Calendar Day
BPSD	Barrels per Stream Day
BTU	British Thermal Units
C ₁	Methane
C ₂	Ethane
C ₃	Propane
C ₃ ^m	Propylene
C ₄	Mixed Butanes
n-C ₄	Normal Butane
i-C ₄	Isobutane
C ₄ ^m	Butylene
C ₅	Pentane
C ₆ ⁺	Hexane and Heavier
C/O	Catalyst-to-Oil Ratio, Weight Basis
CSHT	Crude Shale Hydrotreater
COHT	Cycle Oil Hydrotreater
DCF	Discounted Cash Flow
D-86	ASTM Distillation Procedure D-86
D-2887	ASTM Distillation Procedure D-2887

ABBREVIATIONS (CONT'D)

EP	End Point in a Distillation
°F	Degrees Fahrenheit
FCC	Fluid Catalytic Cracker
FCR	Fluid Catalytic Reactor - Pilot Plant Unit
Fe	Iron
FOE	Fuel Oil Equivalent, at 6.05 MM BTU/BBL
Gal	U.S. Gallon
GCHT	Guardcase Hydrotreater
Gm	Gram
H ₂	Hydrogen
Hr ⁻¹ or hr ⁻¹	Inverse Hours
H ₂ O	Water
H ₂ S	Hydrogen Sulfide
IBP	Initial Boiling Point
in	Inches
JP-4	Military Specification MIL-T-5624K Turbine Fuel
JP-5	Military Specification MIL-T-5624K Turbine Fuel
JP-8	Military Specification MIL-T-83133 Turbine Fuel

ABBREVIATIONS (CONT'D)

lb	Pound
LHSV	Liquid Hourly Space Velocity
LPG	Liquefied Petroleum Gas
LV%	Liquid Volume Percent
MM	Million
M	Thousand
MAT	Microactivity Test
MAX	Maximum
Mf	Mole Fraction
MIN or min	Minimum
ml	Milliliter
MRCC	Modified Reduced Crude Conversion
N	Nitrogen
N _f	Nitrogen in Feed
N _p	Nitrogen in Product
NH ₃	Ammonia
NO _x	Oxides of Nitrogen
n-PARAFFIN	Normal Paraffin
O	Olefins
O:A	Oil-to-Acid Ratio, Weight Basis
OXY	In Situ Shale Oil

ABBREVIATIONS (CONT'D)

Pds	Periods
ppb	Parts per Billion
ppm	Parts per Million
psia	Pounds of Force per Square Inch Absolute
PSIG or psig	Pounds of Force per Square Inch Gauge
R	Gas Constant
r	Correlation coefficient of data
RVP	Reid Vapor Pressure
S	Sulfur
SCFB	Standard Cubic Feet per Barrel
SCFH	Standard Cubic Feet per Hour
TBP	True Boiling Point
V/V	Volume Comparison
VOL	Volume
WBS	Work Breakdown Structure
WHSV	Weight Hourly Space Velocity
W/W	Weight Comparison
WT %	Weight Percent

SYMBOLS

@	At
¢	Cents
\$	Dollar
=	Equals
+	Positive, plus, or greater than as in 600°F+
-	Negative, minus, or less than as in -600°F
%	Percent
>	Greater Than
<	Less Than
"	Inches
#	Pounds
△	Difference

SUMMARY

The Ashland Petroleum Company Research and Development Department has completed a four-phase research program funded under Department of Defense Contract F33615-78-C-2080. This program evaluated, on concept, laboratory, pilot plant, and computer model bases, Ashland's EXTRACTACRACKING process for production of military specification fuels from Occidental and Paraho crude shale oils. This report presents the experimental data analysis and computer modeling results for the final, Phase IV, portion of this contract.

Scale-up evaluations indicated reasonable agreement between laboratory and pilot plant results. Most operating differences were directly reconcilable when operating conditions and/or feedstock properties were considered. There were scale-up problems encountered, however, in the aromatic saturation module.

Computer modeling of these data indicated that Occidental oil would be refined at lower severity in this process than Paraho oil, with a resulting cost advantage of 2 to 3 dollars per barrel. Incremental production of turbine fuel of up to 50M barrels per day above a base level of 23M barrels per day was shown to require only 5 to 10 cents per gallon additional production cost.

Evaluation of changes in apparent plant optimums at different contract stages demonstrates that increasing feedstock costs (from 16 to 40 dollars per barrel) have resulted in much higher proportionate product charges, resulting in a strong driving force for increasing process severity to maximize liquid fuel yields. Future price increases would be anticipated to continue this trend.

SECTION I
INTRODUCTION

The traditional source of aviation fuels has been the refining of petroleum oil. In recent years, the consumption of petroleum products in the United States has exceeded our country's discovery and development of new oil production. The lessening world supply of crude oil, the increased cost of this crude oil, and specifically the dependence of the United States on foreign oil sources were vividly demonstrated during the Arab oil embargo in 1973, as well as the 1979 Iranian crisis. All of these conditions served to emphasize the need for the development of new energy sources within the United States to ensure a continued national energy supply. A secure and reliable supply of military fuels is essential for our national defense. The Department of Defense and the Department of Energy have set into motion programs for the development of fuels from the coal and oil shale reserves located in the United States. Research and Development efforts have shown that oil derived from shale presents one of the best potential alternate sources of military jet fuels (1). Clearly, the incentive to attain self-sufficiency in aviation turbine fuels is great.

Ashland Research and Development Department of Ashland Petroleum Company was awarded Contract No. F33615-78-C-2080 to provide sample quantities of aviation turbine fuel, i.e.,

JP-4 and JP-8, derived from crude shale oil feedstocks for testing and evaluation in programs sponsored by the Air Force Wright Aeronautical Laboratory (AFWAL) and other participating government laboratories. Technical work required under this research and development program was concerned with the production of sample quantities of fuels by processes having the potential for scale-up, as shown in Table 1. The process used to convert whole crude shale oil into military fuels was to be optimized to produce high yields of aviation turbine fuels, type JP-4 or JP-8. It was desired that the process scheme in this research effort be based on the application of promising new refining concepts for increased efficiency and economy.

The goals to be pursued under this program were (1) samples of military fuels were to be provided of variable quality representing fuels which can be economically produced from raw shale oil by methods which shall be disclosed to the Air Force; (2) a complete model of the processing method was to be developed to project economic data based on throughputs which will minimize product costs and maximize overall plant thermal efficiency; (3) a processing method was to be presented having a minimum overall efficiency of seventy percent, based on crude charge, product yield and utility consumptions, including the hydrogen consumption; and, (4) a processing method was desired which produces a full slate of military transportation fuels. This slate of fuels was to

TABLE 1
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 PERCENT.

 4. PROVIDE A PROCESSING METHOD WHICH
 PRODUCES A FULL SLATE OF MILITARY
 TRANSPORTATION FUELS.

include motor gasoline, aviation turbine fuels (grade JP-4 or JP-8 and grade JP-5), diesel fuel, diesel fuel marine and residual fuel products. The yields of residual fuel were limited to no more than ten percent of the product slate while maximizing the yield of aviation turbine fuel, grade JP-4 or JP-8.

This program was divided into four phases, as shown in Table 2. Phase I commenced on February 15, 1979 and was completed on June 15, 1979, with the primary objective of performing a preliminary process analysis. Conceptual flow diagrams, yields, and process economics were developed which demonstrated the potential of this process.

Phase II was initiated on June 15, 1979 and was completed on September 30, 1980. This phase consisted of two major tasks (1) an evaluation of operating conditions on process performance, and (2) production of five small (500 milliliter) samples of variable quality aviation turbine fuels. A total of nine samples were provided.

Phase III was initiated on November 15, 1979 and was completed in June 1981, with the objective of producing larger scale samples of military fuels. Samples were provided of conventional specification JP-4 and JP-8, high aromatics JP-8, and quantities of gasoline, diesel, and residual fuel components.

TABLE 2

MILITARY JET FUEL FROM SHALE OIL PHASES

PHASE I.	PRELIMINARY PROCESS ANALYSIS
PHASE II.	LABORATORY SAMPLES
PHASE III.	COMPONENT TEST SAMPLES
PHASE IV.	OVERALL ECONOMIC OPTIMIZATION

Finally, Phase IV was an overall economic optimization, via computer modeling, of this process. A second objective for Phase IV was analysis of all experimental data. Phase IV efforts were performed during June to September 1981, and these results reported herein.

THE EXTRACTACRACKING PROCESS

EXTRACTACRACKING is an integrated process specifically designed for conversion of non-conventional feedstocks into only finished, conventional products. In the configuration utilized in this program, EXTRACTACRACKING directly addresses the problems involved in shale oil refining.

The process configuration evaluated in this program is shown schematically in Figure 1. Whole crude shale oil is converted by a combination of hydrotreating, extraction and fluid cracking steps into a crude distillate stream demonstrating the desired boiling range characteristics, as well as the

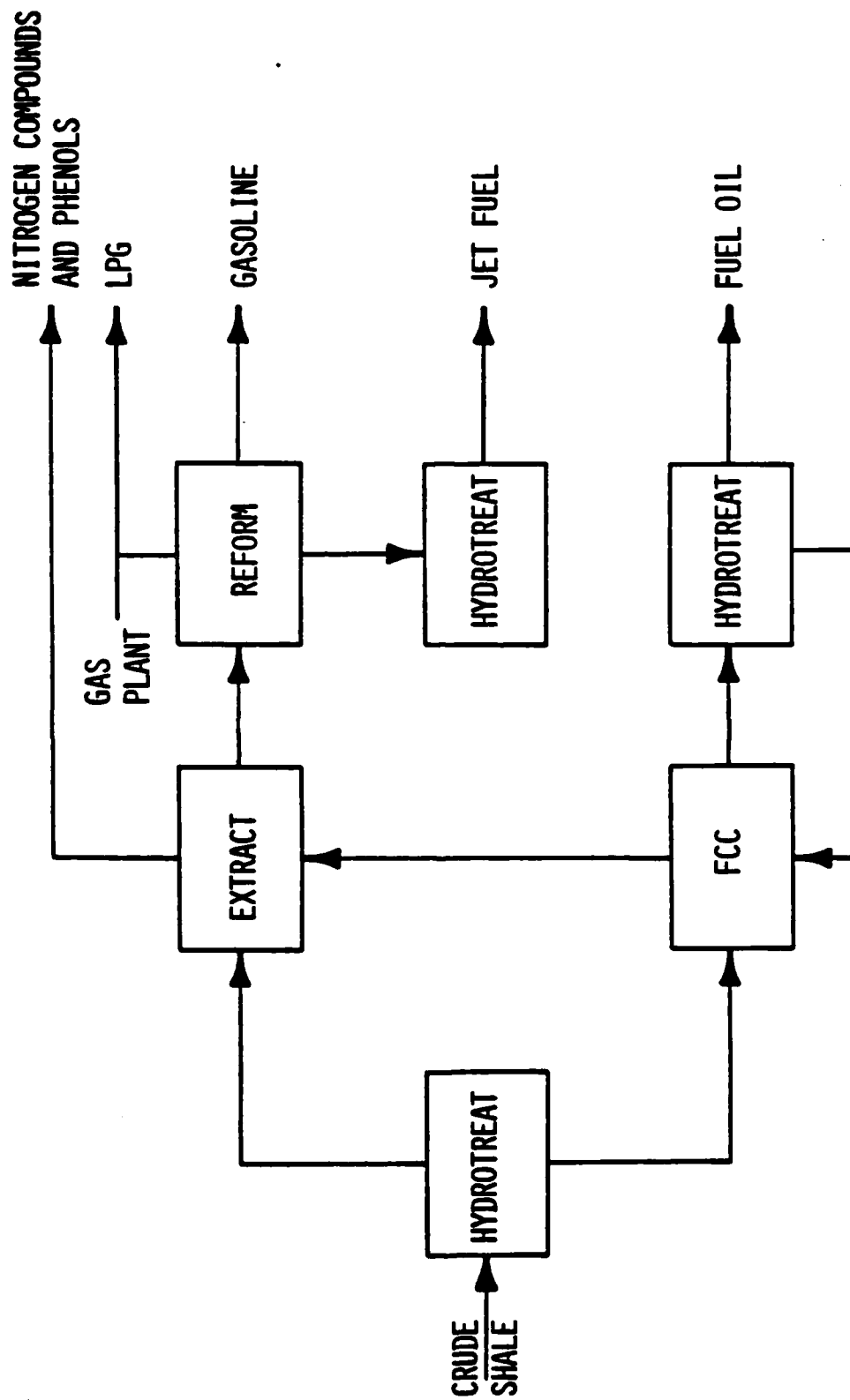


Figure 1. The EXTRACT cracking Process

approximate physical and chemical characteristics required for finished fuel production. Final product treating steps are provided as conceptually necessary for production of finished, on-specification fuels. Since the overall objective of this program is production of an economic maximum of aviation turbine fuels, the process configuration and conditions delineated herein have been defined for that result.

Table 3 demonstrates the direct correlation between problems anticipated for shale oil refining and the provision of specific processing modules in this design.

Further details of this process, as well as technical descriptions of each preceding Phase, are available from previous presentations(2-4) and Interim Technical Reports(5-9). The data utilized in this analysis were obtained from those program portions.

TABLE 3

EXTRACTACRACKING'S ANSWER TO
SHALE OIL REFINING PROBLEMS

<u>PROCESS MODULE</u>	<u>PROBLEM ADDRESSED</u>
• 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

SECTION II
PROCESS MODULE EVALUATION

Two stages of operation, representing one level of scale-up for the most part, were provided during this program using Occidental shale oil. Specific elements from the Phase II laboratory studies were selected, by preliminary optimization, to be evaluated at the pilot scale. This section describes, on a comparative basis, results obtained for each process module shown previously in Figure 1.

CRUDE OIL CHARACTERISTICS

Feedstock parameters demonstrated a very wide variation pattern over the course of the experimental program. A total of twenty Occidental samples were evaluated for crude properties, with the range of results shown in Table 4. In general, the Phase III data showed more scatter than that encountered during Phase II, with the Phase II results commonly distributed at about the midpoint of the Phase III values. The only exceptions to this trend were elemental hydrogen (higher in Phase III) and oxygen (lower in Phase III) contents.

There were few, if any, particular trends in this data. Items were, at least visually, of random distribution. Of particular importance was the observation that hydrogen content during Phase III was consistently at the 12 weight

TABLE 4

RANGE OF FEEDSTOCK PROPERTIES
OCCIDENTAL SHALE OIL

<u>Item</u>	<u>Phase II</u>	<u>Phase III</u>
Element, Wt. %		
Sulfur	0.53-0.64	0.48-0.78
Nitrogen	1.40-1.42	1.21-1.70
Basic Nitrogen	0.859-0.875	0.78-0.96
Oxygen	1.13-1.21	0.877-1.05
Hydrogen	11.0-11.7	11.82-12.1
°API	23.5-23.7	23.5-24.0
Trace Metals, ppm:		
Iron	32-71	20-75
Nickel	11-13	3-13
Vanadium	1-2	1-2
Arsenic	24-39	20-46
Chloride, ppm	4-24	7-113

percent level, or about 0.3 weight percent (or more) higher than those obtained from Phase II. This may well be due to a difference in analytical techniques, as an NMR method was used during Phase III, compared to a Carlo-Erba technique during Phase II. Due to their consistency, and comparison with other reported values, the Phase III hydrogen levels are believed to be more nearly correct. For further hydrogen consumption analysis, however, it should be noted that Phase II feedstocks may be significantly lower in hydrogen content than the Phase III feeds. Since these data were highly variable, extremum averages were used to develop the properties used for computer analysis. Table 5 presents these averages.

CRUDE SHALE OIL HYDROTREATER

The crude shale oil hydrotreater is provided in the EXTRACT-ACRACKING process to saturate olefins and diolefins, remove sulfur, arsenic, and a small amount of nitrogen while providing a relative increase in the distillate oil basic-to-total nitrogen ratio. Since the entire quantity of crude is passed through this module, minimization of hydrogen consumption at this point is of prime importance towards limiting total plant usage. Scale-up effects were evaluated by comparing 100 milliliter (Phase II) and one gallon (Phase III) catalyst charges.

Comparison of lined-out Phase III data with Phase II parameter response and aging data is confounded somewhat, due to

TABLE 5
DESIGN BASIS FEEDSTOCK PROPERTIES
OCCIDENTAL SHALE OIL

Gravity, °API	23.7
Elemental Analysis, Wt. %	
Sulfur	0.61
Nitrogen	1.43
Basic Nitrogen	0.87
Oxygen	1.07
Hydrogen	11.90
Minor Components, ppm	
Iron	52
Nickel	10
Vanadium	1
Arsenic	32
Chloride	37

multiple operating periods, and catalyst charges. However, visual and graphical analysis of these data show that data after July 17, 1980 (after a guardbed change) appear to have equilibrated. Further evaluations herein are based on those values.

Product property comparisons, Table 6, show some very interesting results. Gravity ($^{\circ}$ API) and total nitrogen contents are in substantive (uncorrected) agreement between Phases. Major differences occur in sulfur levels, however, as the Phase III data in total show much higher sulfur removal. However, after the aforementioned lineout period, the data are reasonably consistent. Oxygen data from Phase III are significantly lower than the model values, but in reasonable agreement with Phase II aging data when space velocity differences are reconciled.

A point of major uncertainty in the Phase III analysis is gas (C_1 to C_5) production. High levels of C_1 to C_5 gases in the feed hydrogen (from the adjacent refinery), coupled with a relatively high variability in the supply and measurement of these gases, make any real quantification difficult. Data response estimates in Table 6 are based on the Phase III data, normalized by balancing to 100 percent mass, and hydrogen elemental analysis with the assumptions that: (1) the initial gas yield estimate should be the difference between 100+ observed hydrogen consumption and the sum of measured

TABLE 6

COMPARISON OF PHASE II AND III DATA

	30-Day, Phase II		Phase III		
	Actual Start of Run (Pds 4-6)	Lined Out (Pds 25-28)	Model Start of Run	Start of Run	Lined Out
Temp., °F	677	676	680	680	680
PSIG	1017	1013	1250	1250	1230
LHSV	1.89	2.02	1.5	1.49	1.46
H ₂ Rate, SCFB	3192	3027	3000	3030	2632
H ₂ Purity, mf	1.00	1.00	0.800	0.776	0.676
Yields, Wt. % FD					
C ₁	0.0	0.0		0	0
C ₂	0.10	0.44		0	0
C ₃	0.08	0.38	0.21	0.45	0.68
C ₄	0.27	0.66		0.24	0.16
C ₅	0.01	0.07		0.07	0.07
C ₆₊	99.11	97.77	99.52	98.41	98.20
H ₂ S	0.52	0.55	0.55	0.63	0.59
NH ₃	0.20	0.37	0.45	0.43	0.38
H ₂ O	0.82	0.83	0.59	0.70	0.76
Subtotal	101.11	101.07	101.32	100.93	100.84
Hydrogen	-1.11	-1.07	-1.32	-0.93	-0.84
Liquid Properties:					
°API	27.8	27.2	28.2	28.0	
% S	0.14	0.13	0.09	0.04	0.08
% N	1.23**	1.19**	1.03	1.06*	1.11*
% O	0.41	0.39	0.48	0.30	0.30

* Antek

** Correlated Kjehtdahl

liquid plus calculated heteroatomic species, while (2) maintaining the reported gas distribution. While this may not be an optimum solution, it does limit data impacts to less than 1 percent of feed flow while ensuring normalized elemental balances. This analysis differs slightly from the total Phase III report procedures. For all data, gas measurements represent very high levels of uncertainty, but, again, the magnitude of the gas contribution is relatively small.

Finally, there seems to be a significant difference in hydrogen consumption between modeled and Phase III results. This may well be due to differences in feed hydrogen content, or to differences in measurement techniques. The primary element at present is projected to be the 0.3 weight percent feed composition differential.

A further element of particular importance to the Phase III effort was definition and/or confirmation of Phase II aging trends. Figure 2 demonstrates a comparison of the major elements for aging runs from both phases. Comparative responses are in substantive agreement when specific throughput differences are taken into account. After the aforementioned induction or lineout period, the deactivation slopes are also very consistent. Further, there appeared to be no effective loss of deoxygenation activity during this period in Phase III. Detailed deoxygenation aging parameters were not measured in Phase II.

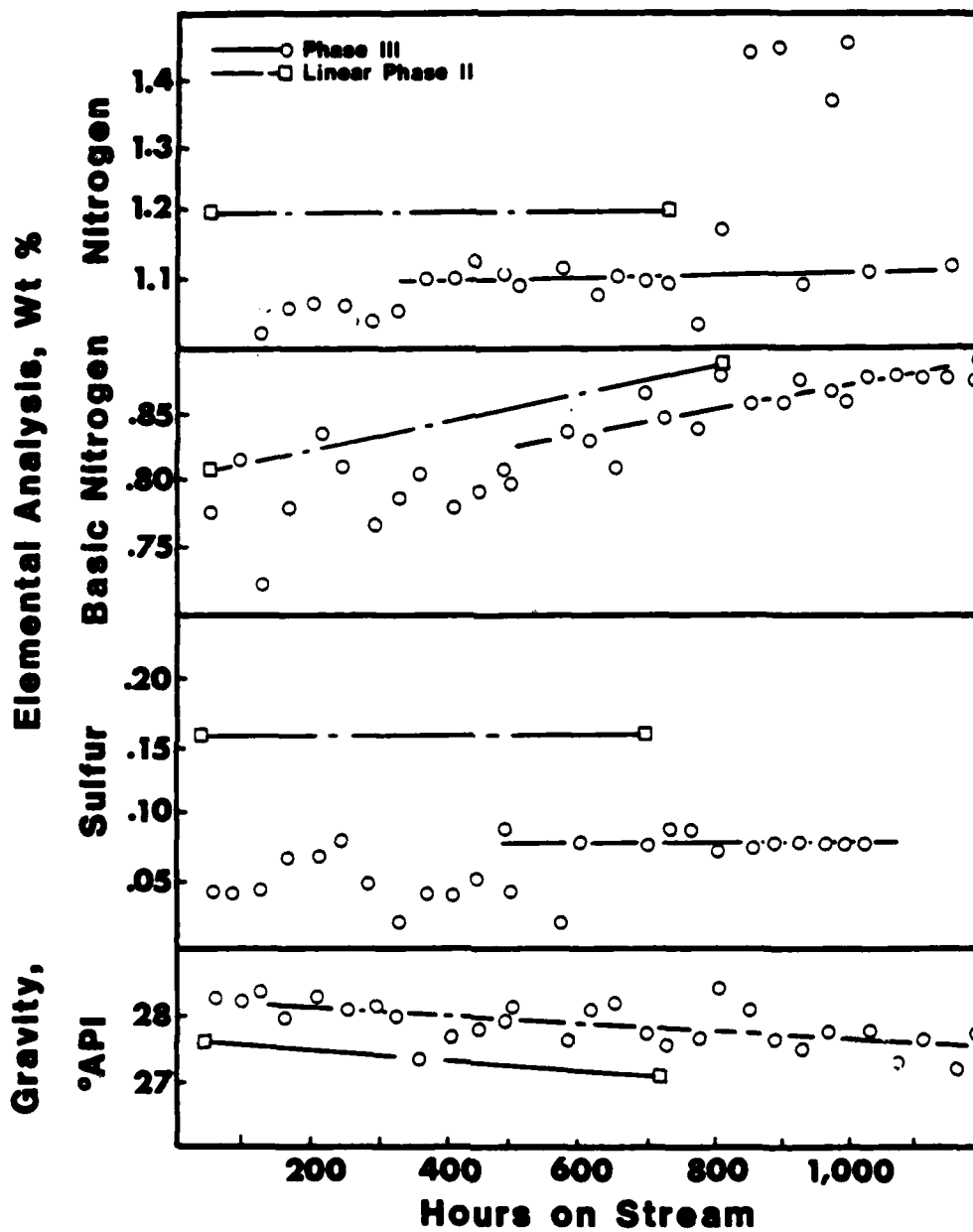


Figure 2. Hydrotreater Aging Comparison

This excellent agreement led to the evaluation that this (Phase III) hydrotreater, starting at a 680°F average temperature, would have a cycle life of at least one year at a 0.2°F/day temperature increase program. This program is that calculated to hold loss of nitrogen removal activity to zero, from the Phase II temperature response, Phase III deactivation curve, and end-of-run requirement of 750°F. This also results in improvement during the year for sulfur and oxygen contents, as well as an increasing basic-to-total nitrogen ratio. The product gravity would be expected to decrease by about 2° API over this period.

Negative factors in this analysis, however, include a severely fouled catalyst bed in both Phases II and III. Both of these runs used singularly unsuccessful guardbeds, with the result that arsenic and iron removal was accomplished by the catalyst bed rather than by the guardbed. It is somewhat surprising that this catalyst maintained the activity that it did. Therefore, any extrapolation of catalyst aging parameters is limited in terms of reliability by these deposits, while almost certain improvement in aging performance could be attained by better guardbed provisions.

Finally, both aging and performance characteristic analyses are clouded by a decrease in hydrogen circulation rate during Phase III and a relatively high variability, in hydrogen consumption in Phase II. For our purposes, hydrogen consumption

has been assumed to stabilize at 80 percent of start-of-run values, as shown by the Phase II data (but not confirmed in Phase III).

Overall, the scale-up from Phase II to Phase III was straightforward and in good agreement. Aging trends and most product properties are directly comparable. For modeling purposes, Phase III deoxygenation data and elemental balanced hydrogen consumption at 80 percent of start-of-run values were used. Gas values from actual Phase II data were used. All other input data for computer modeling were taken directly from Phase II data as necessary.

FLUID CATALYTIC CRACKING

The FCC (or modified reduced crude converter [MRCC]) module is provided to accomplish the necessary degree of boiling range conversion (cascading) to desired distillate products, while providing hydrogen redistribution and some nitrogen removal. Two experimental units were utilized during this analysis, a microactivity unit (MAT) during Phase II and a continuous circulating (FCR) unit during Phases II and III. Due to a lack of reasonable operating time on the Phase III cycle oil hydrotreater, only raw (non-hydrotreated) recycle will be evaluated here.

Evaluation of fresh feed operation in the MRCC system was accomplished by comparing FCR-1 yields with various Phase II

MAT data as shown in Figures 3 and 4. The MAT and FCR-1 data are in substantive agreement on total distillate yields, and in reasonable agreement on individual naphtha and middle distillate yields. The units disagree, however, in terms of gas and coke yields, being lower and higher, respectively, for the FCR data. These results are consistent with previous evaluations.

The discrepancy in coke yield is postulated to be due to (1) an effective temperature difference, and (2) limited spent catalyst stripping capacity. Later thermogravimetric analyses of spent, stripped catalyst show that at least 20 percent of the carbon content of that catalyst is volatile at 1025°F.

Overall, these two items are postulated to explain the majority of differences between these units. The MAT data probably understates the coke yield and overstates gas yield. For modeling purposes, however, the excellent (naphtha + distillate) yield agreement is the key element, as primary liquid yields effectively define performance. Relative errors between gas and coke are not of major economic impact.

Performance of the unit on raw recycle was evaluated both in blend with fresh feed and with recycle alone. No significant differences in yield or conversion were noted, even for multiple pass recycle material at these conversion levels.

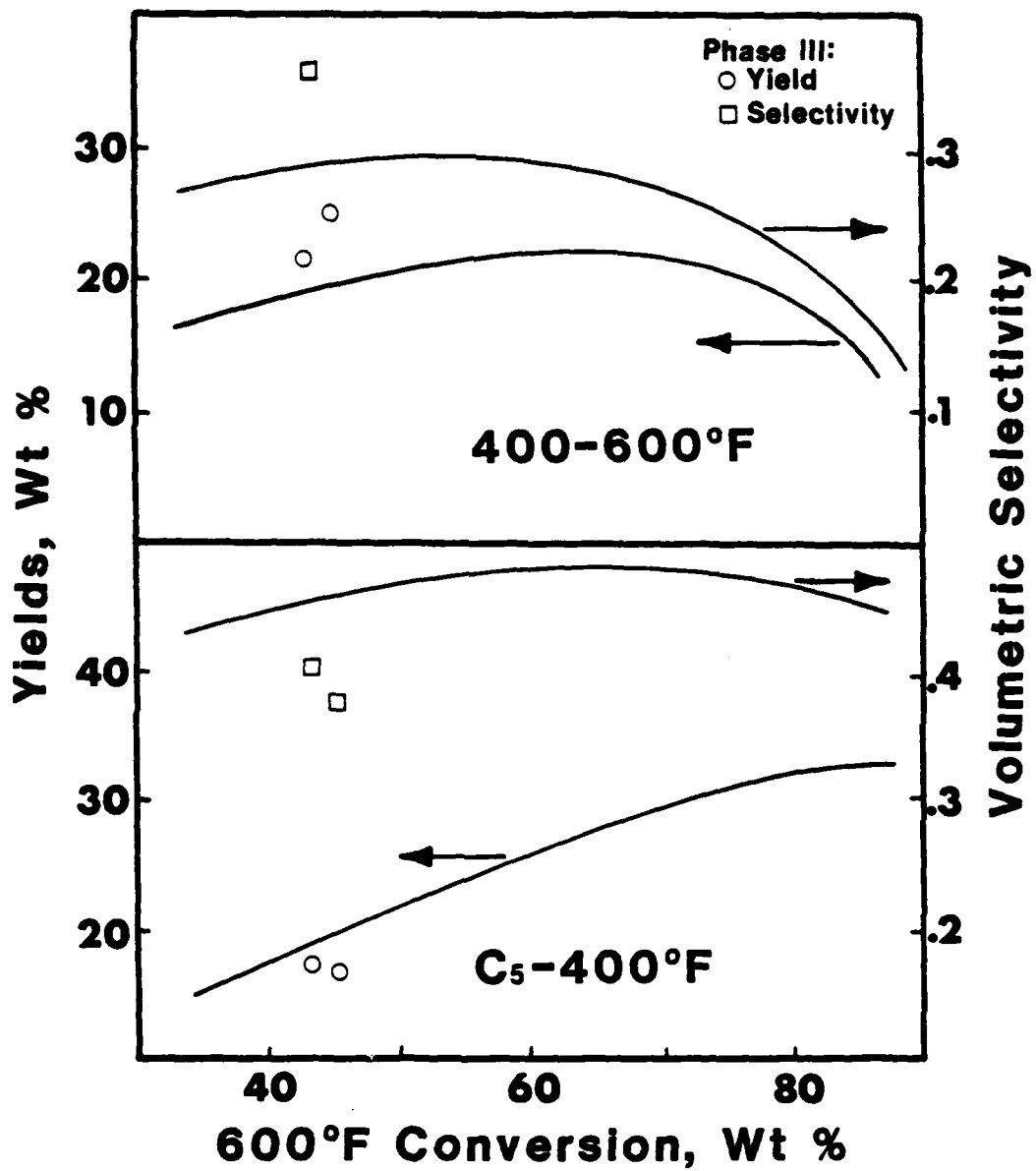


Figure 3. Comparison Of FCC Liquid Product Yields

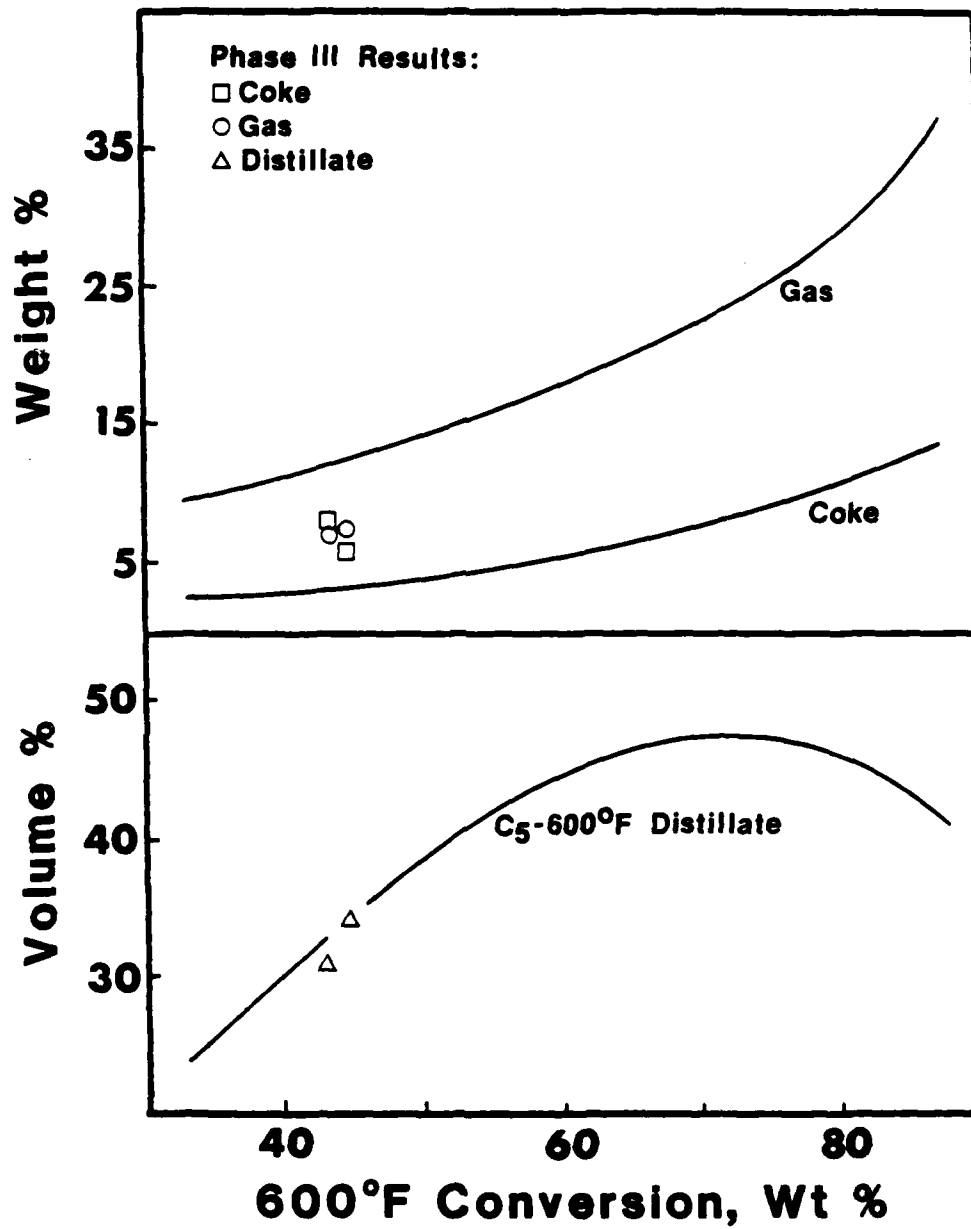


Figure 4. Comparison Of FCC Results Between Phases

Therefore, for modeling purposes, recycle yield structures were defined to be analogous to those for the fresh feed.

Product properties are, for the most part, very comparable to those found in Phase II (on the same unit, under different conditions). Figures 5 and 6, in particular, demonstrate this agreement for sulfur and nitrogen removal. There seems to be some disagreement in terms of hydrogen redistribution, with the Phase III data showing little change between feed and products.

Finally, mathematical analysis was performed on the FCR-1 data to see if time trends could be discerned. There were no apparent data correlating significantly with time, indicating no substantial drift in MRCC performance.

For modeling purposes, these results were defined as allowing use of the Phase II parameter response data, with the caveat that gas yields may be overstated and coke yields understated in the final result. Correlated and actual property data were used from both Phases II and III. Finally, raw recycle was practiced with no differentiation in yield structure required when compared to the fresh feed.

EXTRACTION

The extraction module is provided in this process to accomplish nitrogen removal without external hydrogen addition.

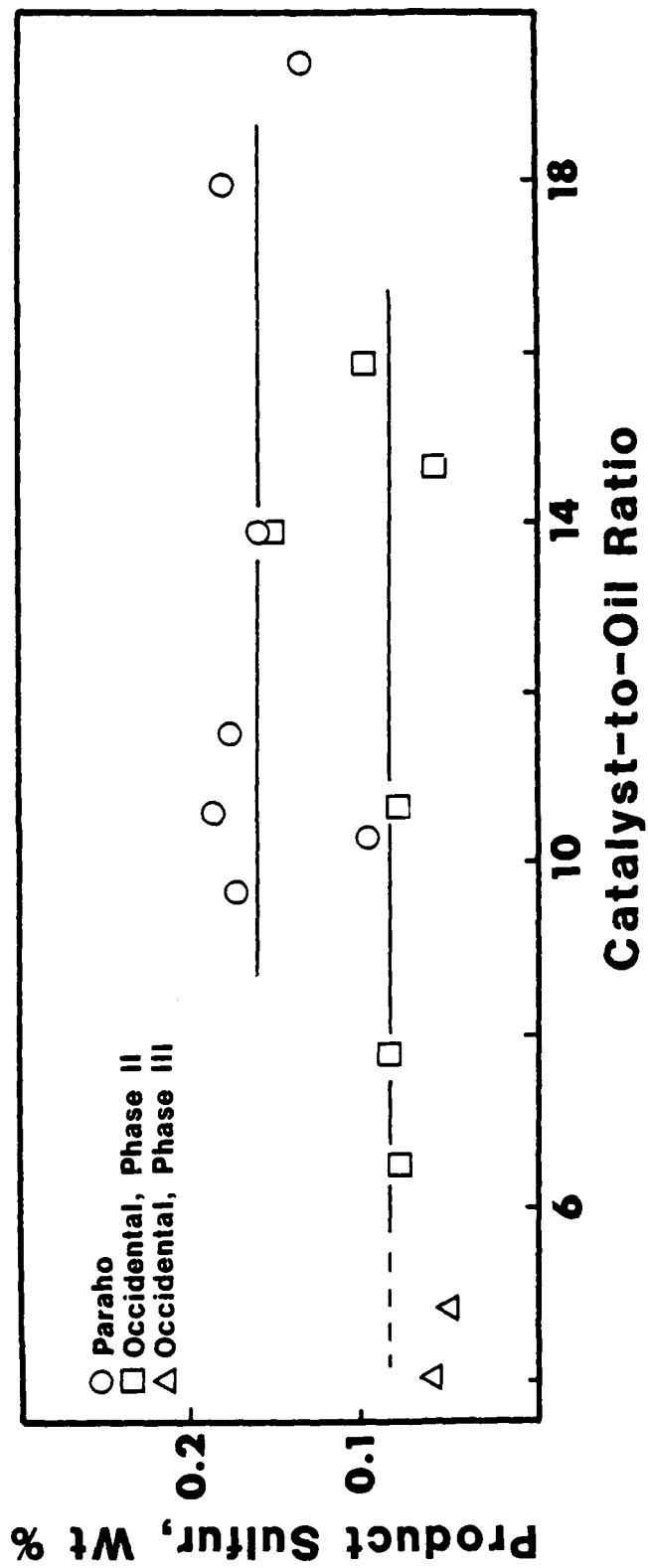


Figure 5. Desulfurization During Fluid Cracking

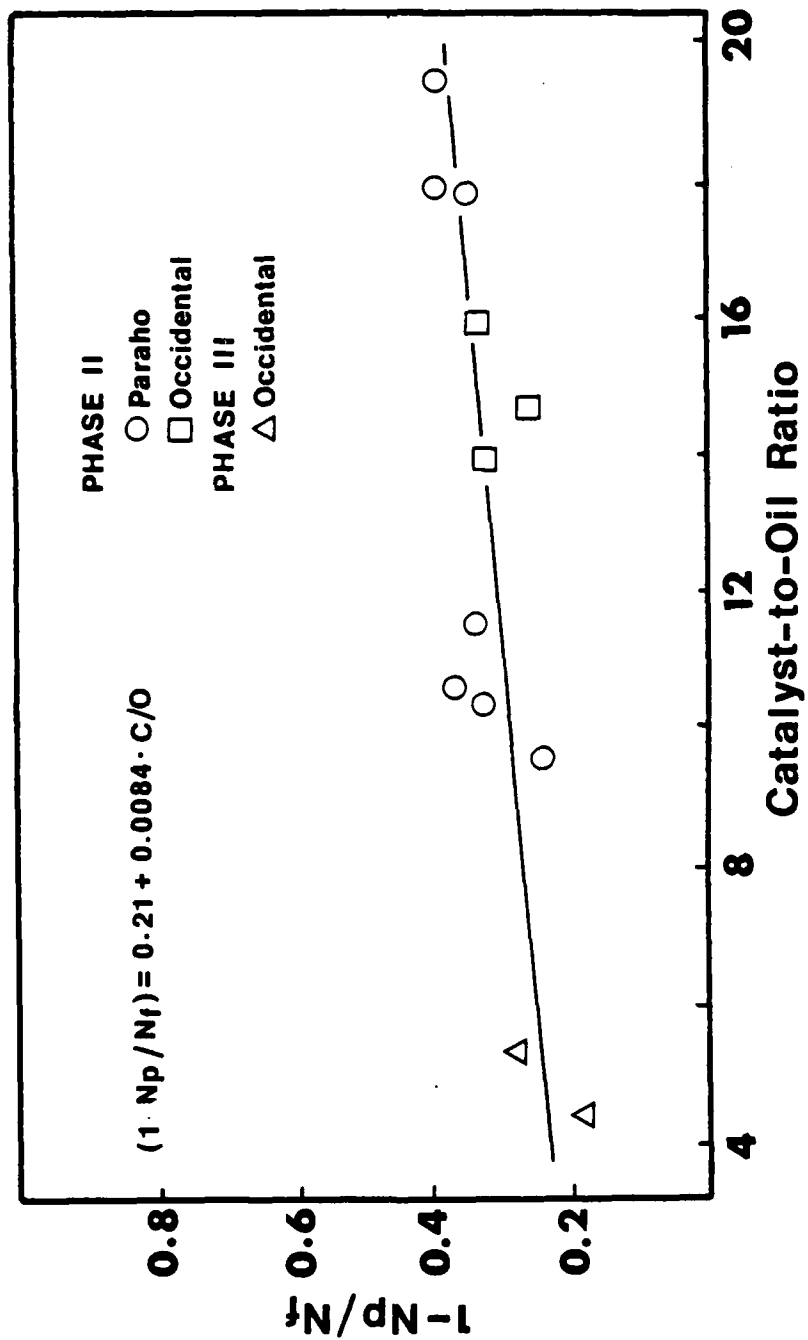


Figure 6. Denitrogenation Comparison - FCC

The process uses chemical action, rather than high severity conditions, to accomplish this objective. Phase II data for this module was accomplished on batch and one inch continuous extraction equipment. The Phase III data was derived on a continuous extraction unit of similar design to that used in Phase II, but with a two inch diameter.

Initial inspections of the Phase III data indicated much lower removal efficiencies than obtained in Phase II. Further evaluation, however, indicated that the major difference between phases was the acid treating rate, which had been allowed to fall below the desired value. Analysis of the Phase III data, in fact, indicated that only varying acid treating rates were significant in the results obtained. Linear least squares evaluation resulted in a correlation coefficient of 0.97 and the plot is shown in Figure 7. As shown by the bar in this graph, the (corrected for other factors) Phase II equivalent results are in reasonable agreement. This indicates that the scale-up was successful, predictable, and that the results from both phases are comparable when stated on equivalent bases.

Inspection of product properties further confirms this analysis. At comparable nitrogen removal levels, for comparable feedstocks, Phase II and Phase III component properties are not significantly different. As a result, Phase II and Phase III (corrected) data were used for modeling purposes. Phase

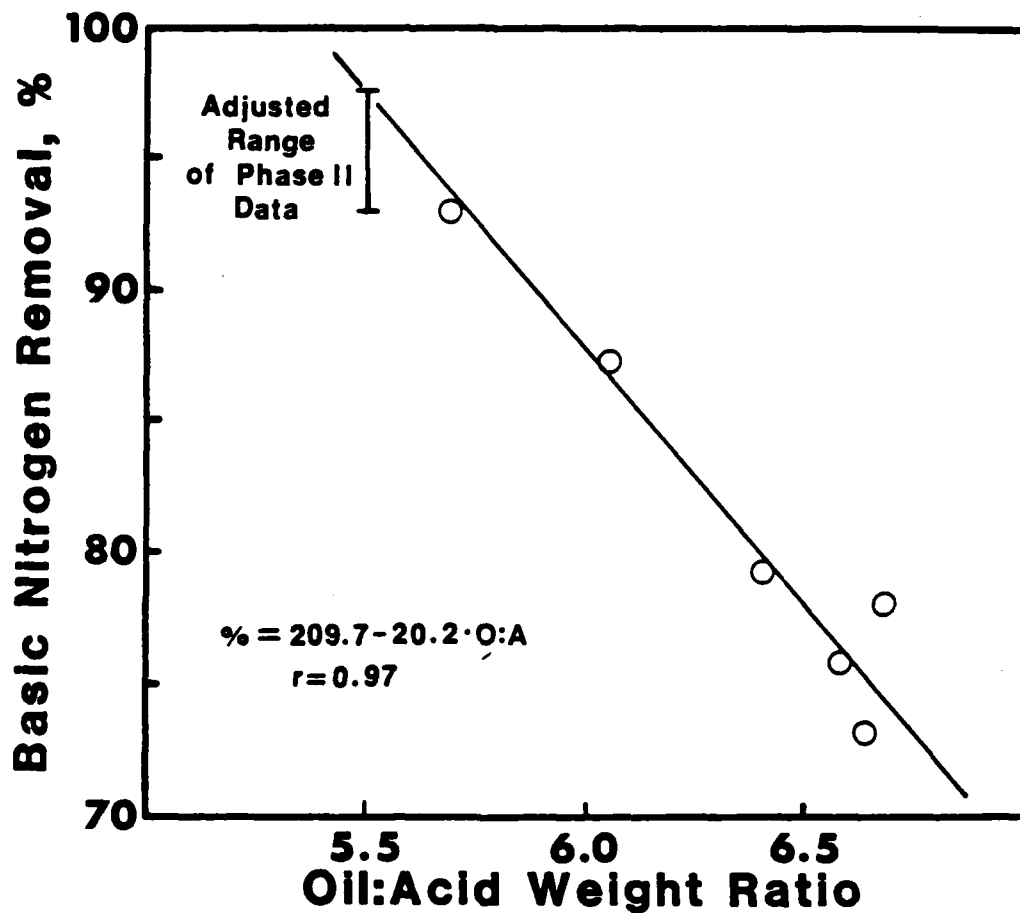


Figure 7. Comparison Of Phase II And III Extraction Response

III extract composition was used, corrected where necessary for excess hydrocarbon loss.

GUARDCASE HYDROTREATING

Guardcase hydrotreating was provided to remove remaining sulfur, nitrogen, oxygen, and/or any remaining contaminants as necessary. Phase II studies were performed in nominal one inch inside diameter laboratory units, while Phase III studies were performed in a nominal two inch inside diameter unit. Both of these systems were analogous in most mechanical respects to those used for crude shale hydrotreating. Fifty to 80 cubic centimeter catalyst charges were used in Phase II, while approximately one gallon of catalyst was used in Phase III. The catalyst used was the same for both cases.

At first analysis, comparative response data (Table 7) appear to show less efficient operation of the Phase III hydrotreater than in Phase II. While the efficiency may be questioned, simple linear analysis indicates that excellent correlation of the data ($r = 0.998$) may be obtained by correcting for temperature, hydrogen partial pressure, and feed nitrogen level. These factors are listed in terms of increasing importance, i.e., the major factor appears to be feed nitrogen level. Less efficient extractor performance apparently led directly to the high severity requirements in Phase III. Table 7 also demonstrates predicted versus actual nitrogen levels for actual preparation samples from Phases II and III.

TABLE 7
COMPARISON OF GUARDCASE RESULTS

Sample ID Fuel Type	PHASE II				PHASE III	
	112 <u>JP-4</u>	121 <u>JP-8</u>	GCl <u>Both</u>	GCl-1 <u>Both</u>	- <u>JP-4</u>	- <u>JP-8</u>
Conditions:						
Temperature, °F	700	700	650	650	730	700
Pressure, psig	1200	1200	1200	1000	1400	1400
Hydrogen Purity, Mole %	100	100	100	100	76.4	77.5
LHSV, hr ⁻¹	0.6	0.65	1.0	1.0	0.7	0.84
Results: Nitrogen Contents, ppm						
Feed	2400	2300	2000	2000	3400	3400
Product	<1	<1	<1	6	2	1
Product, Calculated For Correlation of Phase II and III Data						
	1.0	0.8	0.9	6	1.8	1.4

The second key element, hydrogen consumption, is not a scale-up factor between phases. The key definition of hydrogen consumption will be chemical compound type rather than severity of operation - for all cases, product hydrogen content will tend to a (relatively) constant level. Hydrogen consumption for a given case is defined (assuming comparable boiling ranges) more by hydrogen content of the feed (particularly the amount of olefins and/or aromatics as in the JP-4 pool data) than by any other factor.

For modeling purposes, the highest Phase III severities were used for operating requirements. This should allow adequate slack capacity to handle extractor upsets if and when they occur. Under normal conditions, operations at nominal Phase II levels are shown by the foregoing analysis to be adequate.

FREEZE POINT MODIFICATION

Freeze point modification provides the capability (1) to maximize blending to turbine fuel, and (2) concurrently control hydrogen contents. Phase II efforts were accomplished on nominal one inch units charging 10 to 35 milliliters of catalyst, while the Phase III effort used approximately 0.2 gallons of a similar catalyst in a nominal two inch hydrotreating unit.

Analysis, on a comparative basis, immediately indicates major differences in feedstocks between Phases II and III (Table 8).

TABLE 8
COMPARISON OF PRIMARY DATA
REFORMING SECTIONS

	Phase II			Phase III	
	JP-4 112	JP-8 121	GCI	JP-8	JP-4
Temperature, °F	850	850	910	889	827
Pressure, psig	500	500	500	500	495
LHSV, hr ⁻¹	8	8	24	4.4	6.3
Feedstock Fraction Distilled: 50%, °F	403	430	433	464	344
95%, °F	534	586	565	580	499
°API	43.7	39.1	42.4	41.4	44.8
Product Properties:					
Freeze Point, °F	-78.7	-46.3	-49.0	-67.9	-81.3
% Aromatics	45.8	39.9	42.3	45.4	50.4
Feed Properties:					
Freeze Point	-56	-33.7	-31	-18.4	-73.3
% Aromatics	26.0	30.0	23.0	22.4	25.4

The JP-8 pool material was significantly heavier, and the JP-4 pool significantly lighter, than corresponding fuels prepared in Phase II. These differences are consistent with the manner in which these fuels were prepared. Correlation of fuel properties with freeze points indicates that essentially all feedstock freeze point differences are explained by 50 percent distillation temperature ($r = 0.98$).

Analysis of process response data was made with this factor in the evaluation. Reasonably good reconciliation ($r = 0.96$) was made between Phase II and Phase III aromatization response when processing temperatures, space velocity, and 50 percent distillation temperatures were included. The 50 percent point was of primary importance, followed by temperature.

For the most part, product freeze points were less correlatable than aromatics. However, the combination of temperature, LHSV, and 50 percent distillation temperatures again provided the best fit ($r = 0.89$) with all components of about equal weighting. There is a high probability that paraffin isomerization effects not measured by these properties have a strong impact on the resulting freeze point. This factor will be of particular importance for higher endpoint materials.

Due to product and budget constraints, detailed aging data were not derived for this module. However, indicated aging rates for the JP-8 pool in Phase III tend to suggest relatively high

deactivation rates. In the absence of other data, original Phase I aging estimates were used in the module.

Process response data, as well as required operating conditions, for use in the model, were taken from the Phase III JP-8 pool. Detailed gas component responses were used in conjunction with hydrogen balancing, to define the entire product spectrum. The JP-8 pool condition requirements are the most severe encountered under normal operation, and as such, should provide a conservative estimate for the overall design.

AROMATIC SATURATION

The aromatic saturation unit provides final control of hydrogen content and aromatics level of the finished product. Phase II evaluations were performed in nominal one inch units charging 50 milliliter of catalyst. Phase III evaluations were accomplished in a nominal four inch reactor charging 0.7 gallons of catalyst. Poor saturation efficiency on the first catalyst charge used⁽⁹⁾ has been attributed to contamination, and was not used in this analysis.

Table 9 summarizes primary data from both phases. Analysis between these results indicates that scale-up problems were encountered. Phase II results at 500°F and 200 psig are equivalent to Phase III results at 550°F and 550 psig. The major determinate difference in saturation response was boiling

TABLE 9

DATA SUMMARY AND COMPARISON
FOR AROMATIC SATURATION UNITS

	<u>Phase III</u>		<u>Phase II</u>		
	<u>JP-8</u>	<u>JP-4</u>	<u>JP-4</u>	<u>JP-8</u>	<u>Combined</u>
Conditions:					
Temperature, °F	553	556	500	500	500
PSIG	550	550	200	200	200
LHSV	1.93	1.93	2.0	2.0	2.0
H ₂ , SCFB	8500	8500	8800	8800	8800
Feed Properties:					
°API	39.6	37.8	39.8	37.0	39.6
Aromatics	43.4	52.2	45.8	39.9	42.3
50% Point (D-86)	412	362	(391)	456	(434)
Product Properties:					
°API	41.3	44.7	46.7	46.6	44.2
Aromatics	19.3	11.2	18.3	20.4	11.9
50% Point (D-86)	409	365	379	445	403

() Estimated from D-2887

range of the feedstock as characterized by the 50 percent distillation temperature.

These results require that at least Phase III conditions be used in the computer model. These conditions, Phase III gas yields, and (calculated) hydrogen balancing were input to the model for a complete response matrix.

CONCLUSIONS

For the most part, overall comparison of Phase II and Phase III results indicate reasonable agreement. The major point of difference between phases, as measured by relative influence on processing response, is the boiling range difference between comparable samples. This effect is particularly important in later (downstream) modules.

Table 10 demonstrates key scale-up and operating factors for each module. Reasonably good agreement, particularly for aging trends, was attained in the crude hydrotreater, although total hydrogen input was slightly lower than was predicted or desired. This factor, plus slightly lower catalyst-to-oil operation in the FCC unit, are the probable causes for a low total conversion attained (compared to an original 60 percent target). Problems remain with resolution of gas and coke disagreement in the cracking scale-up.

TABLE 10
SCALE-UP AND DATA ANALYSIS SUMMARY

<u>Item</u>	<u>Relative Scale-up</u>	<u>Major Conclusions</u>
Feedstock	None	Feedstocks drawn from drum samples are highly variable. Phased data agrees except for hydrogen and oxygen contents; primary factor of importance was probable lower hydrogen content for Phase II feedstocks.
CSHT	38 v/v	Total product properties and especially aging curves in substantive agreement. Gas production highly uncertain in both phases. Uncertainties remain in actual aging trend for hydrogen consumption, and independent catalyst aging trends when proper guardcase operation is attained.
MRCC	62,2 w/w	Total distillate in excellent agreement, naphtha and distillate components in good agreement. Gas and coke in disagreement, in counteracting amounts.
Extraction	5 w/w	Good agreement when treating rate and throughput differences are reconciled.
Guardcase	48 v/v	Slightly lower performance in Phase III, but the major factor was increased feed nitrogen content.
Reformer	22 v/v	Major difference was boiling range; may have aging problems.
Aromatic	53 v/v	+50°F, +200 psig condition increase requirement encountered for comparable response.

Extractor results were shown to be in good agreement when acid treating rates were reconciled. However, the lowered rate actually used resulted in a higher than expected nitrogen content in the guardcase charge. This high nitrogen level was the key correlatable difference between Phases II and III guardcase operations.

At this point in Phase III, fractionation of the total distillate pool was performed into JP-4 and JP-8 components. This separation was defined as the key determinant in differences between Phase II and III freeze point modification results. Very little aging information was derived for the reformer module. Scale-up problems were encountered with the aromatic saturation unit and with Phase III processing requiring an additional 50°F and 300 psig for equivalent process response. The major determinant difference between product properties was defined to be boiling range.

SECTION III
EXTRACTACKING COMPUTER MODEL

GOALS

There were six goals to be met in setting up a computer model for the EXTRACTACKING project. First, the model had to be capable of supplying direction to the Phase II screening efforts. Second, the model would be required to optimize Phase IV results to produce the "best" plant design while meeting the constraints imposed by the government guidelines. Third, the tracking of stream nitrogen contents and process unit nitrogen removals was felt to be a key item to be followed through any model developed. Fourth, the basic format of the model was to handle hydrotreating and catalytic cracking units on an "extreme point" basis. Each of these units was to be given the process operating extremes, such as the highest and lowest severity levels, and allowed to choose either extreme or any linear combination between them. Fifth, the model was to be set up to allow the addition of raw process unit data or additional constraints with a minimum amount of data manipulation from the pilot unit data gathering to the model input. Finally, all input data, unit operating conditions, model constraints, etc., were to be fully documented as to source in the model itself to help avoid any identification problems should the model be needed again at a future time.

SYSTEM USED

The system selected to accomplish the goals of this study was the commercially available Refinery and Petrochemical Modeling System (RPMS) developed by Bonner & Moore Management Science of Houston, Texas. This linear programming system had several advantages. First, it was already "in-house", having been used by Ashland since 1971. Second, this system could be adapted to model the EXTRACTACKING process and meet all of the goals identified at the onset of the project. Finally, as an added bonus, final computer runs were produced on microfiche, as well as standard computer paper, with a minimum of effort.

INPUT DATA

All process unit material balance data used in this study were fully weight, sulfur, nitrogen, and hydrogen balanced before being input to the computer model. This data was entered on a weight basis with stream gravities supplied on every stream to allow conversion to a volume basis when needed for blending and final reporting. The hydrogen and nitrogen balances were particularly important to this process in that hydrogen use in the hydrotreaters is one of the key operating parameters in controlling nitrogen removal. The total hydrogen requirements are also one of the key cost items in determining total plant cost, as will be discussed in further detail in the sections dealing with the Phase IV results.

All of the yield data used in this portion of the project was based on the Phase II and Phase III results previously described. This yield data was normalized to 100 percent weight balance and included sulfur and nitrogen contents on each stream. The yields were specific for lighter products such as fuel gas, propane, propylene, C₄'s, and C₅'s. For heavier stream components, a set of pseudocomponents was developed for use in product blending. These pseudocomponents were split out by boiling range as listed below, although the blending properties vary depending upon the source of the stream. Complete blending matrices were developed for reformer, aromatic saturation, and guardcase streams.

TABLE 11
PSEUDOCOMPONENT DEFINITION

<u>Pseudocomponent</u>	<u>Boiling Range, °F</u>
1	C ₆ -300
2	300-400
3	400-520
4	520-600
5	600+

This approach gave the model additional flexibility in product blending which would be required in a full-scale refinery. Component blending data were supplied by correlation in some cases and by basic Bonner & Moore data in others. For example, all of the octane and vapor pressure data for C₄'s and C₅'s going to gasoline blending were supplied from basic Bonner & Moore data.

In each of the model runs, certain units were required which were not included as part of the Pilot Plant investigation. Again, Bonner & Moore basic data were used for auxiliary units such as sulfur recovery and gas plants. Gas plant recoveries were estimated design recoveries based on Ashland's experience for C₃ and C₄ streams. In the cases where the model was allowed to build alkylation or polymerization capacity, the yield data was Bonner & Moore's.

All unit capital cost data were supplied based on updated Phase I investigations. As above, capital costs for auxiliary units were based on Bonner & Moore data. Utility usage and costs were supplied based on experimental work for the usages and government guidelines for the costs. For some additional runs outside of the original project scope, pricing data for the fuels products were taken from Platt's Oilgram US Marketscan (10), an accepted source of industry product prices. Bases and key assumptions for these input items are shown in Tables 12 through 16.

TABLE 12
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 SCALE-UP
FROM PHASE III RESPONSE.

- AGING DATA USED FROM PHASE III.

- PROCESS FLOW: ● AS DEFINED PREVIOUSLY EXCEPT -

- NO COHT

- EXTRACT USED FOR HYDROGEN PRODUCTION

TABLE 13
INVESTMENT AND 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
- 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

TABLE 14
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 SIXTEENTH YEARS
- WORKING CAPITAL CALCULATED FROM:
 - 14 DAYS CRUDE SHALE INVENTORY @ \$40/BBL
 - 7 DAYS PRODUCT INVENTORY @ COST
- WORKING CAPITAL FINANCED AT 15% SIMPLE INTEREST

TABLE 15
OPERATING COST BASES
PHASE IV

● PROCESS HEAT	INTERNALLY GENERATED
● COOLING WATER	3¢/1000 GALLONS
● POWER	4.5¢/KWH
● 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

TABLE 16
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

CONSTRAINTS

Many constraints were standard in every run, especially in the area of product blending specification. Key specifications for the major products are listed in Table 17. Product blending constraints were allowed based on experimental evaluations and product quality judgments.

The major cases were run with the above mentioned constraints as standards with changes either in shale oil type or certain constraints with each run. For example, the Occidental shale was run with the constraints as mentioned to give an optimal solution and allow the calculation of the fuels products price which would result in a 15 percent DCF return. The model was then run with a very high price on the jet fuel products to determine the maximum jet fuel production possible with the existing EXTRACTACRACKING process flow scheme. The same procedure was followed with the Paraho shale oil data.

Additional cases of interest included allowing +10 percent change in the jet fuel aromatics specification to see the effect upon maximum jet fuel volumes, allowing alkylation and polymerization of light gases to enhance the product values and optimizing the process configuration using a set of October 1981 Gulf Coast prices for the major fuels products.

TABLE 17
PRODUCT CONSTRAINTS

	<u>Gasoline</u>	<u>JP-4</u>	<u>JP-5</u>	<u>JP-8</u>	<u>Diesel Fuel</u>
Maximum RVP	9.0	3.0	-	-	-
Minimum RVP	7.0	2.0	-	-	-
Minimum Research Octane	91.0	-	-	-	-
Maximum Lead Level, gm/gal	3.0	-	-	-	-
Maximum Aromatics, Vol. %	-	25	25	25	-
Maximum °API Gravity	-	57	48	51	-
Minimum °API Gravity	-	45	36	37	0
Maximum °F @ 10% Off	-	-	401	401	-
Maximum °F @ 20% Off	-	293	-	-	-
Maximum °F @ 50% Off	239	374	-	-	-
Minimum °F @ 50% Off	193	-	-	-	0
Minimum °F @ 90% Off	-	473	-	-	-
Minimum Cetane Index	-	-	-	-	50

SECTION IV
MODEL RESULTS

The computer model discussed in Section III, and the data discussed in Section II, were used to generate several cases of results. For reporting purposes, these cases are categorized as shown in Table 18. These are the primary variables investigated during this phase.

OCCIDENTAL SHALE OIL

Detailed data from Phases I, II, and III, as discussed in Section II of this report, were used for evaluation of the Occidental shale oil. Development of a base case was followed by model evaluation of several change cases or sensitivities.

Base Case

The base case analysis was provided on Occidental shale oil as our best analysis of optimum operation. No product constraints were provided other than the specifications and prices described earlier. Fuel gas sales were not allowed, as the marketability of this material is highly questionable.

Initial optimization was accomplished at a feedstock equivalent hydrogen plant size of about 1100 standard cubic feet of hydrogen per barrel of crude shale oil. Since linear interpretation of a non-linear world can be risky at times, manual investigation of the data was followed by another optimization, leading to a slightly lowered cost product at slightly over 900 SCFB

TABLE 18
CASE STUDIES EVALUATED

OCCIDENTAL SHALE OIL

BASE CASE

SENSITIVITIES

TURBINE FUEL PRODUCTION LEVEL

TURBINE FUEL AROMATICS SPECIFICATIONS

FUEL GAS SALES

ALKYLATION/POLYMERIZATION CAPACITY

FEEDSTOCK COST

PARAHO SHALE OIL

BASE CASE

TURBINE FUEL PRODUCTION SENSITIVITY

(hydrogen plant size based on crude shale oil). Of particular importance, the apparent optimum curve is relatively flat at total hydrogen input ranging from about 900 SCFB to about 1200 SCFB. Probable operation would occur in the 1000 to 1100 SCFB range to improve total plant operability. Further results reported here as the base case, however, are based on the minimum cost nominal 900 SCFB data.

Table 19 delineates capital cost estimates for this case. Key cost elements are the crude shale hydrotreater and fluid cracking units. There is a high probability that "offsites and other" are significantly understated due to requirements of plants of this type. This cost is a research quality, factored estimate based on modified, updated Phase I results.

This plant operates at the levels shown in Table 20. A 1000 SCFB hydrotreater, operating at 58 percent denitrogenation, feeds a modified reduced crude cracker operating at a total (600°F basis) conversion of 83 weight percent on a fresh feed basis. To attain this conversion level, a 25 percent recycle rate was calculated to be required. The calculated thermal efficiency of 88 percent is very high, and may be due to (1) overestimation of gas yields due to use of MAT data (see Section II), (2) problems in heat balancing in the cracking section, or (3) problems with hydrogen balancing in the FCC section. Other estimates at these operating levels place this value at 82 to 85 percent.

TABLE 19
BASE CASE PLANT RESULTS
OCCIDENTAL SHALE OIL

CAPITAL INVESTMENT 696 MM\$

INVESTMENT DISTRIBUTION:

CRUDE SHALE HYDROTREATER	25%
FLUID CATALYTIC CRACKING	13%
EXTRACTION	3%
UPGRADING	14%
HYDROGEN PLANT	11%
OFFSITES & OTHER	34%

TABLE 20

OPTIMIZATION RESULTS - OCCIDENTAL SHALE OIL BASE CASE

HYDROTREATER:	HYDROGEN CONSUMPTION	1034 SCFB
	DENITROGENATION	58% WT
CATALYTIC CRACKER:	CONVERSION (FRESH FEED BASIS)	83%
	RECYCLE RATE	25%
OVERALL PLANT:	HYDROGEN CONSUMPTION	914 SCFB
	PRIME PRODUCT YIELD, VOLUME % SHALE	92.3
	THERMAL EFFICIENCY	88%

Table 21 presents the overall product slate predicted from this analysis. Gas yields may be slightly high due to previously mentioned factors. A total of 92,300 BPD of prime military fuels (specified at equal value) were produced.

Overall product costs based on these data are shown in Table 22, at a 15 percent DCF rate. Operating costs and working capital are essentially equal to by-product revenues. Feedstock is the key cost component, including about \$3.33 per barrel due to volumetric shrinkage of the products. Capital costs represent about 14 percent of the prime product value listed. Sensitivity to DCF rate is shown in Figure 8. Changing capital return requirements to a 20 percent DCF rate would result in a product value increase of approximately 5 percent.

These cost estimates should not be construed as estimates of the availability cost of products from crude shale oil due to (1) the use of estimated shale oil costs at \$40 per barrel, (2) use of factored capital estimates, (3) the economic constraints used, and (4) possible gas yield inconsistencies in the FCC section. Rather, these estimates are intended for an estimate of the refining impact on incremental product costs, and in particular, are intended to be the basis for the sensitivity analyses following.

Because of the nature of the optimization performed, the reader is cautioned that all fuels produced may be of minimum

TABLE 21

OCCIDENTAL SHALE OIL
BASE PRODUCT SLATE

<u>PRODUCT</u>	<u>BPD</u>	<u>LV % OF PRODUCT SLATE</u>
LPG	1,794	1.8
PROPYLENE	3,844	3.8
N-BUTANE	1,656	1.6
I-BUTANE	2,548	2.5
REGULAR GASOLINE	41,285	40.4
JP-4 TURBINE FUEL	3,594	3.5
JP-8 TURBINE FUEL	18,897	18.5
DIESEL FUEL	19,321	18.9
RESIDUAL FUEL	9,224	9.0
	<u>102,163</u>	<u>100.0</u>

TABLE 22
OVERALL PRODUCT COST SHEET

COST CONTRIBUTION \$/BBL

<u>ITEM</u>	<u>OXY</u>
OPERATING COSTS	\$ 2.23
BY PRODUCTS	(2.66)
WORKING CAPITAL	0.44
FEEDSTOCK	43.33
CAPITAL	6.06
PRIME PRODUCT VALUE	<u>49.40</u>

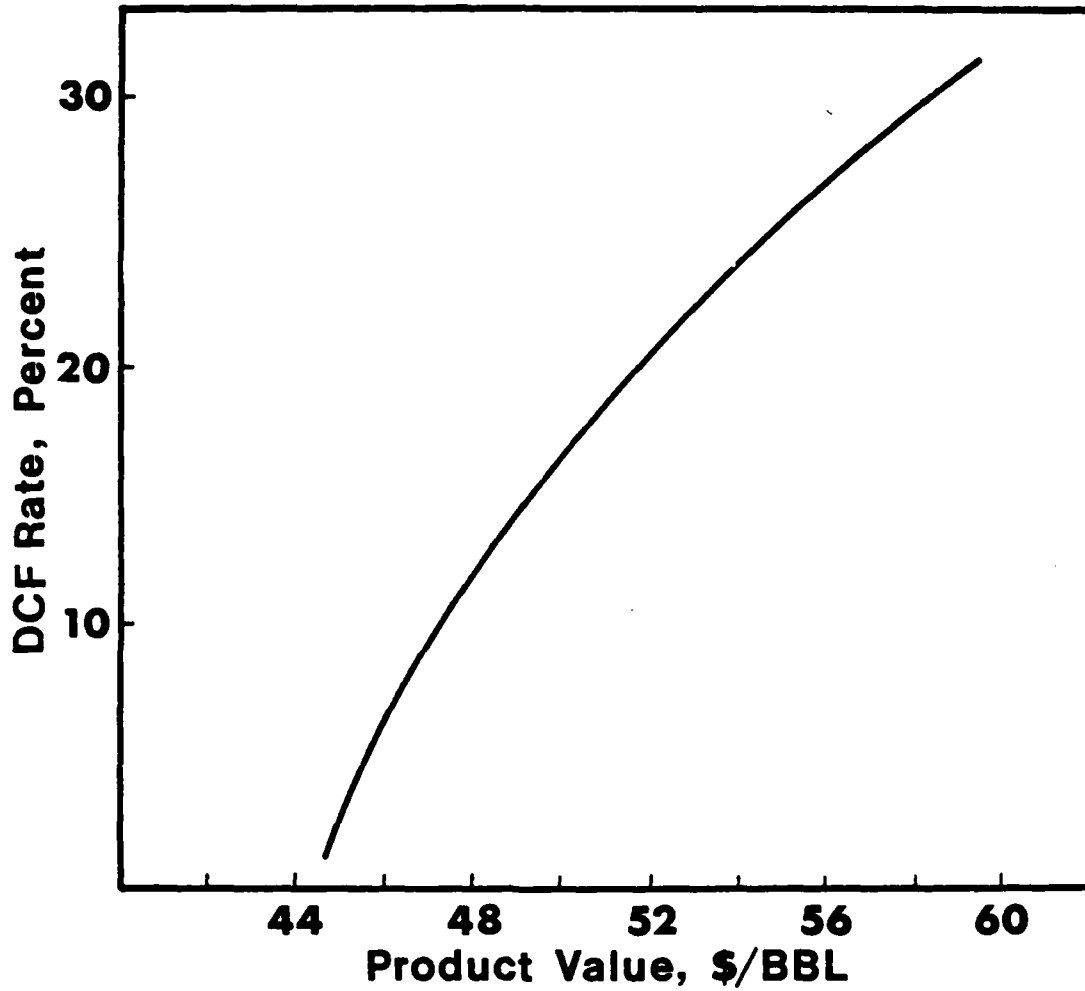


Figure 8. Base Case Product Values As A Function Of DCF Rate - Occidental Shale Oil

required quality. This is a natural result of the optimization requirement, in particular, defined to be least cost of combined fuels and equivalent value of liquid products. As a result, the model in general tends to maximize (1) residual fuel (up to a 10 percent maximum constraint; (2) diesel fuel, since it represents modest hydrogen input and a least total processing requirement; and (3) gasoline, since this stream is the lowest hydrogen content distillate fuel produced. In particular, turbine fuels commonly are provided at or near the maximum (25 volume percent) aromatics level. In some cases (particularly for JP-8), this may result in hydrogen contents less than the specification 13.6 percent. Production of fuels with properties more similar to present DOD fuel experience may be expected to require higher cost levels.

SENSITIVITIES: (1) LEVEL OF TURBINE FUEL PRODUCTION

A primary interest to national defense efforts is the level of turbine fuel production available under unconstrained cost situations, with an estimate of the incremental cost of production showing required increases over base costs for these cases. The model and basic data noted above were operated at three levels of total turbine fuel production. These levels were generated by varying turbine fuel prices relative to other liquid fuel prices.

Figure 9 presents results from this analysis. The production shown is the combined JP-4 and JP-8 plant yield. Somewhat surprisingly, incremental cost of this additional production is relatively low - roughly 5 cents per gallon for about 50 thousand BPD of incremental fuel. This cost increment is primarily due to (1) the additional hydrogen requirement for this turbine fuel, and (2) slightly decreasing total plant yields as turbine fuel production is increased.

The highest yield point shown is not, of necessity, the maximum turbine fuel available, but represents the highest yield evaluated. Slightly higher total yields are probably available, but at exponentially increasing total cost.

SENSITIVITIES: (2) AROMATICS CONTENT OF TURBINE FUELS

The aromatics specification on turbine fuel could have a major impact on total supply as sources of these fuels become poorer in quality. In particular, since the base case evaluation blended to essentially maximum aromatics levels in these fuels, the question arose as to the cost savings potentially available by increasing the aromatic specification. Further, present conventional fuels are generally much lower in aromatic content than allowed; (9) the cost of constraining production from this plant to these conventional levels was also determined to be of interest.

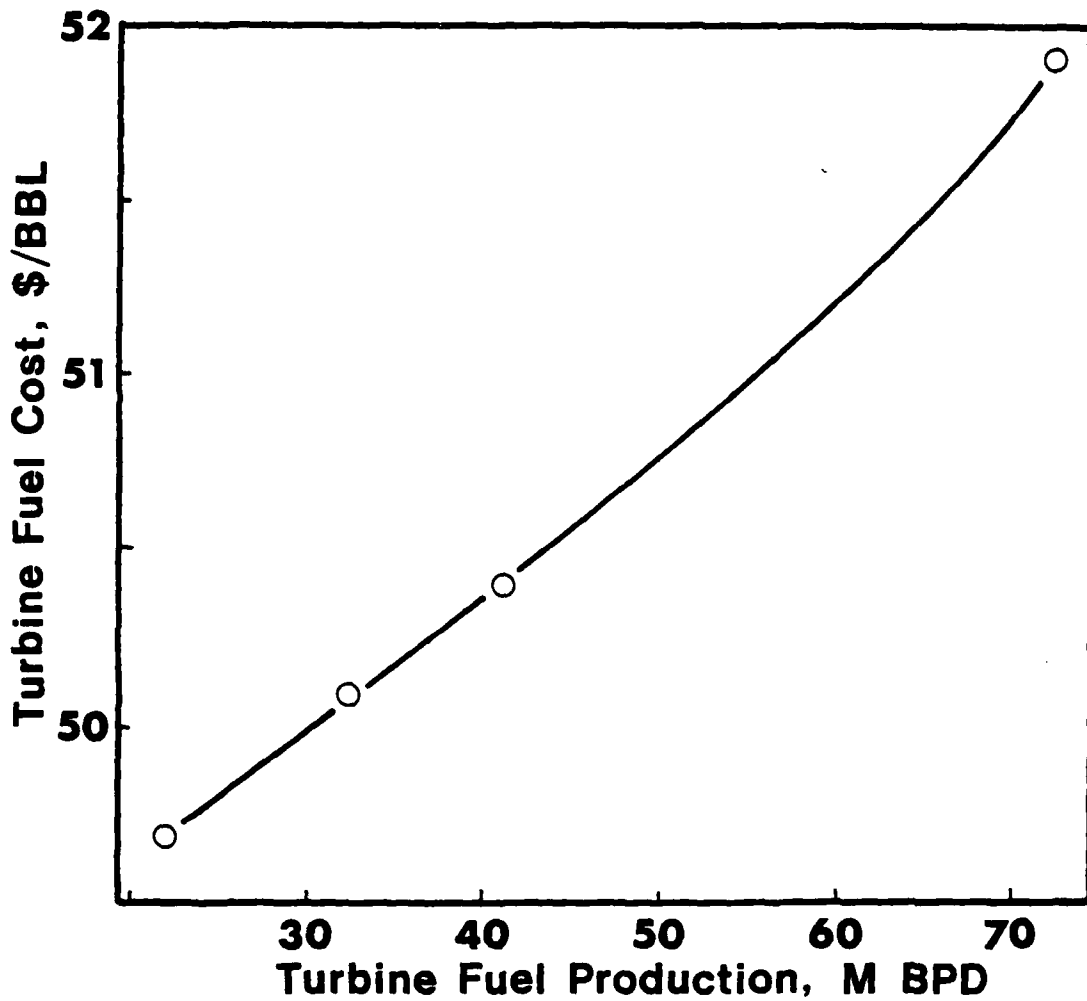


Figure 9. Incremental Production Cost Of Additional Turbine Fuel

As a result, cases were evaluated at 15 percent and 35 percent aromatic specification levels. Results for both cases were surprising, as shown in Table 23.

The 15 percent constraint resulted in zero turbine fuel production from the plant. The model apparently determined that, on a cost basis, optimum performance resulted from higher production of gasoline and diesel fuels rather than supplying incremental hydrogen required for higher turbine fuel yields. To ensure that this was a valid solution (and conclusion), a high value was placed on JP-4 and the model again processed with a 15 percent aromatics limit. Fifteen percent aromatics JP-4 was produced in accordance with all required specifications, indicating that the original solution was, in fact, valid.

Evaluation of the 35 percent limit was surprising in that additional turbine fuel was not produced; in fact, slightly less production was encountered. The key change, however, was a slight reduction in hydrogen consumption and, therefore, total cost. Additional turbine fuel was not produced because, due to cost/processing considerations, the main target fuels are gasoline and diesel fuel. The model only produces turbine fuels from excess components and/or other components resulting in essentially a maximum total distillate fuel production. If additional processing cost could be recovered in the turbine fuel price, additional volumes could be produced.

TABLE 23

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

SENSITIVITIES: (3) FUEL GAS SALES ALLOWED

Individual analysis of the process indicated that a major potential cost reduction might accrue from allowing external refinery fuel gas sales. This results directly from the experimental findings that gas yields rapidly rise in the cracking unit as hydrotreating severity in the crude shale hydro-treater is reduced. This phenomenon results in the opportunity to reduce capital investment at the expense of higher gas (and, therefore, lower liquid) yields. This sales provision was not provided in the base case, since refinery fuel gas is emphatically not pipeline quality, and actual sales potential is relatively low except to a nearby captive industrial user.

When the model was allowed to produce and sell fuel gas (at FOE equivalent), the results shown in Table 24 were found. Significantly lower capital investment, at higher feedstock costs and by-product credits, were attained. Total product cost was reduced by about 3 cents per gallon (\$1.40 per barrel) when compared to the base case.

Cautions with regard to this result should be re-emphasized: (1) refinery fuel gas is not a normal, commercial product, and (2) selection of data to be used in the evaluation and model development, as discussed in Section II, probably bias this analysis. The actual magnitude of this difference is, therefore, of high uncertainty; the demonstrated direction and opportunity for cost reduction is, however, quite valid.

TABLE 24

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

ITEM	WITH	
	GAS SALES	BASE CASE
CAPITAL INVESTMENT, MM\$	558	596
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
	<u>48.00</u>	<u>49.40</u>

SENSITIVITIES: (4) ALKYLATION/POLYMERIZATION

As expected in our original contract proposal, under most conditions (and at least under the base case optimization) relatively large quantities of gases, particularly olefins, are available in excess over that required for fuel gas or blending purposes. Sales of these materials as by-products is risky at times due to highly uncertain markets, and negatively impacts economic estimates due to these uncertainties. There is obvious potential for addition of capacity to produce high value distillate liquids from these materials.

The model was allowed the option to use either C₃/C₄ alkylation or C₃ polymerization modules or both of them in the modeling system library to build additional capacity as determined by cost potential (at 15 percent DCF rate and all previous economic assumptions). The model determined that addition of both modules was of economic advantage, with the results shown in Tables 25 and 26. The key result is an equivalent reduction in product cost of about \$0.50 per barrel (1 cent per gallon).

SENSITIVITIES: (5) FEEDSTOCK COST

The final dependency determined to be of key interest at this level of analysis was the impact of using actual market values for products, especially in terms of calculating an equivalent feedstock value. In particular, providing a more appropriate value differential between residual fuel and gasoline (or other high-value distillates) was of interest.

TABLE 25

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

TABLE 26

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

<u>ITEM</u>	<u>COST CONTRIBUTION, \$/BBL</u>	
	<u>WITH ADDED CAPACITY</u>	<u>BASE CASE</u>
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

Product postings or equivalents from Platt's Oilgram were input to the model as shown in Table 27. The feedstock cost was then allowed to take on the required amount to produce a 15 percent DCF rate. The product spectrum shown in Table 27 resulted in the cost data shown in Figure 10. At 15 percent DCF, the feedstock equivalent value was about \$31 per barrel for Occidental oil.

A somewhat surprising observation from this analysis is that total fuel production, except for gasoline and residual fuel, did not change a major amount. The major difference is higher gasoline production at the expense of residual oil due to the large value differential.

There are three major limitations to the analysis. First, the analysis and value calculation is plant and situation specific, i.e., only for new construction using this technology. Second, the model recycled residual fuel to extinction, probably causing some discrepancies from normally attainable results. And third, previous cautions concerning gas production are particularly applicable here due to the extinction (high levels) recycle encountered.

SUMMARY - OCCIDENTAL ANALYSIS

Overall, the Occidental shale oil analysis was relatively straightforward with stable solutions. Large variations in constraints allowed during these (and other) sensitivity

TABLE 27

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	-----	<u>13,117</u>
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	-----	<u>90,675</u>

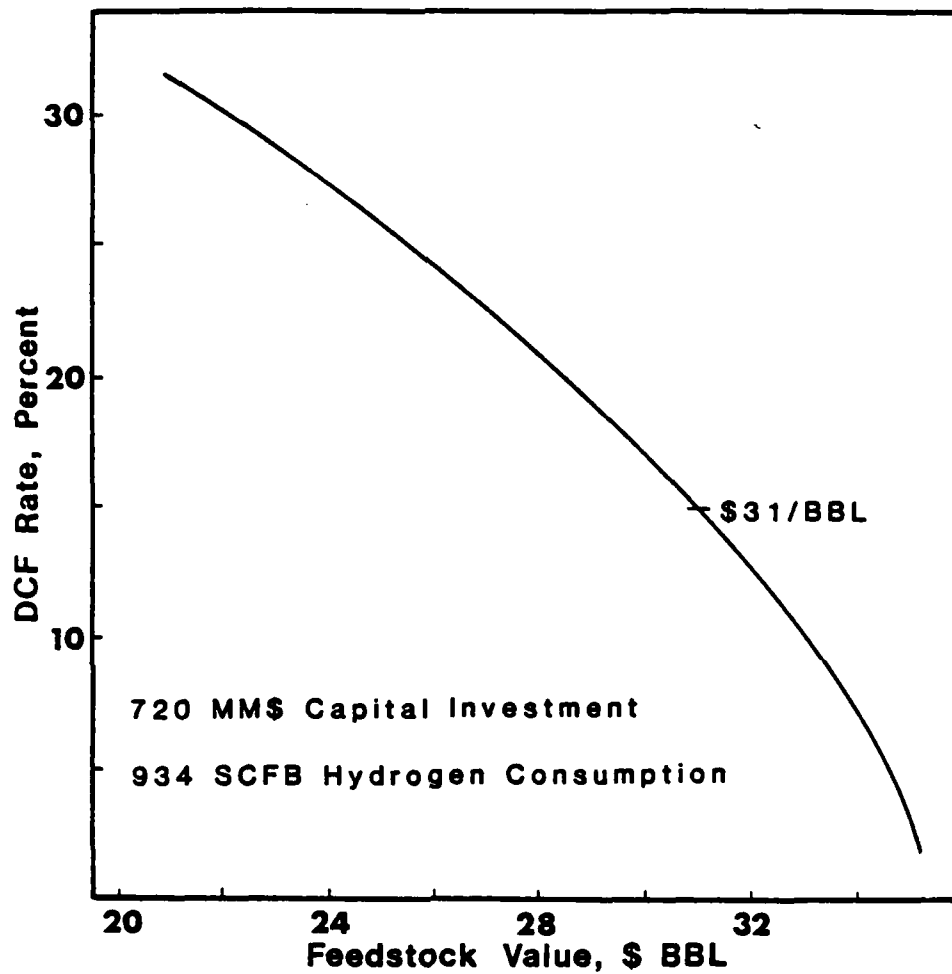


Figure 10. Value Of Occidental Oil At Present Market Prices

calculations demonstrated that the location (in terms of operating conditions) of the optimums defined were very similar for essentially all operations.

Product slates obtained under essentially comparable conditions in Phase IV were remarkably similar to those estimated in Phases I and II, particularly in terms of liquid fuel production levels.

During development of this model, and as progress was made in terms of contract completion, one key factor became obvious from process optimization. The initial Phase I model tests indicated that the cost optimum occurred at very low crude shale hydrotreater severity as originally projected during process development. During Phase II, selection of Phase III conditions by process modeling indicated that slightly higher severities (corresponding to Phase III hydrotreater operations) were optimum. This was followed by our final optimization for this report which indicated further (although still moderate) severity increases were dictated.

This optimum/severity level shift is probably due to three primary factors. Obviously, inclusion of better and more detailed data, particularly for aging curves, resulted in better estimates. The inclusion of the aging requirements, plus more severe requirements than anticipated for the guardcase, reformer, and aromatic saturation (from Phase III results),

provided a driving force towards higher severity front-end operation.

Second, and possibly of key importance, are the increasing costs assigned to crude shale oil in each analysis. Initial optimizations at \$16/barrel were followed by valuations of \$30/barrel (for definition of Phase III conditions) and \$40/barrel (for this report). These cost changes are of tremendous magnitude, particularly considering that the Phase I (\$16/barrel) shale cost represented 73 percent of final product cost, while the base case estimate for this report (\$40/barrel) resulted in 88 percent of the total cost being attributable to feedstock at essentially the same production level of distillate fuels. This rapid expansion in feedstock cost is a direct, high magnitude driving force towards maximization of production (i.e., higher severity crude shale hydrotreater operation). On a relative basis, capital has become less expensive and there is more incentive to invest to obtain additional barrels of product.

Finally, the data matrix of operating conditions used in these evaluations changed slightly during these analyses. Use of selected FCC data from a very non-linear region (as in the original and Phase IV base case evaluations) can make some difference in the model solution. However, this difference is probably slight, as noted previously in discussing an original, versus the final, base case result.

PARAHO SHALE OIL

Only experimental data from Phase II was used for the Paraho shale oil analysis. Where appropriate, Phase III Occidental scale-up data were also used to improve the quality of results. Overall, however, these results should be interpreted with the caveat that they represent a higher degree of uncertainty than the foregoing Occidental analysis.

BASE CASE

The base case for Paraho oil was input in a manner analogous to that performed for the Occidental oil. Complete extreme-point matrices were developed from Phase II data. Optimization results are shown in Tables 28 and 29 in comparison to the Occidental products. Capital investment requirements were significantly higher than for the Occidental material, although essentially equivalent yields were obtained. This resulted in a product differential versus the Occidental case of about \$2.80 per barrel as shown in Table 30 and Figure 11.

The optimum defined for the Paraho material was at about 1600 SCFB total hydrogen input. Further, the crude hydrotreater case selected was the highest severity operation input to the model. This indicates that further extensions of severity could reduce resulting costs reported herein.

TABLE 28
BASE CASE RESULTS COMPARISON

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

TABLE 29
BASE PRODUCT SLATE

<u>PRODUCT</u>	<u>OXY</u>	<u>PARAHO</u>
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
	<u>102,163</u>	<u>93,384</u>

TABLE 30
OVERALL PRODUCT COST SHEET

ITEM	COST CONTRIBUTION \$/BBL	
	OXY	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

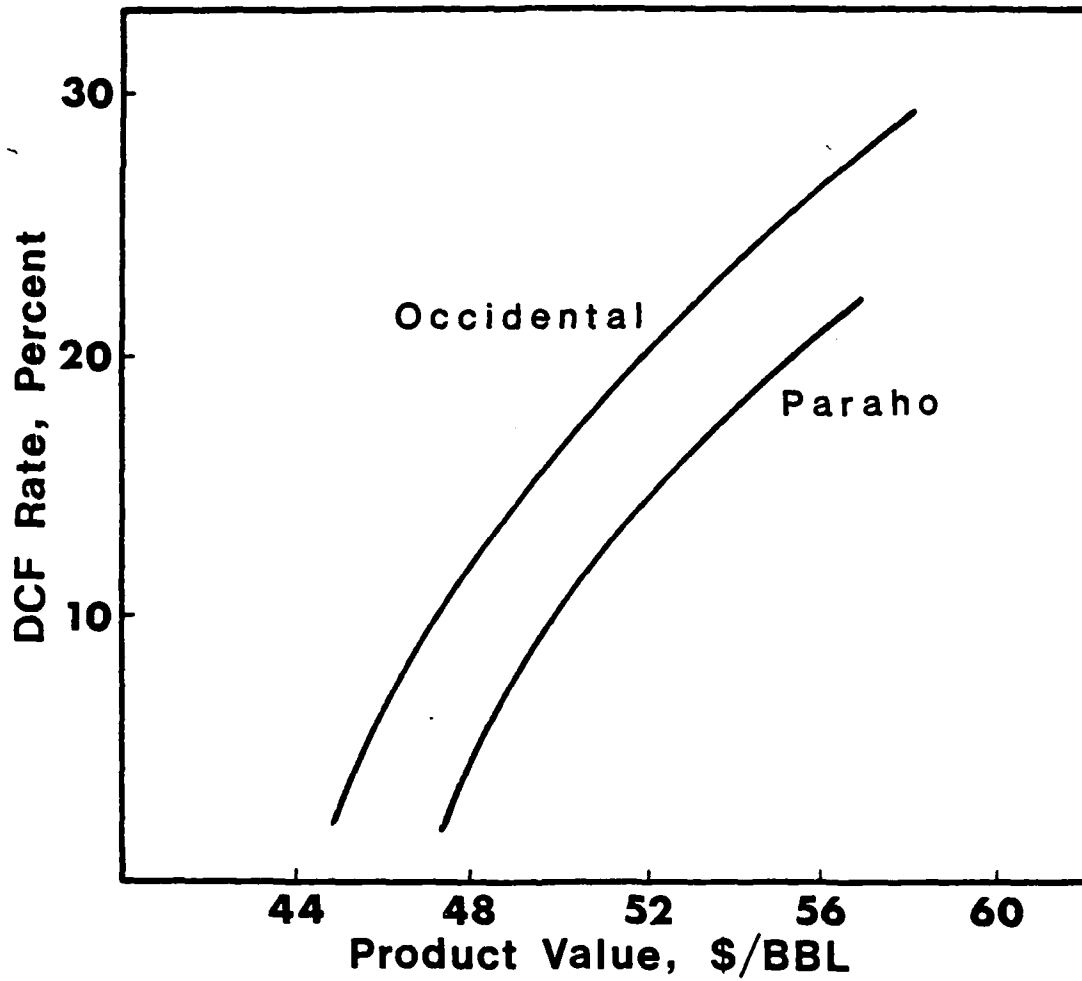


Figure 11. Product Values As A Function Of DCF Rate

SENSITIVITY: INCREMENTAL TURBINE FUEL PRODUCTION

An incremental turbine fuel production case was provided for the Paraho oil on a basis similar to that shown earlier for the Occidental material. Figure 12 demonstrates these results, showing essentially parallel curves for the two oils. About 80 thousand BPD of production was obtained from the Paraho material.

SUMMARY - PARAHO SHALE OIL

Although the Paraho analysis represents a higher level of uncertainty than the Occidental results, very similar cost and yield responses were obtained. Operations on the Paraho oil, however, are at higher operating severity and resulting product costs at equivalent feedstock costs. Optimum operation for the Paraho material may be at higher severity than provided in this analysis, although there are strong indications that a different hydrotreater catalyst choice would be of a major contribution to improved performance.

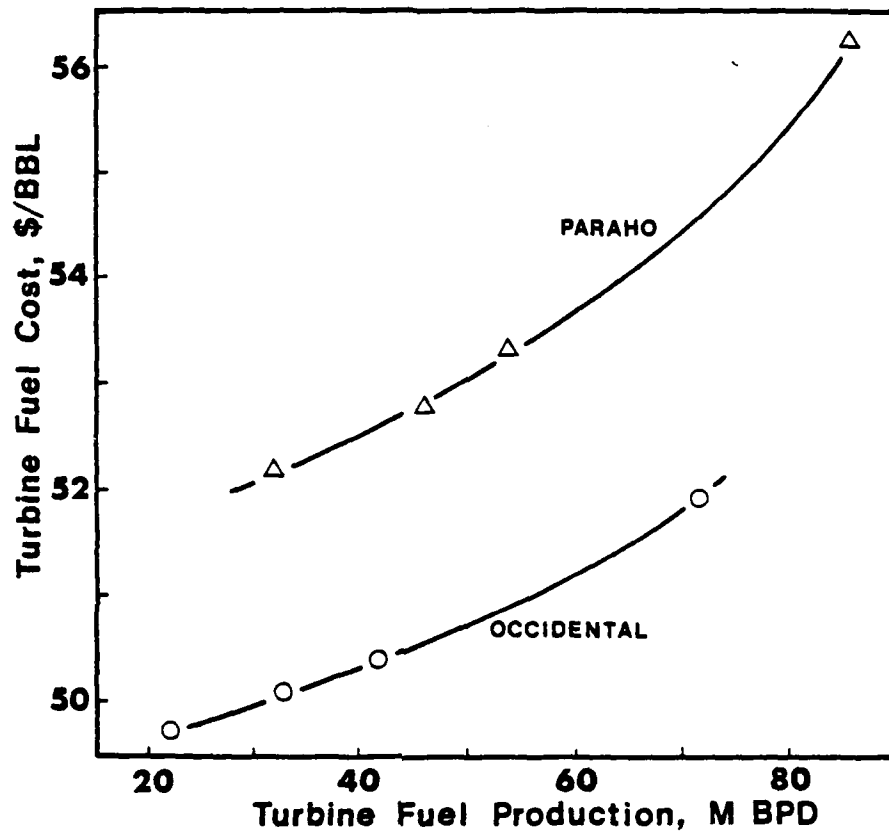


Figure 12. Incremental Turbine Fuel Cost

SECTION V
CONCLUSIONS AND QUESTIONS

Essentially all Phase IV objectives have been completed by this report. Good agreement with previous reports and conclusions has been demonstrated, with the following conclusions of major importance:

- 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 occurs at relatively low hydrogen consumption (about 900 SCFB).
- Optimum operation for the Occidental oil is relatively flat in the region of 900 to 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.
- Total volumes of prime military fuels produced exceed 90 volume percent of crude shale oil.

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REFINING OF MILITARY JET FUELS FROM SHALE OIL PART IV
PROCESS COMPUTER MODELING STUDIES(U) ASHLAND PETROLEUM
CO KY H F MOORE ET AL. AUG 82 AFWAL-TR-81-2056-PT-4
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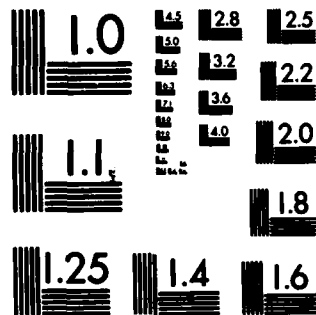
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- On a comparable basis, products from the Occidental oil are \$2 to 3/barrel less expensive than the Paraho oil.
- Allowing sales of fuel gas can reduce product costs by \$1/barrel or more.
- Turbine fuel yields of 85 volume percent or more result in incremental costs of up to 10¢/gallon.
- Modification of turbine fuel aromatic specification to 15 volume percent reduces plant production of turbine fuel to zero at equal product prices, 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 percent.
- Evaluation of the process at today's market values results in a calculated value of \$31/barrel for Occidental oil.
- Neither addition of alky/poly capacity nor use of present market value for products significantly impacts location of the defined optimum.

Obviously, however, in any major research program, questions are raised during the work which are not addressed due to unforeseen constraints. For this program, major questions remaining at the conclusion of this contract include:

- CSHT performance with improved guardbeds
- Emissions from the FCC unit
- Actual FCC coke and gas yields
- Evaluation of COHT addition
- Response of extract to partial oxidation
- Guardcase, reformer long term aging

This report completes all program efforts funded under this contract.

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