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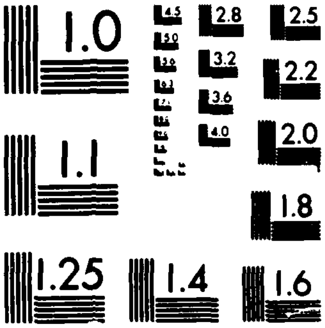
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TURBINE FUELS FROM TAR SANDS BITUMEN AND HEAVY OIL

VOL I - Phase III Pilot Plant Testing, Final Design, and Economics

A. F. Talbot, T. C. Carson, L. G. Magill, and J. R. Swesey

Applied Research and Development
Sun Refining and Marketing Company
P.O. Box 1135
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August 1987

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Pilot Plant-scale demonstration of an upgrading/refining scheme to convert bitumen or heavy crude oil into high yields of specification quality aviation turbine fuel was performed. An atmospheric residue from San Ardo (California) crude was converted under hydrovisbreaking conditions to synthetic crude for further refining. Naphtha cuts from the straight run and synthetic crude were combined and catalytically hydrotreated. The respective distillate cuts were also combined, catalytically hydrotreated, then hydrocracked. Products from these operations were combined to produce two prototype specification fuels (JP-4 and JP-8) as well as two heavier, variable quality fuels.

An engineering design (Volume II) was developed for a 50,000 BPSD grass-roots refinery, from the pilot plant operations. Capital investment and operating costs were estimated, and fuel manufacturing costs projected. Conclusions and recommendations for further work are included.

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SUMMARY

In Phases I and II of this program, it was established that domestic tar sands bitumens and heavy crude oils represent a significant resource potential with respect to this country's need for high quality military transportation fuels. A process scheme capable of very high yields of aviation turbine fuel was identified and demonstrated on laboratory scale with a variety of low grade feeds.

In this concluding Phase III work, short duration, continuous mode pilot plant tests were performed, converting San Ardo crude oil into high yields of aviation turbine fuel. The same process sequence as was identified earlier was employed, viz., upgrading residuum by hydrovisbreaking, plus naphtha hydrotreating and distillate hydrocracking. Major process parameters affecting these primary conversion steps were explored briefly, prior to carrying out short production runs at design conditions. Product from these production runs was combined to permit preparation of prototype turbine fuel samples. Testing of the prototype samples showed them to be of acceptable quality, when compared with specification requirements for either JP-4 or JP-8. Several variable quality turbine fuels, similar to high quality diesel fuels, were also produced.

Pilot plant results became the basis for the design (Volume II) of a 50,000 barrel per stream day grass-roots refinery for converting San Ardo crude into JP-4 type fuel. A JP-4 yield of 88.6 volume percent was projected from the process simulations, while refinery overall thermal efficiency was estimated at 84 percent. Net production of residual fuel for sale was less than 2 percent.

Total fixed capital required was $1.126 billion for the refinery, which reflects the high degree of hydroprocessing necessary to achieve this high yield of turbine fuel. Based on the economic parameters established for the analysis, fuel cost under base case assumptions was projected to be approximately $52 per barrel.

FOREWORD

This report presents the results of a study performed by the Applied Research and Development (ARD) Department of the Sun Refining and Marketing Company, a subsidiary of Sun Company. The program was supported by the Aero Propulsion Laboratory of the U.S. Air Force Wright Aeronautical Laboratories under Contract No. F33615-83-C-2352, awarded 8 July 1983. It addresses the technology of converting tar sands bitumens, heavy petroleum crude oils, or low quality refinery intermediate streams into aviation turbine fuels for military use.

The work was performed at the Sun Company ARD laboratories in Marcus Hook, Pennsylvania during the period 1 June 1985 through 31 March 1987. The Air Force Project Engineer during this period was Mr. William E. Harrison, III; AFWAL/POSF. The ARD Program Manager was Mr. Alfred F. Talbot. This report was released by the author in March 1987.

The Program Manager acknowledges the valued contributions of co-workers V. Elanchenny, L. G. Magill, R. S. Matyas, V. K. Patel, D. R. Scheibe and J. R. Swesey in the execution of this program. The dedicated efforts of C. J. Bennett and M. T. Reed in preparing the manuscript for this report and in maintaining the timely flow of numerous periodic reports are also acknowledged, and greatly appreciated.

Provision of vital personnel and capital resources by ARD and Sun Refining and Marketing Company managements enabled construction of the new heavy oil pilot unit in which the continuous hydrovisbreaking runs were performed. The Facilities and Design Section of ARD, under Mr. A. T. Finlayson, are commended for the fabrication, assembly, and start-up of the new unit under a very demanding timetable.

The Program Manager acknowledges the continued support of Mr. William E. Harrison throughout all four phases of this program. His valued guidance in addressing the various non-technical as well as technical challenges associated with the project was very helpful.

This final report is the culmination of a four-phase assessment of the potential for producing aviation turbine fuels from low-grade domestic resources. In Phase I, a series of case studies identified a preferred process route, from among several examined, for accomplishing this conversion. In Phase II, the selected process route was demonstrated on a bench-scale, and representative fuels produced. In Phase IV, several thousand gallons batches of test fuels of controlled composition were produced from intermediates such as catalytic cycle oil and pyrolysis oil.

In this Phase III segment, the process sequence which emerged from the Phase I and Phase II work was demonstrated in pilot plant equipment in order to generate a preliminary engineering design of a commercial refinery, to confirm earlier projections of manufacturing costs, and to provide samples for comprehensive testing.

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SECTION I

INTRODUCTION

The United States continues to consume more crude oil than it produces or discovers. The trend, uninterrupted for at least the last decade, is not expected to reverse while crude oil prices remain depressed. As a result, the nation's vulnerability to supply disruptions by socio-political events in less stable parts of the world continually increases. This program, initiated by the Air Force Wright Aeronautical Laboratories, responds to that exposure by assessing the potential of converting domestically produced low-grade feedstocks into high quality aviation turbine fuels.

This assessment addresses both the processing technology capable of converting these low quality feeds and the quality of the fuels produced therefrom. In addition, it provides information on the costs of accomplishing this conversion.

Overall program objectives include the following:

- to identify a preferred process scheme for producing JP-4, JP-8, or variable quality fuels from bitumens, heavy crudes, or refinery intermediates.
- to demonstrate its performance in laboratory and pilot plant scale operations, providing appropriately sized prototype fuel samples.
- to evaluate the economics of the processing scheme selected.
- to determine the relationships between fuel quality variations, economic parameters, and fuel costs.

The program consists of four distinct phases. The first three were established at the time of contract award --July 1983. The fourth phase was added via contract modification issued in November 1985. The program elements consist of:

Phase I - Preliminary process analysis included an evaluation of domestic tar sands and heavy oil resources and a preliminary screening of selected processing schemes for converting these resources into specification quality transportation fuels. The findings: 1) the resources have significant potential, 2) the resources present a significant processing challenge, 3) high turbine fuel yields are possible when employing a two-step approach consisting of upgrading the residuum feed to a syncrude plus hydrorefining the syncrude into finished fuels, and 4) assorted case studies favored upgrading by hydrovisbreaking, combined with naphtha hydrotreating and distillate hydrocracking (Reference 1). Figure 1 illustrates the process concept proposed. A recommendation to apply this concept in Phase II, utilizing high conversion hydrovisbreaking for residuum upgrading, was accepted.

Phase II - Laboratory sample production included laboratory or bench-scale demonstration of the recommended process sequence, as applied to four different low-quality feedstocks. Results included: 1) principal operating parameters for each of the important conversion steps were identified, 2) the effect of feedstock origin on process operating parameters were defined, 3) feedstock source had a very minor effect on the physical or chemical characteristics of prototype fuel samples, 4) properties of samples representing JP-4 type or JP-8 type turbine fuels compared favorably with specification limits(Reference 2). The recommendation to proceed to Phase III for more quantitative studies, including detailed engineering design of a commercial plant, was accepted.

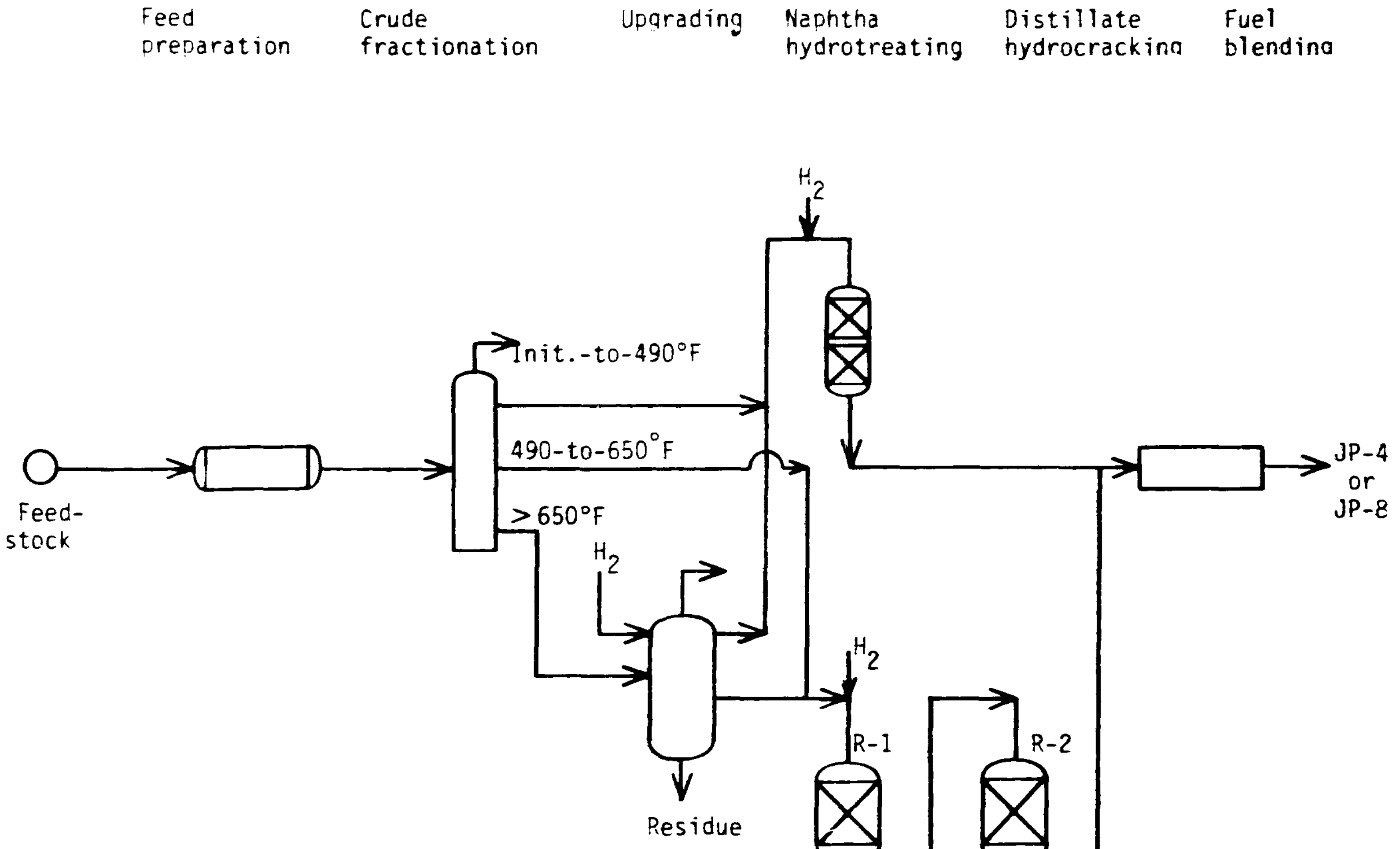

FIGURE 1 PROCESS CONCEPT

Phase III - Pilot plant testing, final design and economics is the subject of this report. It included confirmation of the laboratory-estimated process operating parameters for a single feedstock in continuous mode pilot plant facilities. Other objectives were selection of design bases for detailed equipment cost estimates, economic analysis of fuel manufacturing cost estimates, and preparation of pilot plant sized samples of specification quality and variable quality turbine fuels.

Phase IV - Production of test fuels from heavy oil feedstocks entailed production of larger quantities (e.g., 2,000 gallons) of test fuels from refinery or petrochemical plant intermediates such as catalytic light cycle oil and light pyrolysis fuel oil by two-stage hydrogenation. Physical and chemical characteristics of the test fuels produced were within the specified ranges (Reference 3).

This report presents the results of the Phase III work, performed at Sun Co.'s Applied Research and Development (ARD) Department laboratories in Marcus Hook, PA. For project management purposes, the Phase III program was subdivided into the following elements:

Task	Activity
1	Feedstock preparation
2	Preliminary engineering
3	Hydrovisbreaking studies
4	Hydrotreating studies
5	Hydrocracking studies
6	Fuel sample preparation/testing
7	Design basis
8	Engineering design package
9	Fuel cost calculations
10	Phase III report

Results of these activities are summarized in the report sections which follow.

SECTION II

FEEDSTOCK PREPARATION

1. Introduction

The Air Force selected San Ardo crude oil for these comprehensive Phase III studies. It is a 12.8 °API gravity heavy crude produced from the onshore San Ardo field in the southern Monterey County coastal region of California. Physical and chemical properties of the whole crude, as determined and reported in the Phase II work, are listed in Table 1. Typical of heavy crudes, the amount of non-distillable fraction is relatively high (~40 volume percent), and ambient temperature flowability is low. Sulfur content is moderately high at 1.9 weight percent. The nitrogen content of 1.3 weight percent is exceptionally high and likely to require relatively severe processing. Metals content is tolerable.

The reported salt content of 34 lb/1,000 barrels necessitated desalting of the crude before further processing. Following desalting, the crude was fractionated into several overhead fractions plus a residuum, as described in the following sections.

2. Crude Desalting

Processing of the 1,100 gallon inventory of San Ardo crude is illustrated in Figure 2. The desalting operation consisted of two steps: water-washing of the solvent-diluted crude at elevated temperature, and subsequent stripping of the solvent from the crude. The desalted crude was distilled into the desired straight run fractions, also in two steps.

TABLE 1

PROPERTIES OF SAN ARDO CRUDE OIL

Physical properties

Gravity, °API	12.8
Sp. gravity, 60/60°F	0.9806
Distillation, °F (by ASTM D1160)	
IBP	183
5%	401
10%	494
20%	589
30%	675
40%	769
50%	880
60%	968
Flash point, °F	194
Pour point, °F	35
Salt, lb/1000 bbl.	34
Carbon residue, wt.%	8.7
Viscosity, cSt	
77°F	12,700
100°F	3,294

Chemical characteristics, by weight

Carbon, %	81.62
Hydrogen, %	10.51
Oxygen, %	1.82
Sulfur, %	1.89
Nitrogen, total, %	1.32
basic, %	0.23
Ash, %	0.12
Trace metals, ppm(1)	
Nickel	41, 78
Vanadium	37, 96
Iron	37, 42
Copper	0.3, 0.9
Hydrocarbon type, %	
Saturates	24.0
Aromatics	32.7
Polar compounds	27.2
Asphaltenes	16.1

(1) Two values shown for repeat tests.

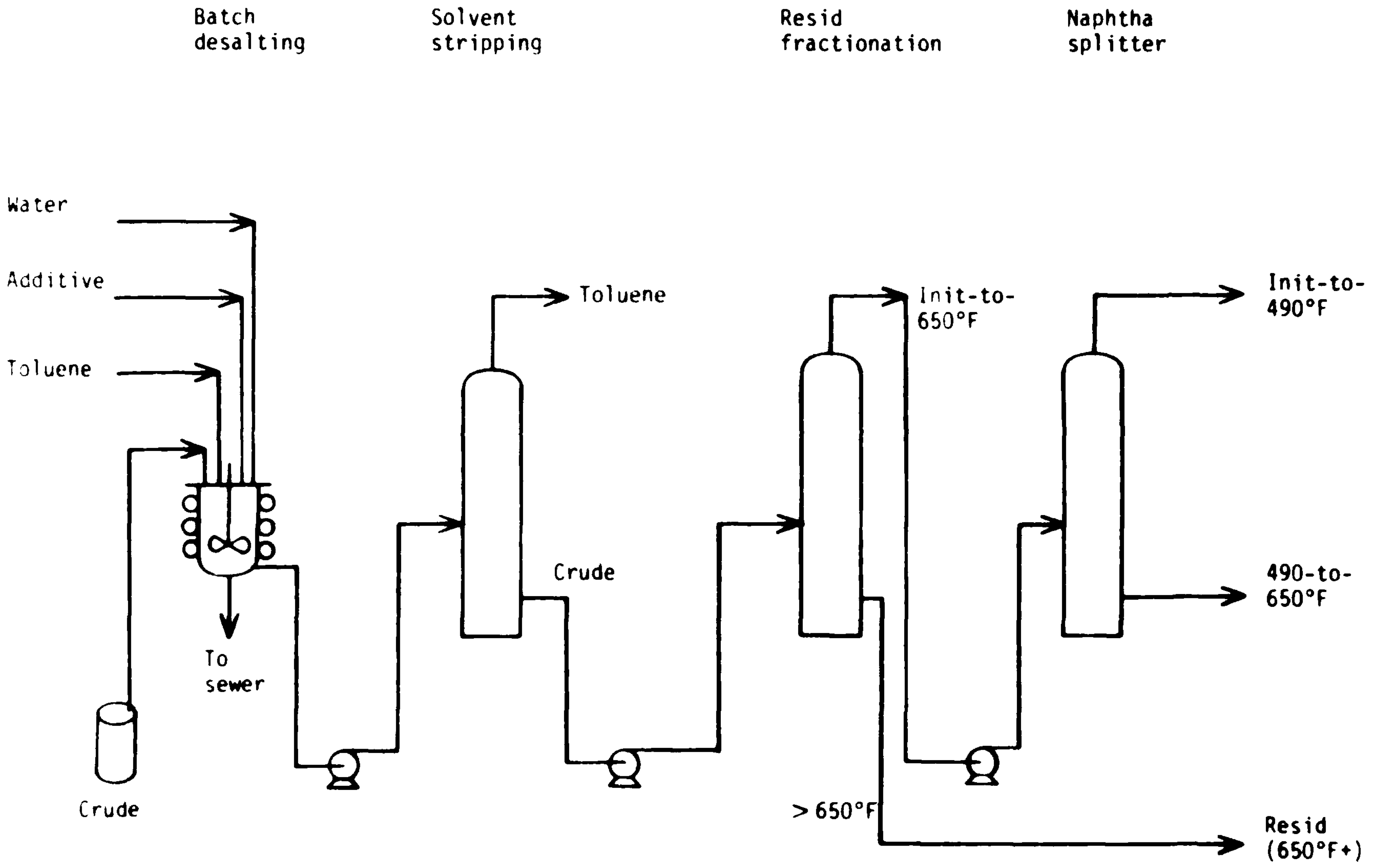

FIGURE 2 FEEDSTOCK PREPARATION

Crude desalting was performed batchwise in ARD's 500-gallon steam-jacketed glass-lined reactor. Operating conditions were similar to those employed during Phase II, as follows:

Temperature, °F	180
Solvent	Toluene
Dilution, vol.% crude	25
Water wash, vol.% crude	40
Desalting aid, ppmw crude	43

Desalting was accomplished in five charges to the reactor. After the dirty water layer was drained to the refinery sewer, the crude/solvent upper layer was removed and stored in drums until all five batches were processed.

Toluene stripping of the crude was performed in ARD's continuous stripping still ("S" still, with 8 inch column diameter and 6 theoretical trays) at the following conditions:

Pressure	Atmospheric
Charge rate, gal/hr	6 to 7-1/2
Reflux ratio	3:1
Vapor temperature, °F	215-225
Column feed, °F	285-325
Column bottom, °F	305-320
Reboiler, °F	435-450
Overhead/bottoms split, % by weight	16:84

Periodic gas chromatographic analyses of the overhead fractions indicated toluene content exceeding 99 weight percent.

3. Crude Fractionation

The desalted, solvent-stripped crude was distilled in two steps into the following fractions:

Fraction	Nominal distillation range,°F
1	Initial to 490
2	490 to 650
3	>650

As also illustrated in Figure 2, the separation required two passes through the stills because there are no facilities for taking a sidestream cut during fractionation.

In the first pass, the desalted whole crude was separated into a nominal initial-to-650°F cut and a >650°F residuum in ARD's continuous vacuum still ("V" still, with 6 inch column diameter and 10 theoretical trays) at the following conditions:

Pressure, mm Hg	25-35
Charge rate, gal/hr	5-1/2 to 7-1/2
Reflux ratio	0.5:1
Vapor temperature,°F	245-260
Column feed, °F	320-340
Column bottom, °F	350-435
Overhead/bottoms split, % by weight	18:82

Distillate yield was 20 volume percent. At the conclusion, both the overhead and bottoms fractions were composited by charging them (individually, of course) to the jacketed 500-gallon reactor for several hours of agitation. The composites were then drummed off to await further processing.

Physical and chemical characteristics of the two fractions are summarized in Table 2. Figure 3 illustrates the distillation (by ASTM D-1160) ranges for the two fractions, and indicates a relatively clean separation, with very little overlap at the target 650°F cut point. Sulfur distributed between the two fractions, whereas nitrogen concentrated in the bottoms.

The residuum was used in subsequent upgrading studies, described in Section III. The overhead straight run distillate fraction was further distilled into light and middle distillate cuts, which were subsequently combined with the respective fractions from the hydrovisbreaking operations, for hydrorefining.

The straight run <650°F fraction was distilled in ARD's continuous high resolution still ("HR" still, with 6 inch column diameter and 60 theoretical trays) at typical operating conditions of:

Pressure	Atmospheric
Charge rate, gal/hr	3-1/2
Reflux ratio	0.5:1
Vapor temperature,°F	470
Column feed,°F	85
Reboiler, °F	575
Overhead/bottoms split, % by weight	24:76

Naphtha overhead yield was 24.8 volume percent. Table 3 summarizes physical and chemical characteristics of the two fractions. Elemental analyses compare as expected; i.e., the light fraction contains more hydrogen, less of the heteroatoms. The efficiency of the HR still is apparent from the distillation curves in Figure 4; there is essentially no overlap between the two fractions.

TABLE 2

SAN ARDO DISTILLATE AND ATMOSPHERIC RESIDUUM

Fraction	<650°F Distillate	>650°F Residuum
Sample code	DRS 7016	DRS 7017
Yield, volume % crude	20.0	80.0
Physical properties		
Gravity, °API	26.2	8.5
Sp. gravity, 60/60°F	0.8970	1.0107
Distillation, °F (by ASTM D1160)		
IBP	148	552
5%	294	684
10%	320	735
20%	350	804
30%	511	860
40%	525	938
50%	547	992 (cracking)
60%	566	
70%	584	
80%	612	
90%	637	
95%	651	
FBP	-	
Viscosity, cSt		
160°F	-	7,761
210°F	-	841
Chemical characteristics		
Elemental analysis, wt.%		
Carbon	86.27	86.10
Hydrogen	12.05	10.93
Sulfur	0.929	2.36
Nitrogen	0.0588	1.204
Aromatics, wt.% by J-7 (1)	45.7	-

(1) In-house procedure similar to ASTM D2007

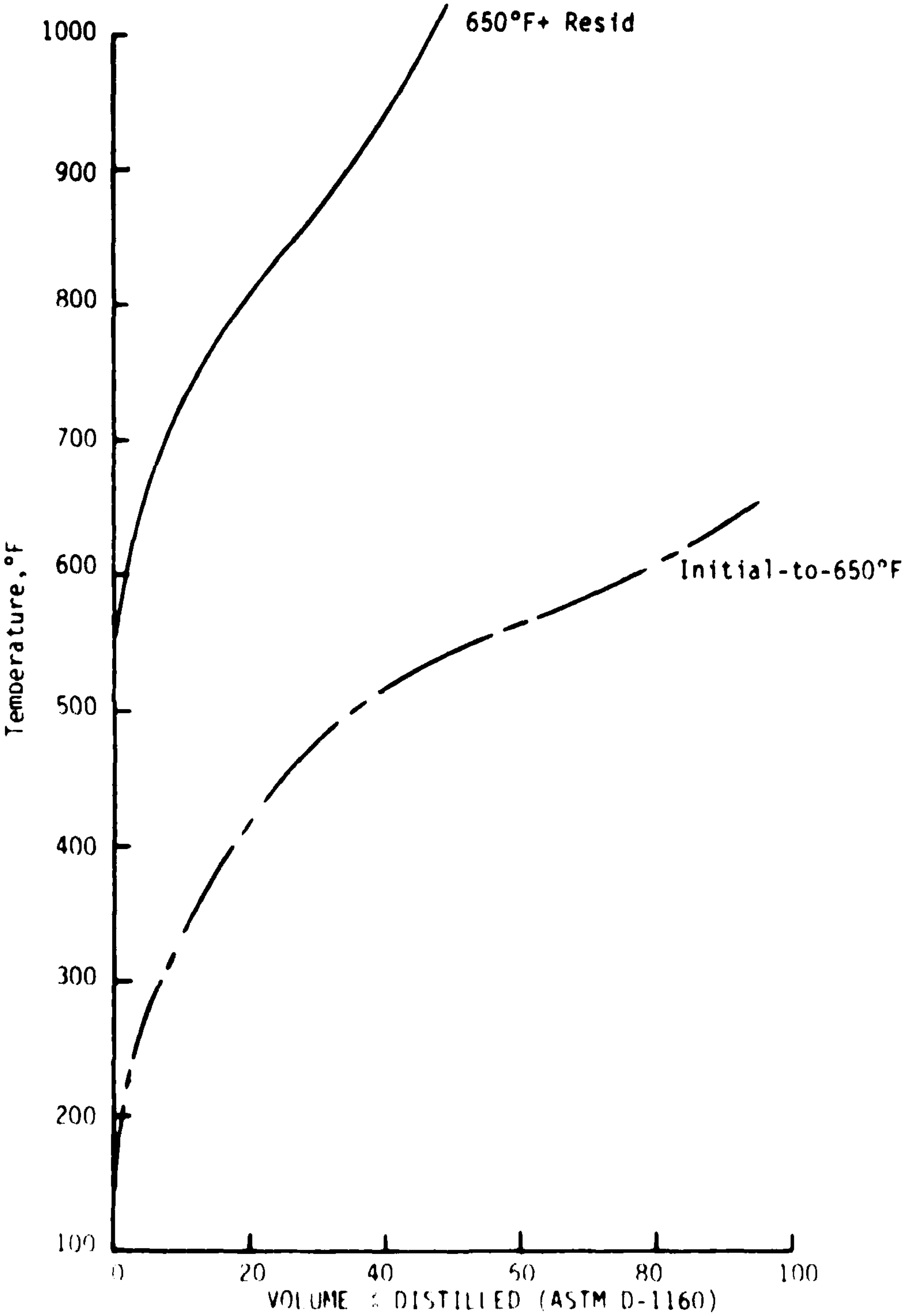

FIGURE 3. DISTILLATION RANGES OF SAN ARDO STRAIGHT RUN DISTILLATE AND ATMOSPHERIC RESIDUUM

TABLE 3

SAN ARDO NAPHTHA AND MIDDLE DISTILLATE

Fraction	Initial-490°F	490°F-bottoms
Sample code	JDT-25	JDT-26
Yield, vol.% still charge	24.8	75.2
Physical properties		
Gravity, °API	32.5	24.4
Sp. gravity, 60/60°F	0.8628	0.9076
Distillation, °F (by ASTM D86)		
IBP	387	421
5%	404	491
10%	410	532
20%	418	539
30%	425	547
40%	429	560
50%	434	568
60%	437	575
70%	441	596
90%	446	603
90%	451	631
95%	453	666
FBP	463	672
Chemical characteristics		
Elemental analysis, wt.%		
Carbon	86.72	87.21
Hydrogen	13.27	12.07
Oxygen	0.32	0.64
Sulfur	0.382	0.823
Nitrogen	0.007	0.082
Hydrocarbon type(1); method	FIA, vol.%	D2007,wt.%
Saturates	67.7	51.1
Olefins	2.4	-
Polars	-	3.4
Aromatics	29.9	45.5

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(1) Procedures differ; results should not be compared.

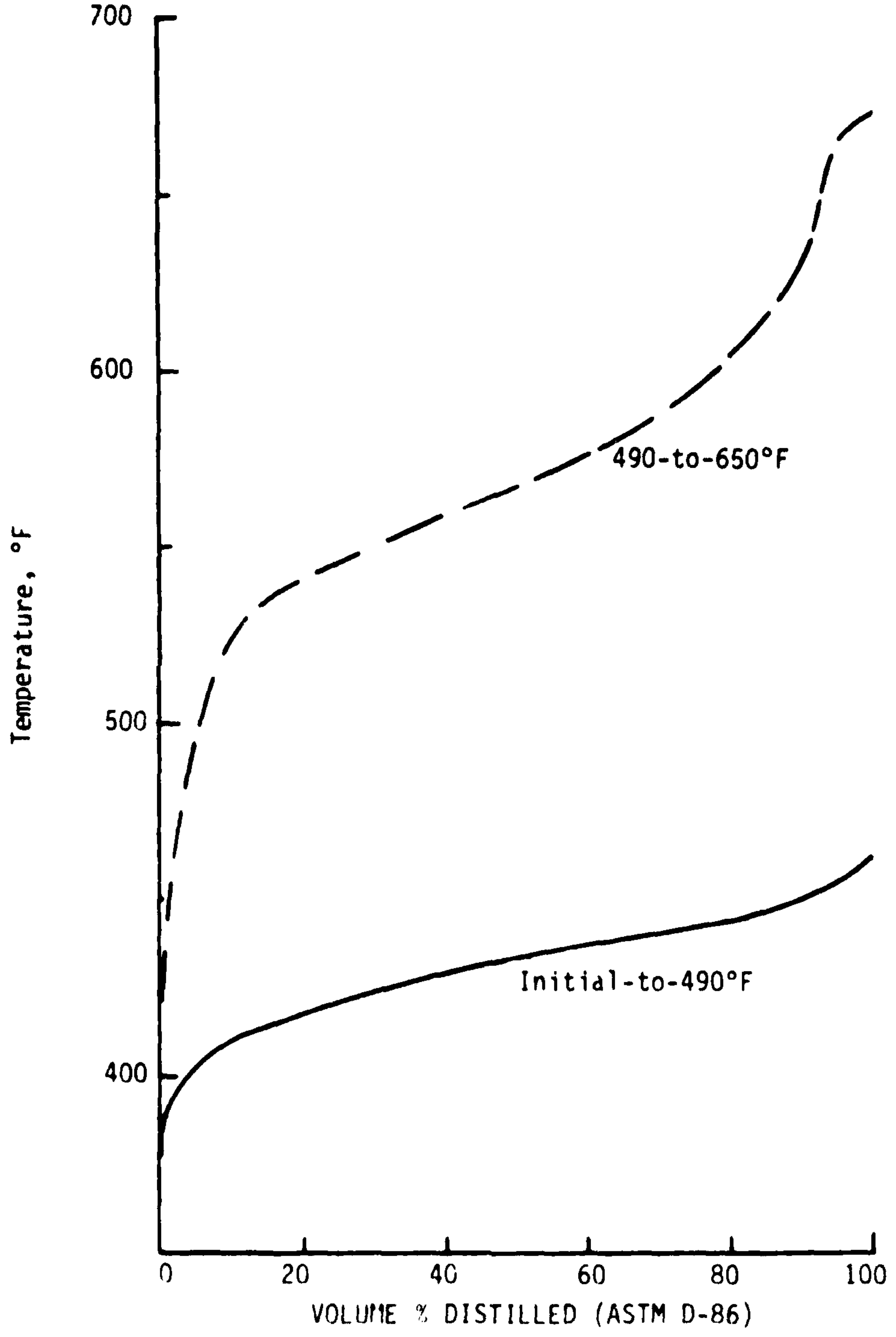


FIGURE 4 DISTILLATION RANGES OF SAN ARDO STRAIGHT RUN NAPHTHA AND MIDDLE DISTILLATE

SECTION III

HYDROVISBREAKING

1. Introduction

Applying the process concept illustrated in Figure 1, residuum is upgraded by hydrovisbreaking. In the context of this project, hydrovisbreaking implies significant conversion of the non-distillable material in the feed to lighter products through the application of heat and high hydrogen partial pressures. These two aspects -- high conversion and a hydrogen environment -- distinguish hydrovisbreaking from conventional visbreaking. Hydrovisbreaking may, therefore, be viewed as a form of thermal hydrocracking.

In some circumstances, it is advantageous to include a processing aid in the hydrovisbreaker feed to control the amount of, and/or the location of, coke deposits that form during the cracking and condensation reactions. The inclusion of such a coke-suppressing additive is not considered a contradiction of the thermal hydrocracking concept, in that the additive appears not to affect the rates of the cracking reactions. It does seem, however, to influence the relative reaction rates of the cracked products. The result is an enhanced yield of liquid product and reduced yield of insoluble or solid material.

The Phase II hydrovisbreaking studies broadly defined operating conditions necessary to achieve high conversion of four different low-grade feeds. The experiments were performed in a batch environment, and feed reactivity differences, if any, were very small. Representative operating conditions were:

Parameter	Range
Temperature, ^{o}F	700-800
Pressure, psig	1,500-2,500
Residence time, hours	1-5

As might be expected, higher residuum conversions were favored by higher temperatures and longer residence times. Interestingly, higher conversions were also favored by lower operating pressures, although heteroatom removal appeared to be unaffected. Sulfur removal appeared to be more facile than nitrogen reduction, while product distribution at constant residuum conversion was fairly insensitive to feedstock type.

Objectives of this Phase III hydrovisbreaking work included 1) definition of the effects of major process parameters in continuous-mode operations, 2) determination of detailed product distributions and engineering design basis, and 3) preparation of sufficient hydrovisbroken liquids to support the downstream refining studies.

San Ardo crude, one of the four feeds evaluated in the Phase II studies, was nominated the design feed for this Phase III program. However, the start-up and debugging work on the heavy oil pilot unit was performed with a different residual feed, to conserve inventory of the design feed. Since this alternate feed had been prepared from another of the Phase II feedstocks, the results are of more than passing interest. Accordingly, occasional reference will be made to results obtained with a residuum from Honda Monterey crude.

Operations with a third feed, as-received Kensyntar bitumen, during the start-up trials were not successful. Investigation suggested the unstable unit operation observed with this feed was caused by rapid erosion of the heavy oil letdown valve. We believe the erosion was the result of a relatively high solids level in the bitumen, combined with use (inadvertent) of non-hardened internals in the heavy oil letdown valve. We do not believe the performance observed with the Kensyntar bitumen is necessarily indicative of its processability under hydrovisbreaking conditions. However, defining approaches to achieve stable operations with the bitumen was considered beyond the scope of our start-up effort and was not pursued.

2. Procedure

Continuous mode residuum hydrovisbreaking runs were performed in ARD's heavy oil pilot plant, which was newly constructed by ARD personnel during the time period covered by this report. The unit is described in Appendix A. The reaction section of the unit consists of three 2-liter stirred stainless steel reactors in series. Transfer lines are manifolded such that any of the three reactors can be included or excluded from the flow path. In these studies we used either one or two reactors, reserving the third as a spare. A gas recycle system allows unreacted hydrogen to be recycled, after caustic scrubbing to remove hydrogen sulfide.

Reactor effluent is separated into liquid and vapor in two high pressure separators, one operating at elevated temperature (e.g. ~500°F) and the second at cooling water temperature (e.g. 70-90°F). Thus, liquid product consists of both a heavy oil and a light oil. Because the separation is very rough, there is considerable overlap in distillation range for the two streams. The unit contains no facilities for recycling unconverted liquid feed, since to do this effectively requires a fractionation system for the heavy oil stream. Consequently, achieving high conversion on a once-through basis is considered a more severe operation than if achieved in a recycle operation. Defining the benefits of recycle hydrovisbreaking would be a fruitful area for further study.

A small quantity of processing aid was metered into the residual feed upstream of the preheater coil for the purpose of controlling coke production. For the studies reported here, we used an oil-soluble molybdenum compound (molybdenum octoate) which had been shown in laboratory testing to be very effective in lowering coke production.

Preliminary start-up and debugging operations were with Hondo Monterey residuum, during which qualitative trends of some major operating parameters were established. Once stable, continuous operation was demonstrated, attention shifted to the design feed to obtain design basis data and carry out the production run.

3. Process Studies

Where appropriate, some results with the start-up feed (Hondo Monterey resid) have been included in the ensuing discussion of the hydrovisbreaking of San Ardo residuum. The objective is not to compare feedstocks but to provide additional support for some of the observations made with the San Ardo residuum. Properties of the Hondo Monterey residuum are listed in Table 4. Properties of the San Ardo design basis feed were previously presented in Table 2, and are repeated in Table 4.

A major point to be established in these preliminary studies was the combination of operating conditions that would produce once-through residuum conversions in the range of 70 to 90 volume percent. While the Phase II results were indicative of these requirements, several distinguishing features prevented direct translation from Phase II. First, Phase II results were obtained in batch-type processing, whereas Phase III operations were to be continuous. In the batch mode, heat-up was slow due to the thermal inertia of the autoclave mass. Thus, time-at-temperature conditions were poorly discriminated. Secondly, in the batch operations fresh hydrogen supply was limited. It could be added to replace that consumed, but there was no continuous purge of the vapor space during a run. Entirely different relationships between hydrogen partial pressure and total reaction pressure would prevail, in the two different operational modes. Thirdly, coke suppressant was not used during the batch work in Phase II, but was considered essential for extended operation of the continuous unit.

Other operating conditions for the continuous hydrovisbreaking process studies were:

TABLE 4

HONDO MONTEREY AND SAN ARDO RESIDUA

Source	Hondo Monterey	San Ardo
Physical properties		
Gravity, °API	5.8	8.5
Sp. gravity, 60/60°F	1.0306	1.0107
Distillation, °F (by ASTM D1160)		
IBP	813	552
5%	878	684
10%	914	735
20%	974	804
30%	-	860
40%	-	938
50%	-	992
FBP	1,000 @ 26.5 %	(cracking)
Viscosity, cSt		
160°F	91,148	7,761
210°F	5,762	841
Chemical characteristics		
Elemental analysis, wt.%		
Carbon	83.61	86.10
Hydrogen	10.29	10.93
Oxygen	1.37	-
Sulfur	7.51	2.36
Nitrogen	1.80	1.204
Carbon residue, wt.%	9.7	-

Parameter	Level(s)
Reaction temperature, °F	800-855
Reaction pressure, psig	2,000 and 2,500
Nominal residence time, hrs.	0.7 to 1.9
Number of reactors (2-liter)	1 or 2
Total hydrogen to oil, SCF/bbl	5,000
Agitator speed, RPM	800
Additive, in ppm molybdenum	367

Brief discussion of the effects of some of these variables follows. It should be noted that the true residence time of the liquid feed within the reaction zone is not known. This parameter would be a function of the volume fraction of gas and liquid present at any set of conditions. Presently, we have no way of determining those values. Global residence times have been calculated based on fresh liquid feed rate, the 60°F density of the feed, and nominal volume of 2.0 liters per empty reactor.

For much of the process variable study, resid conversion was estimated by comparing ASTM type vacuum distillations of the feed and product heavy oil. A more rigorous procedure, employing true boiling point type distillations of the combined light and heavy oil products, was used for the design basis runs.

a. Temperature effect

Figure 5 illustrates the effect of reaction temperature on the estimated >1000°F conversion for San Ardo resid feed when processed through a single reactor. Conversion increased with temperature over the range studied. The modest scattering of the data is believed due to inconsistencies in the vacuum distillation of the heavy oil product. Results with the Hondo start-up feed are represented by the dashed line in Figure 5. The trend is similar to that for the San Ardo. The displacement of the Hondo results toward higher conversion is considered real, and is believed due to 1) the Hondo feed contains more >1000°F material and may be more readily cracked, and/or 2) the higher sulfur content of the Hondo resid may also render it more susceptible to cracking.

Conditions

2,500 psig
One reactor
1 hour residence time (nominal)
5,000 SCF H_2/bbl feed
367 ppm Mo additive
resid feed: as indicated

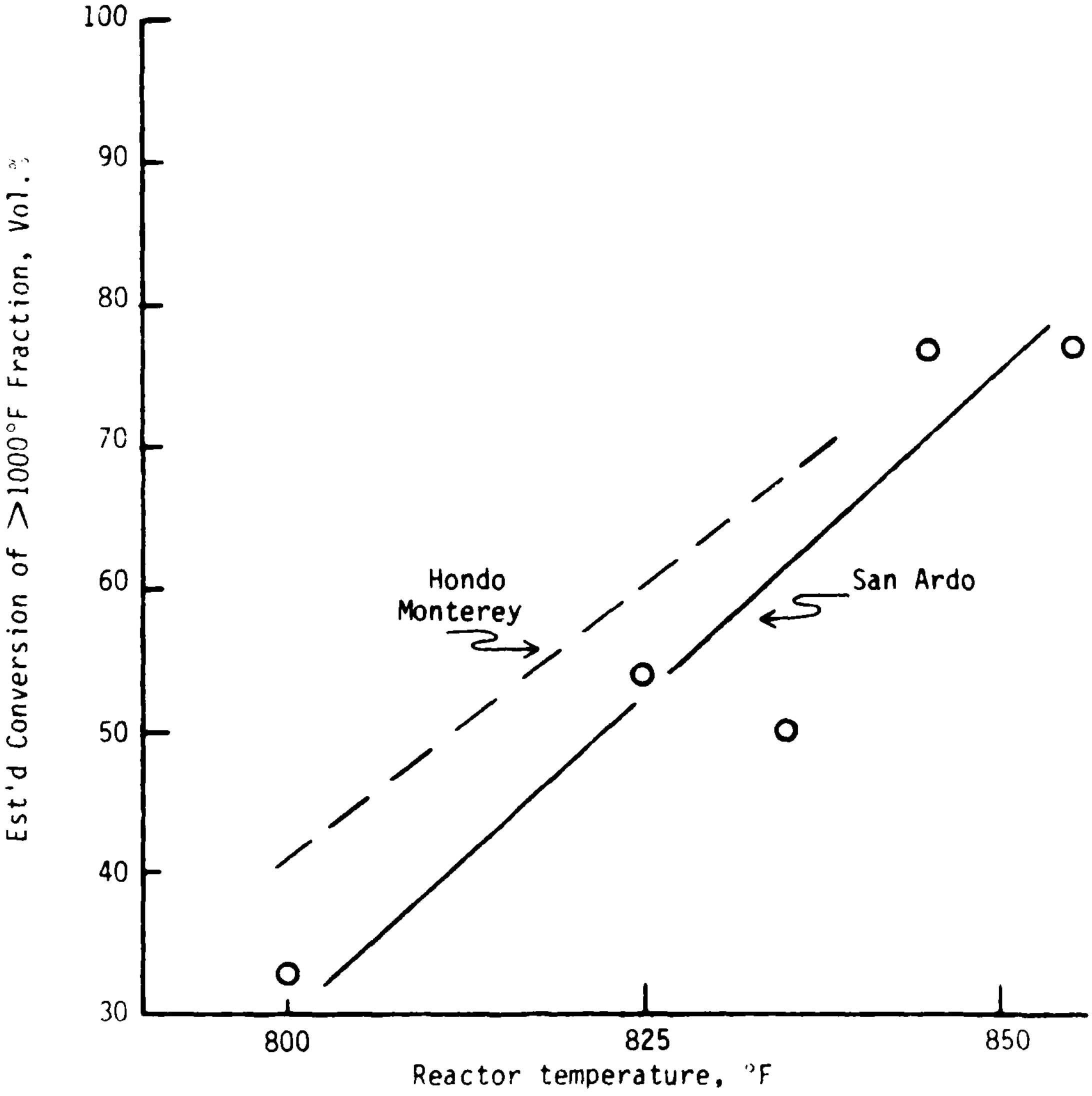


FIGURE 5 TEMPERATURE EFFECT IN HYDROVISBREAKING

Other changes accompany the increase in resid conversion with higher reaction temperatures. The split between light and heavy oil products shifts toward light oil, while flash gas volume and specific gravities increase. These trends are illustrated in Table 5, which summarizes data from processing the San Ardo resid at three different temperatures.

In Table 5, light oil yield increases and heavy oil decreases with increasing temperature. The composition of the combined gas streams is also shown. Yields of light hydrocarbons and hydrogen sulfide increase as resid conversion rises (Note: the light hydrocarbon breakdown in Table 5 represents only the gas streams and does not include any C_5 and lighter materials contained in the light oil stream). The net hydrogen, or apparent hydrogen consumed, also increases with reaction temperature, as would be expected. The material balance data (>97.5 weight percent recovered) are encouraging.

b. Effect of number of reactors

The results described above were obtained using a single reactor, whereas the heavy oil unit is capable of processing feed through two or three reactors in series. In theory, as the number of reactors increases, the operation approaches a plug flow regime rather than a fully backmixed condition. It was of interest to determine if two-reactor operation (the mode planned for the production run) was significantly different from single-reactor operation for the same nominal residence times. As illustrated in Figure 6, two-reactor processing appeared to give about the same conversion as was obtained in a single reactor. Other aspects of the operations were not compared, however, so the conclusion should be treated cautiously.

c. Residence time effect

While true residence times of liquid feed could not be determined, it would be expected that variations in apparent hold-up time would affect

TABLE 5

TEMPERATURE EFFECT IN HYDROVISBREAKING SAN ARDO RESIDUUM

Run no.	25	29	31
Avg. reactor temp., °F(1)	800	835	845
Material balance			
Supplied, wt.% fresh feed			
Fresh feed	100.0	100.0	100.0
Additive	2.4	2.6	2.3
Hydrogen	1.0	1.5	1.5
Recovered, no-loss, wt.% f.f			
Light oil	7.9	13.7	16.2
Heavy oil	93.2	85.6	81.1
High pressure gas	1.0	1.4	1.5
Low pressure gas	1.3	3.4	5.0
Mtl. bal. closure, wt.% total	97.6	98.5	99.0
Results			
Est'd conversion of >1000°F, %	33	51	77
Gas phase composition, wt.% f.f.			
H_2	0.6	0.6	0.5
C_1-C_3	1.0	2.7	4.1
C_4	0.2	0.7	0.9
C_5	0.1	0.4	0.4
H_2S	0.3	0.3	0.4
Hydrogen disappearance, wt.% f.f.	0.4	0.9	1.0

(1) Other conditions: 2,500 psig, 1 hr. (nominal) residence time in single reactor, H_2:oil ratio 5,000 SCF/bbl, 367 ppmw Mo

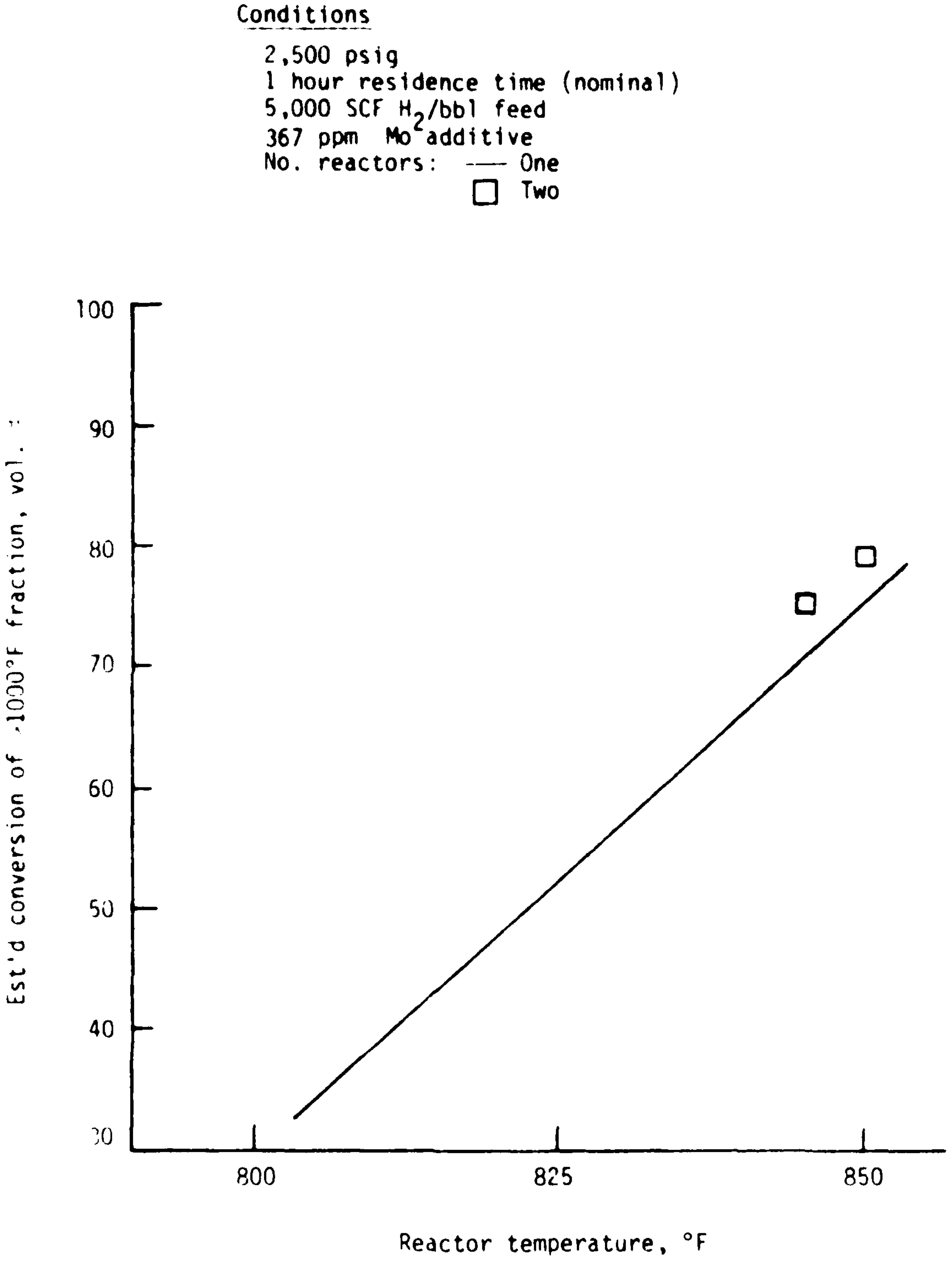


FIGURE 6 HYDROVISBREAKING SAN ARDO RESID IN MULTIPLE REACTORS

conversion level. Figure 7 illustrates this effect. The data shown are for both one-reactor and two-reactor operations at 845°F. Again, the number of reactors in use appears to have no effect. The dashed line indicates the trend obtained with Hondo Monterey residuum at 835°F, or 10°F lower than for the San Ardo. This accounts for the positioning of the San Ardo data above the Hondo line. In both series, higher nominal residence times produced greater resid conversion.

The resulting postulate of time-temperature interchangeability with respect to resid conversion would have a significant impact on plant design. Tradeoffs between reactor size, charge heater duty and heater coil coking cycle could be substantial. However, considerably more detailed studies would be necessary to determine 1) the optimum combination, and 2) process parameters other than resid conversion level which might be affected.

d. Effect of reaction pressure

During the batch mode operations of Phase II, hydrovisbreaking pressure was observed to have a significant effect on resid conversion level. This raised the question whether the effect would also occur in continuous mode processing. Feedstock and schedule limitations prevented a comprehensive study of the pressure effect. A single comparison of 2,000 vs. 2,500 psig operations, a somewhat narrower range than the 1,500 vs. 2,500 psig comparison of Phase II, was obtained during the production run.

For this study, liquid products were analyzed in detail, because the run at 2,500 psig was nominated as the design basis run for the plant design. Table 6 summarizes pertinent data from the two operations. Although the 2,000 psig run was at a 5°F lower temperature, the yield patterns are extremely similar. We concluded the change in hydrovisbreaking pressure from 2,500 to 2,000 had no significant effect. Extrapolation of this single observation to wider pressure ranges would be unwise, however. At some point, regular decreases in total or hydrogen partial pressure would certainly be expected to influence process results significantly.

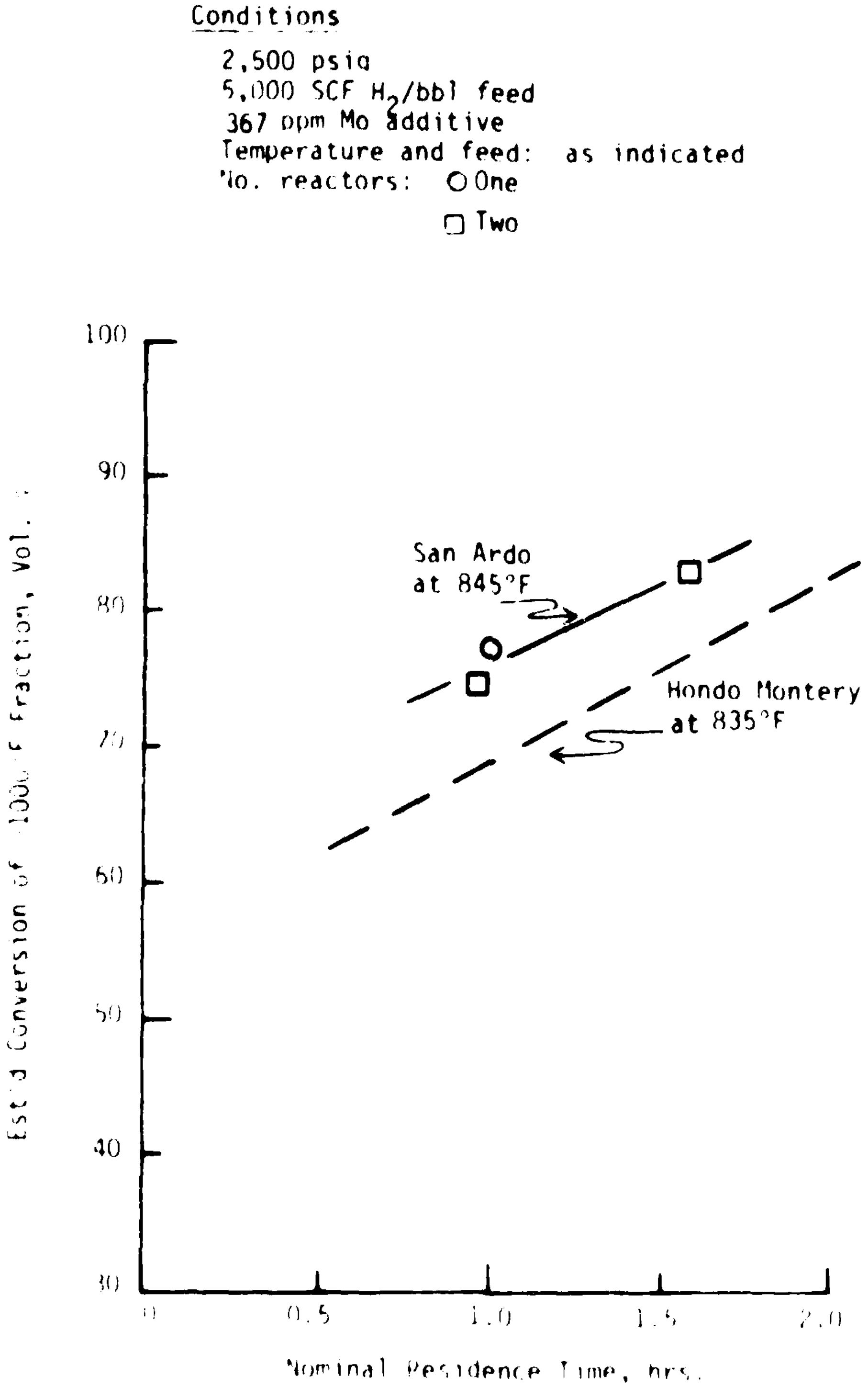


FIGURE 7 RESIDENCE TIME EFFECTS IN HYDROVISBREAKING

TABLE 6

PRESSURE EFFECT IN HYDROVISBREAKING SAN ARDO RESIDUUM

Run no.	14	08
Pressure, psig(1)	2,000	2,500
Avg. reactor temp., °F	845	850
Material balance		
Supplied, wt.% fresh feed		
Fresh feed	100.0	100.0
Additive	2.2	1.6
Hydrogen	2.3	2.2
Recovered, no-loss, wt.% f.f		
Light oil	19.2	20.5
Heavy oil	78.2	76.3
High pressure gas	2.9	2.9
Low pressure gas	4.5	4.2
Mtl. bal. closure, wt.% total	95.3	98.7
Results		
Est'd conversion of >1000°F, vol.%	66.4	64.0
Product dist'n, wt.% f.f.		
H_2	1.1	1.1
C_1-C_3	4.0	4.3
C_4	1.6	1.5
C_5	1.5	1.5
H_2S	0.7	0.6
C_6+liquid	95.2	94.5
Hydrogen disappearance, wt.% f.f.	1.2	1.1

(1) Other conditions: 1 hour (nominal) residence time in two reactors in series, H_2: oil ratio 5,000 SCF/bbl, 367 ppmw Mo

4. Design Basis Run

The design basis run was performed following the process variable scouting studies. Operating conditions were maintained as nearly as possible at levels anticipated for the commercial unit. Analysis of the operating results was also somewhat more quantitative than employed in the process scouting work described above.

The two liquid streams from the unit were re-combined in yield proportions for fractionation into several boiling range fractions by true boiling point (TBP) distillation. This type separation gives more sharply defined fractions than does the ASTM type distillation used to estimate resid conversion in the process studies. It also permits accounting for light hydrocarbons (e.g. C_3's through C_6's) contained in the light oil stream, when developing the detailed product distribution.

Table 7 summarizes results of the design basis run. Internal temperature in both reactors was 850°F. Nominal oil residence time was 1.0 hour and reaction pressure was 2,500 psig. Overall material balance accounting resulted in a 1.3 weight percent loss.

Table 7 includes a more detailed breakdown of products, as accounted for in the two gas streams and the light and heavy oil streams. The preponderance of the light hydrocarbons are saturated, as might be expected from the high operating pressure. Nevertheless, there is a showing of olefinic hydrocarbons that tends to increase with carbon number. Based on the accounting of molecular hydrogen, a net reduction (or consumption) of hydrogen of 1.15 weight percent of fresh feed (2.25 percent supplied minus 1.1 percent recovered) occurred. This is equivalent to 760 standard cubic feet per barrel of liquid feed.

Estimated resid conversion level for this operation, based on routine vacuum distillations (modified ASTM D1160) of the feed and heavy oil product, was 78 percent. Conversion as determined by the TBP distillation residue was 69 percent, somewhat below that estimated from D1160 fractionations.

TABLE 7

DESIGN BASIS RUN - HYDROVISBREAKING

Operating conditions

Reaction zone	Two 2-liter autoclaves in series	
Impeller	Turbine blade at 800 RPM	
Residence time, hrs	1.0 (nominal)	
Pressure	2500	
Hydrogen: oil, SCF/bbl	5800	
Temperature, °F	#1	#2
Preheater sand bath	450	550
Reactor inlet	596	742
skin	774	765
internal	850	850

Material balance, wt.% f.f.

Supplied	
Feed	100.0
Additive	2.25
Hydrogen	1.63
Recovered	
Light oil	20.49
Heavy oil	76.27
High pressure gas	2.89
Low pressure gas	4.23
Closure, wt.% total	98.67

Product distribution, % f.f.	Wt.	Vol.
Hydrogen sulfide	0.6	-
Hydrogen	1.1	-
Methane	1.6	-
Ethane	1.2	-
Propane	1.4	2.8
Propylene	0.1	0.2
i-Butane	0.5	0.9
n-Butane	0.8	1.4
Butylenes	0.2	0.3
i-Pentane	0.6	1.0
n-pentane	0.6	1.0
Pentenes	0.3	0.5
Others	0.3	-
Liquid fractions		
120-to-490°F	22.8	29.1
490-to-650°F	13.9	15.7
659-to-950°F	37.6	39.8
>950°F	20.2	18.0
	103.8	

The breakdown of >120°F liquid is also shown in Table 7. The four distillation ranges of the liquid products (120 to 490°F, 490 to 650°F, and 650 to 950°F, and >950°F) were selected to reflect the downstream processing scheme. Volumetric yields relative to the >950°F residuum fraction were 1.6:1, 0.9:1 and 2.2:1 for the naphtha, middle distillate, and vacuum gas oil, respectively. Table 8 lists some physical and chemical characteristics of the four liquid fractions comprising the synthetic crude. The distillation residue (>950°F) is extremely intractable and some of the analytical results are suspect. Properties of vacuum resid prepared in pilot plant distillation equipment are discussed later.

During operation of the heavy oil pilot unit, there is neither material balance accounting nor analysis of the quench sour water and caustic absorbent streams. Thus, these streams could carry to the sewer significant amounts of dissolved inorganics (ammonium sulfides, ammonia or hydrogen sulfide). This precludes independent calculation of nitrogen and sulfur balances. Conversion of sulfur and nitrogen compounds in the feed was estimated from analyses of the various TBP fractions of the synthetic crude:

Element	Est'd conversion,%
Sulfur	66.2
Nitrogen	19.1

The inability to close fully the sulfur and nitrogen balances suggests these data be used conservatively. Some reinforcement is provided by similar calculations for the hydrovisbreaking run at 2,000 psig, at comparable resid conversion. In that run, sulfur and nitrogen conversions of 65.6 and 18.1 percents, respectively were estimated.

Inclusion of coke suppressant is considered necessary for once-through high conversion hydrovisbreaking. Product handling procedures precluded determination of the amount of solids or coke being produced, while the project scope did not include studies of coke suppressant effectiveness (i.e., concentration, compound type).

TABLE 8

PROPERTIES OF SYNCRUDE FRACTIONS

TBP still fraction, °F	120-490	490-650	650-950	>950
Yield, vol.% still charge(1)	27.5	14.8	37.6	17.0
Physical properties				
Gravity, °API	47.1	26.0	16.8	<1.0
Sp. gravity, 60/60°F	0.7923	0.8984	0.9541	-
Distillation, °F (2)				
IBP	169	431	596	-
5%	220	481	632	-
10%	237	490	650	-
20%	262	530	684	-
30%	289	530	704	-
50%	345	532	750	-
70%	397	535	803	-
80%	419	536	835	-
90%	441	578	873	-
95%	454	583	906	-
FBP	459	593	906	-
Pour point	-	-	-	>120
Ash, wt.%	-	-	-	13.07
Asphaltenes, wt.%	-	-	-	43.9
Carbon residue, wt.%	-	-	-	38.7
Viscosity, cSt				
100°F	-	15.51	-	-
160°F	-	12.55	16.15	-
210°F	-	1.64	6.67	-
Chemical characteristics				
Elemental analysis, wt.%				
Carbon	85.46	86.29	87.47	87.06
Hydrogen	13.60	12.05	10.95	8.20
Oxygen	0.33	0.62	1.08	2.16
Sulfur	0.55	0.88	0.75	1.33
Nitrogen	0.22	0.53	1.05	2.24
Metals, ppmw				
Iron	-	-	<0.1	91.3
Nickel	-	-	<0.1	192
Vanadium	-	-	<0.1	121
Copper	-	-	<0.1	1.9

(1) Initial-to-120°F cut of 3.1 volume % analyzed by G.C. and included in product distribution of Table 7.

(2) By ASTM D-86 for 120-to-490°F and 490-to-650°F cuts; by ASTM D1160 for 650-to-950°F cut.

5. Syncrude Production

The heavy oil unit operated for two extended periods, accumulating synthetic crude for subsequent pilot plant refining studies. During the first period, operating conditions were maintained at the design basis conditions (850°F, 2500 psig, nominal one hour residence time through two reactors) for a total of 124 hours. The unit was shut down for mechanical work, then re-started at nearly similar conditions (845°F, 2000 psig, nominal one hour residence time through two reactors). After 132 hours operation the unit was intentionally shut down, terminating the production run. The detailed material balance and product distribution data presented in the preceding two sections of this report were obtained during these two production runs and are believed representative of the entire 256 hour period.

6. Syncrude Fractionation

Light and heavy oil accumulated during the hydrovisbreaking production run were distilled prior to their use in the refining studies to follow. While recombination of the two streams would have simplified the distillation procedure, we elected to handle them separately to avoid possible sediment formation due to compatibility differences.

Approximately 60 gallons of light oil from the production run were composited and fractionated in ARD's high resolution still into naphtha and middle distillate cuts. Nominal cut point was 490°F. The overhead condenser on the still was operated at an elevated temperature, to vent light hydrocarbons along with the inert gas bleed. We were thus able to stabilize and fractionate the still charge in a single operation, at considerable savings.

The still was operated in a semi-continuous manner, because there was not enough light oil feed for continuous operation. Periodically, feed was admitted to the reboiler and still temperatures increased until the major portion of the still charge was taken overhead. The reflux ratio from the 110°F condenser was 0.5 to 1.0 during these operations. The bottoms fraction accumulated in the reboiler until the final charge was made, whereupon temperatures were increased to reach the intended 490° vapor temperature. The still was then cooled and both fractions recovered.

Distillation data for the still charge and the two fractions recovered are listed in Table 9. The data indicate good separation of the two product streams, with essentially no overlap in their distillation ranges. In addition, the naphtha cut was very effectively stabilized, with initial boiling point increasing from 101°F to 121°F.

Approximately 211 gallons of heavy oil were composited from the production run, pressure filtered to remove any suspended particulates, and fractionated in two separate passes through the ARD vacuum still. The first, at atmospheric pressure, had a target cut point of 490°F. The >490°F still bottoms from the first pass was redistilled in a vacuum operation to a nominal cut point of 975°F. Operating conditions for the two separation were:

Pass	1	2
Pressure	atmospheric	5 mm Hg
Charge rate, lb/hr	50	35-40
Reflux ratio	0.1 to 1.0	0.1 to 1.0
Reflux temperature, °F	280-300	400-425
Column feed, °F	525-535	555-565
Reboiler, °F	525-535	650-665
Overhead/bottoms split, % by weight	6:94	77:23

This series of distillations produced two naphtha fractions, two distillate fractions, and one residual fraction from the hydrovisbroken syncrude. The two naphtha fractions were combined in yield proportions with the San Ardo straight run naphtha. The distillate cuts were blended with straight run distillate from the San Ardo crude. All blends were then stored in drums until needed for the hydrotreating program. The syncrude vacuum tower bottoms was stored in pails.

TABLE 9

DISTILLATION RANGES - LIGHT OIL FRACTIONATION

Fraction	Light oil from Hydrovisbreaking (Still charge)	Still Overhead (I-490°F)	Still Bottoms (>490°F)
Yield, wt.% still charge(1)	100.0	66.4	26.1
Distillation, °F (by ASTM D86)			
IBP	101	121	505
5%	176	169	539
10%	202	186	545
20%	224	213	548
30%	241	236	553
40%	258	260	564
50%	285	284	579
60%	366	319	600
70%	439	348	675
80%	509	381	661
90%	613	415	726
95%	621	433	-
FBP	668	440	-

(1) Overhead and bottoms fractions do not total 100% because overhead condenser was maintained at 110°F to drive condensibles up vent, thereby stabilizing overhead cut.

Properties of the straight run/hydrovisbroken blends are included in the following section which covers the hydrotreating work. Characteristics of the vacuum still bottoms from the syncrude fractionation were also determined, because those measured on the TBP vacuum bottoms from the design basis run were suspect. Properties are shown in Table 10.

The pilot plant vacuum still residue was a black, brittle solid at room temperature. In the commercial plant design, this stream would be used as refinery fuel and any excess sold. Although removed from the still bottom as a liquid, its pour point was too high for measurement by the conventional procedure (ASTM method D97). Attempts to blend it with a catalytic light cycle oil cutter stock were unsuccessful, due to poor compatibility. However, the properties shown in Table 10 indicate the undiluted material is suitable as a boiler fuel. It would have to be kept in heated storage, but at a firing temperature of 450°F, viscosity should be less than the 200 cps needed for steam atomization. Flue gas desulfurization would be required in view of the 1.5 weight percent sulfur content. Boiler ash could be a rich source of molybdenum and vanadium.

TABLE 10

VACUUM RESIDUE FROM HYDROVISBROKEN SAN ARDO

Appearance	Brittle, glassy, black solid
Softening temp., °F	240-260°F
Viscosity, cp⁽¹⁾	
285°F	94,000
300°F	43,800
Heat of combustion, Btu/lb	
Gross	17,138
Net	16,408
Composition, wt.%	
Sulfur	1.46
Nitrogen	2.88
Carbon	8.0
Hydrogen	86.0
Ash	0.38
Other	Soluble in toluene Incompatible with a catalytic, light cycle oil

(1) via Brookfield rotational viscometer

SECTION IV

HYDROTREATING

1. Introduction

For downstream refining, two streams require catalytic hydrotreatment. The lighter of the two is a broad boiling range (C_6 to 490°F) naphtha; the second is a very wide boiling range (490 to 975°F) distillate fraction. Both are combinations of straight run fractions from the San Ardo whole crude oil with fractions produced by hydrovisbreaking the San Ardo >650°F residuum.

In the Phase II scouting studies, it was established that both streams could be satisfactorily hydroprocessed over the same cobalt-molybdenum-on-alumina catalyst, albeit at very much different operating conditions. The objectives of this study included further investigation of the effect of the primary operating variables, quantitative definition of product distribution, and the generation of sufficient inventory of hydroprocessed material to support subsequent studies. Concurrently, pilot plant operations were to provide the basis for the engineering design of the commercial plant.

2. Procedure

Hydrotreating studies were performed in a continuous mode, fixed-bed pilot plant. Each of two tubular stainless steel downflow reactors (effective reactor dimensions are 94 inches long, 1-1/2 inches inside diameter, with a 9/16 inch outside diameter central thermowell) is immersed in a circulating molten salt bath. The unit can be operated with one reactor or with two reactors in series. Auxiliaries include a hydrogen recycle system in addition to the fresh hydrogen supply, an integral product fractionation column, and an oil recycle system. The latter two items provided a high degree of versatility, allowing both the hydrotreating and hydrocracking studies to be performed in the same pilot plant facility.

The hydrotreating studies employed a non-proprietary, commercial nickel-molybdenum-on-alumina extrudate. It was the same product used in the Phase II scouting studies, and had been selected from among three candidates on the basis of bench-scale comparisons of fresh catalyst activities. Catalyst properties included:

Composition, wt %	
NiO	4.0
MoO_3	19.5
Support	Alumina
Form	Shaped extrudate
Size	~ 1/16 inch diameter by ~ 1/8 inch length
Surface area	~ 200 m^2/g

The catalyst charged to either reactor was supported on a base of -6/+10 mesh inert tabular alumina. The first reactor (R-1) contained 300 cc catalyst, diluted to a 25 volume percent active mixture with Ottawa sand. The second reactor (R-2) contained 1,200 cc of 100 percent active (i.e. no dilution) catalyst. The remaining volume of the reactors above the catalyst beds was filled with more tabular alumina which served as a preheat zone.

The unbalanced catalyst loading was to accommodate the varying program requirements. The light loading in R-1 suited the naphtha hydrotreating work, where relatively high liquid space velocities were anticipated and product inventory requirements were modest. For distillate hydrotreating, much lower space velocities would be required, and a relatively long production run was needed to produce the large inventory of low nitrogen content feedstock for hydrocracking studies. To maintain reasonable flow rates during the production run, both reactors would be employed, providing five times the catalyst volume available in R-1.

After catalyst loading and successful pressure testing, the catalyst in both reactors was pre-sulfided in a hydrogen atmosphere using carbon disulfide in a straight run petroleum distillate fraction. Following the sulfiding treatment, during which approximately twice the theoretical amount of sulfur was introduced, catalyst temperatures were increased and a straight run naphtha/middle distillate blend hydroprocessed for a period of several days. Process studies with San Ardo naphtha blend began when effluent samples indicated the period of high initial activity had passed. Since the naphtha studies were to be conducted first, the R-2 reactor was cooled, purged of residual hydrocarbons, and isolated from the system in a hydrogen atmosphere until needed for the distillate studies.

3. Naphtha Hydrotreating

The feedstock was a blend of San Ardo straight run and hydrovisbroken naphthas, with nominal distillation range of 120 to 490°F. The proportion of straight run to hydrovisbroken naphtha was determined by the yields obtained in the preceding pilot plant operations. However, because the syncrude from the hydrovisbreaking production run was collected as separate light oil and heavy oil streams, three components were actually blended together to obtain the desired naphtha composition. They were 1) the initial to 490°F straight run cut, 2) the 120 to 490°F cut from the hydrovisbroken light liquid product, and 3) the 120 to 490°F cut from the heavy oil stream from hydrovisbreaking. Overall, the blend proportion was:

Component	Volume % in blend	Volume ratio
Straight run naphtha	27.1	1
Hydrovisbroken naphtha	72.9	2.69

During the naphtha hydrotreating studies, 300 cc/hr of distilled water was injected into the reactor effluent line upstream of the high pressure separator to prevent plugging the gas recycle line with ammonium sulfides. The integral fractionating column downstream of the low pressure receiver was operated as a stripper/stabilizer (i.e., inert gas purge, total reflux, 125°F reboiler temperature) to remove light hydrocarbons and any dissolved hydrogen sulfide from the liquid product.

Shortly after switching feedstocks from the break-in feed to the San Ardo naphtha blend, the pilot unit suffered repeated severe plugging in the inlet transfer lines and top portion of the reactor bed. After several shutdowns for clearing plugs (black, carbonaceous, gritty) and unloading contaminated catalyst from R-1, we concluded the feed itself was the source of the deposits. Since the feed passes through filters on the suction side of the pilot unit charge pump, it appeared the deposits were caused by soluble sediment pre-cursors which were left behind in the heated transfer lines as the bulk of the charge was vaporized. Evidently, the hydrovisbroken naphtha was not particularly storage stable, in spite of the fact that it had been produced under conditions of high hydrogen partial pressure. In addition, exposure to air or light during handling may have accelerated polymer formation.

To remove the offending material, the naphtha blend was redistilled as rapidly as possible in continuous pilot plant fractionation equipment. As it was charged to the still, the naphtha was combined with about one half its volume of a high boiling naphthenic lube fraction in order to 1) obtain as high a yield as possible of redistilled naphtha, and 2) provide a medium for removing any high boiling polymer from the reboiler without plugging, as the pilot unit had. The redistilled naphtha was immediately treated with 80 ppm hindered phenol type anti-oxidant and stored in drums under nitrogen blanket. This procedure was effective, and pilot plant processing of the freshly distilled naphtha resumed with no further flow problems.

Table 11 presents physical and chemical characteristics of the redistilled naphtha feed blend. The distillation range is about as expected from the data for the blend components. Those characteristics indicative of hydrotreating requirements are the olefin content of about 17 volume percent and the nitrogen content of over 1100 ppmw. The hydrogen and sulfur contents are very close to limiting values for turbine fuels, and should improve markedly on hydrotreating.

TABLE 11

NAPHTHA HYDROTREATING FEEDSTOCK

Composition	Straight run/hydrovisbroken blend(1)
Physical properties	
Gravity, °API	45.7
Sp. gravity, 60/60°F	0.7985
Distillation, °F (by ASTM D86)	
IBP	177
5%	224
10%	242
20%	269
30%	298
40%	329
50%	356
60%	384
70%	402
80%	417
90%	431
95%	439
FBP	446
Chemical characteristics	
Elemental analysis	
Carbon, wt.%	85.6
Hydrogen, wt.%	13.4
Oxygen (by difference), wt.%	0.4
Sulfur, ppmw	4,760
Nitrogen, ppmw	1,134
Hydrocarbon type, vol.%	
Paraffins	31.1
Olefins	16.7
Naphthenes	36.9
Aromatics	15.3

(1) Proportions: 27.1 vol.% straight run naphtha, 72.9 vol.% hydrovisbroken naphtha

Process scouting emphasized variations in the operating parameters which were likely to have the greatest impact on the plant design, and covered the following:

Parameter	Range
Space velocity, hr^{-1}	2.0 to 3.5
Pressure, psig	750 to 1,500
Hydrogen:oil, SCF/bbl (1)	2,500 to 10,000
Average catalyst temperature, °F	610, 650

(1) Includes fresh plus recycle

Figure 8 summarizes the effects of varying combinations of reaction pressure and liquid space velocity on the quality of the hydrotreated liquid product, as indicated by sulfur content. The integers enclosed within the symbols represent the sequence in which the six runs were made. The numbers adjacent the symbols indicate the sulfur content of the product obtained at those conditions. Hydrotreating severity increases as either pressure rises or space velocity decreases, while the most rapid increase occurs as both parameters change, approximately in the direction represented by the large arrow in Figure 8. Over wide ranges of process parameters, it should be possible to construct lines of constant product quality--in this case, sulfur content--that generally orient perpendicular to this severity line. However, as indicated in Figure 8, other factors appeared to be operative which obscured this severity relationship. In particular, the first two runs in the sequence were inconsistent with the remainder, for undetermined reasons. Runs 3 through 6 suggested that hydrodesulfurization is very thorough ($\gtrsim$ 99.9 percent removal), and that at this removal level, the imposed severity variations had only a small effect on product sulfur content. A similar observation applied to the Phase II naphtha hydrotreating work, wherein the process variables spanned a much narrower range.

Conditions

Ni-Mo-on-alumina catalyst
650°F catalyst temperature
5,000 SCF H_2/bbl feed
4,760 ppmw sulfur in feed

Note: Number within symbol indicates run sequence; number next to symbol indicates sulfur content (in ppmw) of liquid product

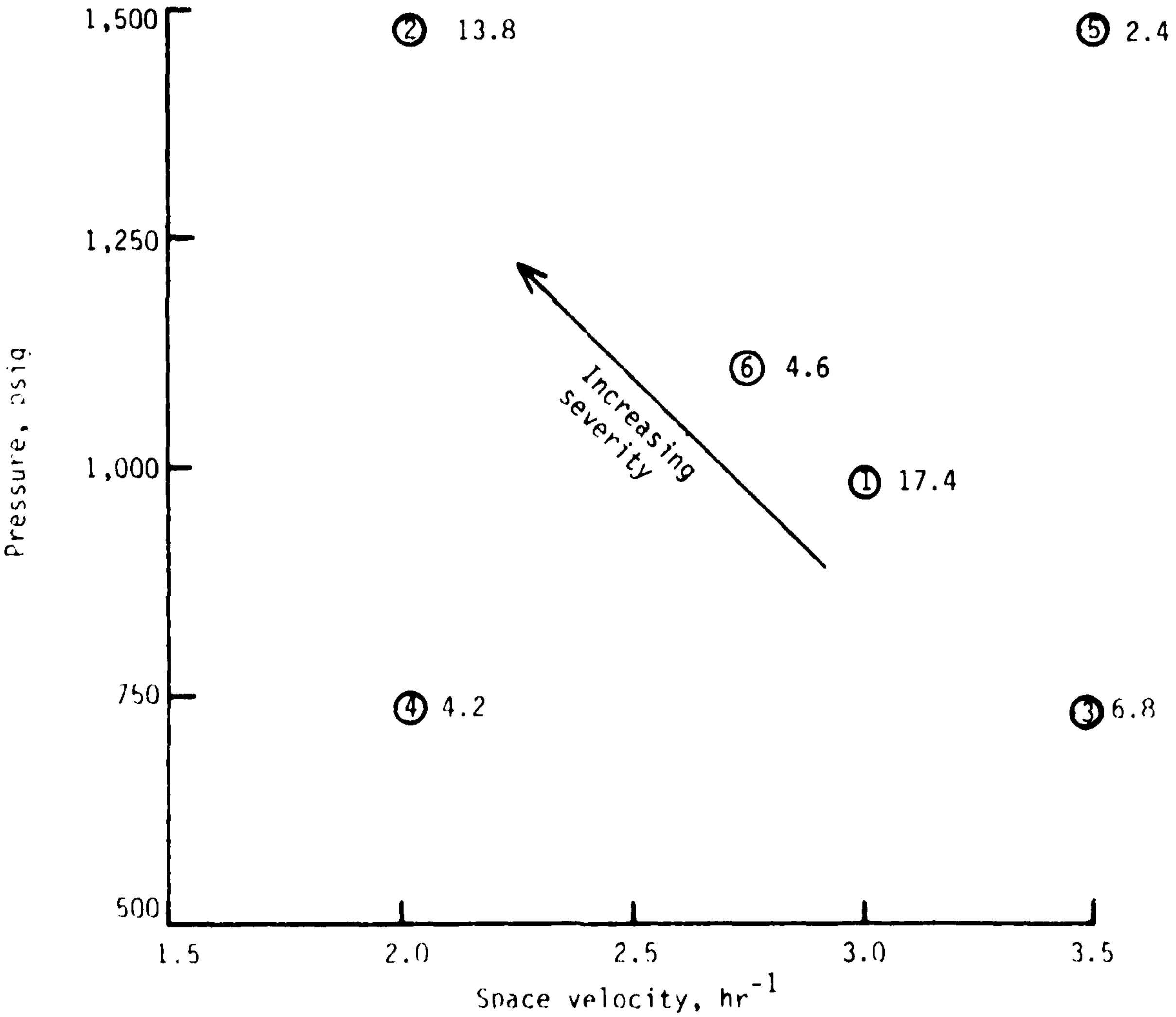


FIGURE 8 EFFECT OF HYDROTREATING SEVERITY ON NAPHTHA SULFUR CONTENT

Figure 9 depicts similar relationships for nitrogen content of the hydrotreated naphtha product. In this case, a more consistent pattern of nitrogen content with operating severity was obtained, although run #2 appeared slightly high. The results indicated that the least severe combination (750 psig and 3.5 hr^{-1}) was too mild to achieve the <10 ppm nitrogen levels considered necessary for acceptable thermal or storage stability in finished fuel blends.

Parameters of constant product nitrogen were constructed to illustrate the trade-offs between operating pressure and liquid space velocity (omitting run #2) by interpolating linearly across either variable. Results are illustrated in Figure 10 for product nitrogen contents of 1, 5 and 10 ppm. In this manner, optimum process designs could be generated for various concentrations of nitrogen in the finished product. Inasmuch as current turbine fuel specifications do not address nitrogen content, a comprehensive series of performance type tests would be required to establish an acceptable upper limit.

The effect of processing severity on other parameters was evaluated by comparing results from several runs distributed along the severity line of Figures 8 and 9. Run #1 was omitted due to the uncertainties in the results already cited. Results from runs #2, #6 and #3, in order of increasing severity, are listed in Table 12. Pilot unit material balances were uniformly good, although hydrogen consumption data are uncertain due to a fresh hydrogen metering problem. The detailed product distribution shown for run #6 indicates few light hydrocarbons are produced during processing.

With increasing severity, liquid product specific gravity decreased and product distillation range shifted very slightly. Although the variations in carbon and hydrogen contents were small, the trend was in the expected direction. Consistent with these data, a slight decrease in aromatics content occurred as hydroprocessing severity increased. The large reduction in product freeze point with hydroprocessing is of interest. Most of the decrease occurred over the first severity increment, although the

Conditions

Ni-Mo-on-alumina catalyst
650°F catalyst temperature
5,000 SCF H_2/bbl feed
1,134 ppmw nitrogen in feed

Note: Numbers within symbol indicates run sequence; number next to symbol indicates nitrogen content (in ppmw) of liquid product.

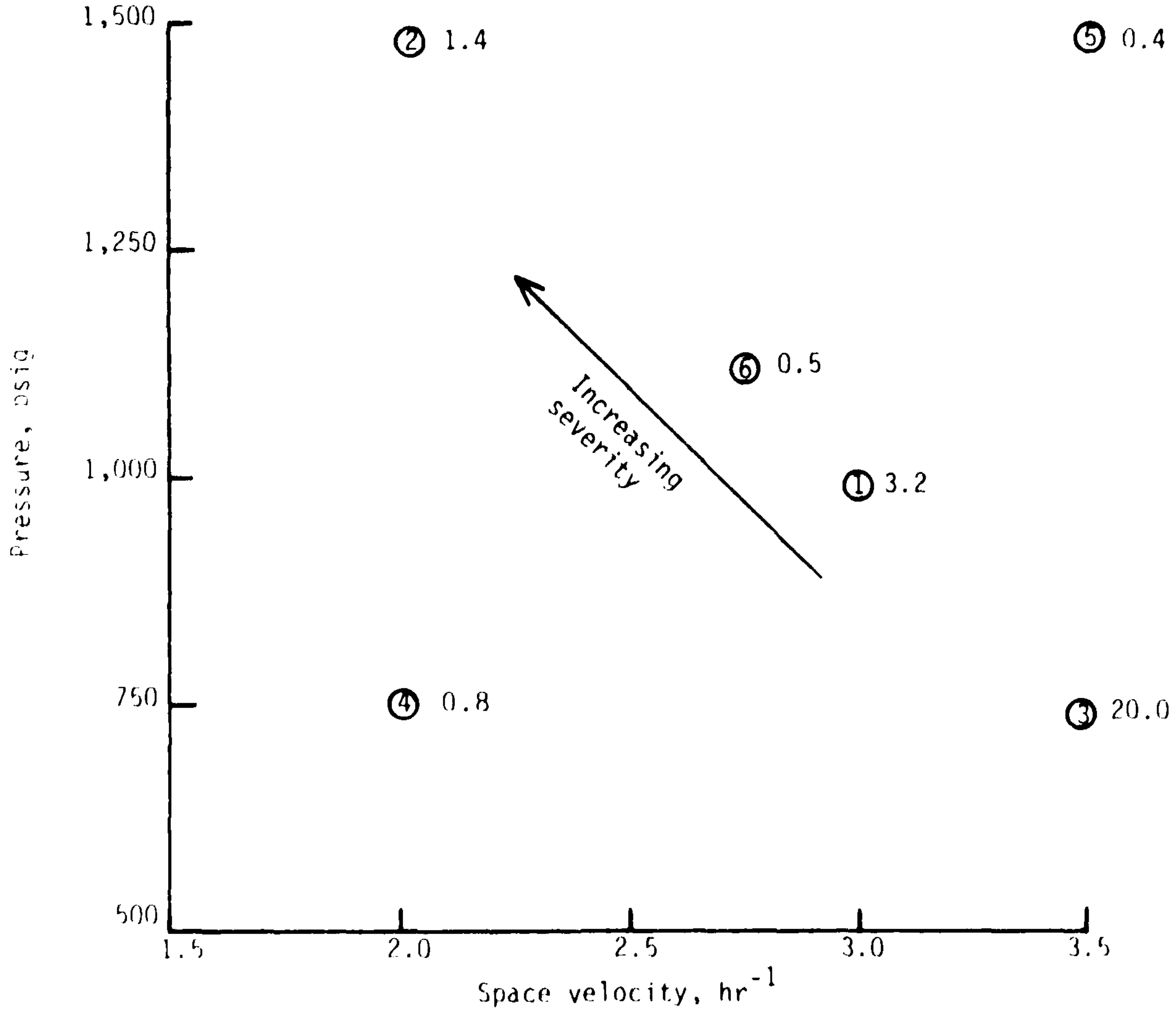


FIGURE 9 EFFECT OF HYDROTREATING SEVERITY ON NAPHTHA NITROGEN CONTENT

Conditions:

Ni-Mo-on-alumina catalyst
650°F catalyst temperature
5,000 SCF H_2/bbl feed
1,134 ppm nitrogen in feed

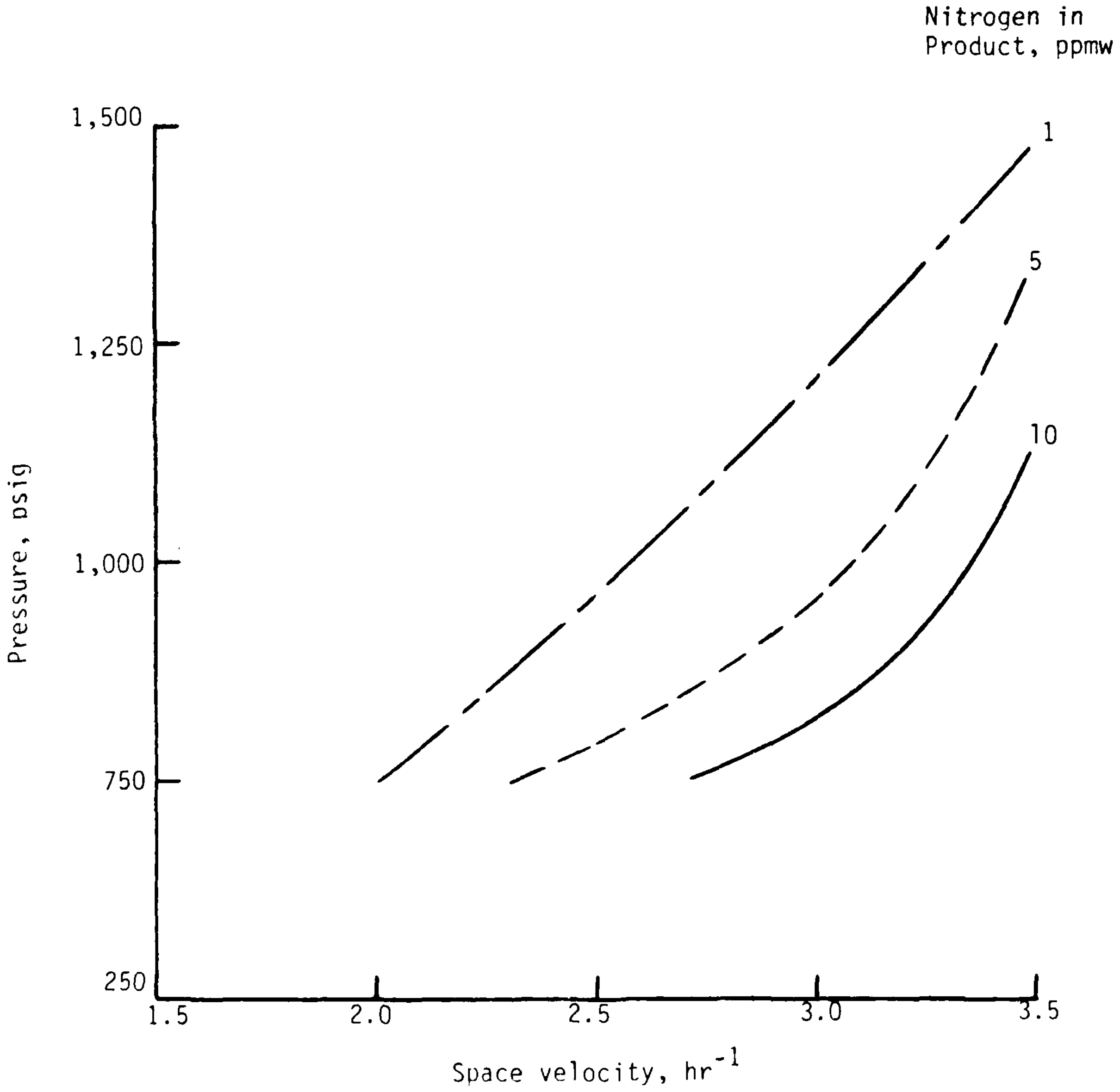


FIGURE 10 PRESSURE-SPACE VELOCITY TRADEOFFS IN NAPHTHA HYDROTREATING

TABLE 12

SEVERITY EFFECTS IN NAPHTHA HYDROTREATING

Relative severity	Low	Intermediate	High
Operating conditions(1)			
Pressure, psig	750	1,125	1,500
Space velocity, hr^{-1}	3.49	2.74	1.93
Material balance			
Supplied, wt.% fresh feed			
Naphtha	-	100.0	-
Hydrogen	-	0.46	-
Products, no-loss wt.% f.f.			
Hydrogen	-	0.45	-
C_1-C_3	-	0.12	-
C_4's	-	0.37	-
C_5's, others	-	0.46	-
H_2S	-	0.30	-
Liquid product	-	98.76	-
Properties of liquid product			
Gravity, °API	47.2	47.6	48.0
Sp. gravity, 60/60°F	0.7918	0.7901	0.7883
Distillation, °F (by ASTM D86)			
IBP	193	188	208
5%	237	232	236
10%	253	249	252
20%	278	273	280
50%	364	357	358
80%	422	416	414
90%	437	431	430
95%	452	441	440
FBP	497	462	470
Freeze point, °F	-46	-64	-68
Elemental analysis			
Carbon, wt.%	86.2	86.0	85.9
Hydrogen, wt.%	14.0	14.2	14.2
Sulfur, ppmw(2)	7.4, 6.2	5.5, 3.6	10.6, 17.1
Nitrogen, ppmw(2)	18.0, 21.9	0.43, 0.50	1.2, 1.5
Hydrocarbon type by ASTM D1319, vol.%			
Saturates	88.0	88.1	92.5
Olefins	0.0	0.9	0.0
Aromatics	12.0	11.9	7.5

(1) All runs at 650°F catalyst temperature, 5,000 SCF/bbl H_2 to oil ratio on nickel-molybdenum-on-alumina catalyst. Feed described in Table 11.

(2) First of two sets of analyses represents selected weight balance period; second is for composite for entire run.

selected increments in severity should not necessarily be interpreted as equivalent. The effect is especially intriguing, since it is believed that processing conditions were mild enough that there would have been little cracking or skeletal isomerization occurring.

A brief study of the effect of hydrogen (recycle plus fresh) to naphtha feedstock ratio is summarized in Table 13. At the design conditions of 650°F, 1125 psig and 2.75 hr^{-1} space velocity, runs were made at one half and at two times the design hydrogen to oil ratio of 5,000 SCF/bbl. As the results indicate, there was no significant effect on either product distribution or product quality as reflected in nitrogen and sulfur contents. These results suggest a potential for significant reduction in costs associated with hydrogen circulation.

A single run was made at a lower average catalyst bed temperature than the design basis conditions (610°F vs 650°F), with the following results:

Run sequence	7	10
Avg. catalyst temp., °F	650	610
Product quality		
Sulfur ppmw	4.5	2.9
Nitrogen ppmw	0.4	4.0

Product nitrogen content was higher by an order of magnitude at the lower run temperature. While the product nitrogen content was still very low, the result suggests little room for additional reductions in reaction temperature.

4. Distillate Hydrotreating

a. Introduction

Preliminary scouting of the distillate hydrotreating process used the same reactor load (300 cc in R-1) of catalyst which had been used for the naphtha studies. After a series of qualitative runs to establish acceptable operating conditions, the second reactor containing 1,200 cc catalyst was opened to the system and the design basis and the production runs carried out.

TABLE 13

HYDROGEN-TO-OIL RATIO EFFECT IN NAPHTHA HYDROTREATING

Operating conditions			
Avg. catalyst temp., °F	← 650 →		
Pressure, psig	← 1,125 →		
Space velocity, hr^{-1}	← 2.75 →		
Hydrogen/oil, SCF/bbl(1)	10,000	5,000	2,500
Material balance			
Supplied, wt.% fresh feed			
Naphtha	100.0	100.0	100.0
Hydrogen	0.49	0.46	0.46
Products, no-loss wt.% f.f.			
Hydrogen	0.41	0.45	0.47
C_1-C_3	0.1	0.1	0.1
C_4's	0.3	0.4	0.4
C_5's	0.6	0.4	0.3
H_2S	0.2	0.3	0.2
Liquid product	98.7	98.8	98.7
Properties of liquid product			
Elemental analysis			
Sulfur, ppmw	1.9	4.6	1.9
Nitrogen, ppmw	0.3	0.4	0.3

(1) Includes fresh plus recycle.

The distillate feedstock was a blend of San Ardo 490 to 650°F straight run fraction produced during the crude fractionation step, plus the 490 to 975°F long range hydrovisbroken distillate. As with the naphtha blend, the hydrovisbroken distillate component consisted of two portions, one recovered from the light oil product stream from the heavy oil unit and one recovered from the heavy oil product. Overall blend proportion was:

Distillate Component	Volume % in blend	Volume ratio
490 to 650°F straight run	22.3	1.0
490 to 975°F hydrovisbroken	77.7	3.47
	100.00	

The difficulties encountered while processing the naphtha blend caused concern about distillate blend stability. In addition to being of higher distillation range and potentially less stable, the distillate blend contained an even larger proportion of hydrovisbroken component. Furthermore, the components had been kept in storage even longer than the naphtha. Unfortunately, it was impractical to redistill either the hydrovisbroken distillate or the distillate blend without suffering large losses. This was because there was no suitable higher boiling liquid that could be used as a chaser during distillation. However, one factor possibly working in our favor was that the distillate processing was to be primarily a trickle phase operation. Potential deposit formers might remain in the liquid phase to be carried through the system, or at least be deposited in the reactor beds rather than in the narrow gauge transfer lines.

Table 14 lists physical and chemical characteristics of the distillate feed blend. With a gravity of 18.8° API, the feed is relatively heavy, compared to many gas oil hydrotreating applications. This is reflected in the 95 volume % point of 958°F. At 0.9 weight percent, sulfur content is reasonable; however, the 7519 ppmw nitrogen content indicated relatively severe processing conditions would be required.

TABLE 14

DISTILLATE HYDROTREATING FEEDSTOCK

Composition	Straight run/hydrovisbroken blend[1]
Physical properties	
Gravity, °API	18.8
Sp. gravity, 60/60°F	0.9415
Distillation, °F (by ASTM D1160)	
IBP	182
5%	456
10%	524
20%	565
30%	595
40%	630
50%	669
60%	705
70%	758
80%	816
90%	886
95%	958
FBP	958@ 95%
Chemical characteristics	
Elemental analysis	
Carbon, wt.%	86.2
Hydrogen, wt.%	11.2
Oxygen (by difference), wt.%	1.0
Sulfur, ppmw	8,841
Nitrogen, ppmw	7,519

(1) Proportions: 22.3 vol. % straight run middle distillate, 77.7 vol. % hydrovisbroken vacuum distillate.

The nitrogen content of the hydrotreated liquid product was to be the primary indicator of hydrotreating effectiveness. This parameter was important because the hydrotreated distillate became the feedstock for the hydrocracking process. Excessive amounts of nitrogen in the hydrocracker feed can depress the acidic cracking function of the catalyst. Our preliminary target was to limit the effluent nitrogen content to <<100 ppmw, and preferably to $\lesssim$10 ppm. Sulfur content of hydrocracker feed has less impact on the hydrocracking catalyst and therefore was less critical.

b. Process scouting

The first scouting run was at somewhat milder operating conditions than were necessary to yield product nitrogen contents within the target range. The purpose was to avoid over-coking the catalyst with too rapid a change from the operating conditions of the naphtha studies, and to compare with the Phase II work. The results:

	Source	
Conditions	Phase II	This study
Temperature, ^{o}F	725	725
Pressure, psig	2,000	2,000
LHSV, hr^{-1}	0.75	1.0
Product N, ppmw	968	991
Product S, ppmw	135	257

The agreement with Phase II results was acceptable, while the product nitrogen content of ~1,000 ppmw confirmed that higher severity operations were required.

A series of runs at 750^{o}F average catalyst bed defined the effects of reaction pressure and liquid space velocity, variables which greatly impact the engineering design. Because feed space velocities were relatively low, long line-out times between runs were necessary to avoid cross contamination of products within the system. In spite of this, or perhaps because of it, early results were inconsistent. After five runs in the series were completed, a repeat of the first run conditions confirmed that catalyst activity had decreased substantially during that period:

Run No. Conditions	#1	#6	
Temperature, °F	← 750 →		
Pressure, psig	← 2,000 →		
LHSV, hr^{-1}	← 1.0 →		
Elapsed time, hrs.	N.A.	251	
Product analyses, ppmw			Mean
Sulfur	111.5	152.3	132
Nitrogen	555.1	1145.0	850

Thus, after 251 additional hours of operation on distillate feed, product sulfur content had increased by about one-third, whereas nitrogen content had more than doubled. On the premise that the average values were more representative of this set of conditions, the mean values shown above were used in the data presentation.

Figure 11 illustrates the effects of operating pressure and liquid space velocity on quality of the hydrotreated distillate. All runs were at average catalyst temperature of 750°F. Product sulfur contents were generally lower than the nitrogen contents by nearly an order of magnitude. Both nitrogen and sulfur contents decreased markedly when the space velocity was halved, as one would expect. On the other hand, the relative change in operating severity with pressure was fairly modest, a 25 percent increase from 2,000 to 2,500 psig. This increase had no apparent effect on the degree of sulfur removal. By contrast, this change produced a major response in product nitrogen content, as shown in Figure 11.

Conditions:

Ni-Mo-on-alumina catalyst
750°F catalyst temperature
pressure: as indicated
5,000 SCF H_2/bbl feed
feed content: 7,519 ppmw nitrogen
8,841 ppmw sulfur

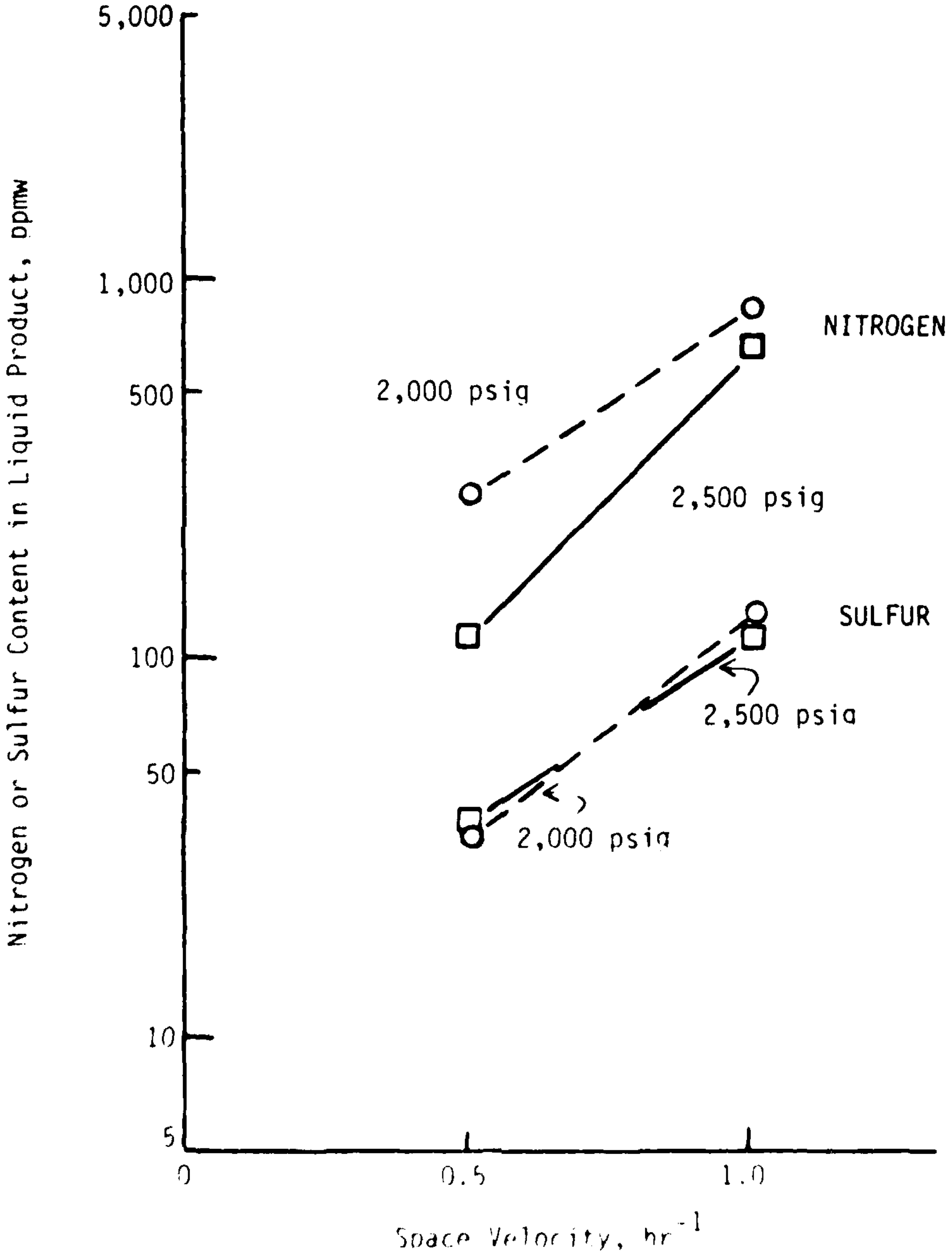


FIGURE 11 SEVERITY EFFECTS IN DISTILLATE HYDROTREATING

The experimental plan for the distillate hydrotreating studies originally included catalyst temperature as the third independent variable in a 2^3 factorial design. The four conditions shown in Figure 11 represented one face of the 3-dimensional experimental space. However, an upper limit of 750°F catalyst temperature had been set to avoid overcracking and rapid catalyst deactivation, and four more runs at a lower temperature would have had little value. Therefore, the extended temperature portion of the program was abbreviated to a single run at a lower temperature, made at the center of the experimental space represented by the four 750°F runs. Comparison of the mean results from the four runs at 750°F with the lower temperature center-point run provided an estimate of the temperature effect:

	Runs Compared	
Conditions	Center-point, actual	Mean of four(1)
Av'g. catalyst temperature, °F	737	750
Pressure, psig	2,250	2,250
Liquid space velocity, hr^{-1}	0.78	0.75
Results		
Product nitrogen, ppmw	752	477
Product sulfur, ppmw	139	79

(1) Not an actual run, but arithmetic average of four runs at 0.5 and 1.0 hr^{-1} and at 2,000 and 2,500 psig.

The temperature sensitivity of both nitrogen and sulfur contents is quite strong and of the same magnitude as was observed over a wider temperature range in Phase II. The above series confirmed that hydrodenitrogenation was limiting, and required relatively severe conditions (e.g. 750°F, 2,500 psig) to achieve nitrogen removal of 99.9 percent.

c. Design basis results

The run to provide the basis for the engineering design of the distillate hydrotreater utilized both reactors of the pilot plant in series operation, providing a total catalyst volume of 1,500 cc. The design basis run also initiated the production run, which was made at essentially the same operating conditions.

For these runs, the pilot unit's integral fractionation column operated in a true distillation mode rather than as a stripper/stabilizer. The nominal cut point target was 490°F. Since the distillate hydrotreater feed contained very little material boiling below 490°F, any liquid recovered as fractionator overhead would have represented hydrocracked material produced during the hydrotreating step. If allowed to remain, it would further crack to lighter products during the hydrocracking step, which was undesirable. The overhead cut was retained for inclusion in the final product blends, since its nitrogen content was acceptably low.

The results of the design basis run are summarized in Table 15. Operating conditions were those projected from the scouting studies, viz., 750°F, 2500 psig, and 0.5 hr^{-1} space velocity. Yield data for several distillation range fractions were determined by true boiling point analysis of recombined -- in yield proportions -- fractionator overhead and bottoms. As shown in Table 15, the yield of C_6 to 490°F TBP fraction was 23 volume percent of the reactor feed. This is somewhat less than the 44 weight percent recovered as fractionator overhead during the run, primarily because the still had not yet been lined out at the conditions required to obtain the nominal 490°F cut point.

Indicative of high severity operation, the dry gas (C_1-C_3) yield of 1.4 weight percent of fresh feed compared to only 0.1 weight percent in the naphtha hydrotreating design basis run. Olefin contents of the dry gas and condensibles (C_4's and C_5's) were low, ranging from 5 to 10 percent of the individual fractions.

TABLE 15

DESIGN BASIS RUN - DISTILLATE HYDROTREATING

Operating Conditions

Catalyst	Ni-Mo-on-alumina
Reactor loading	
R-1	300^{cc} diluted to 20 vol. % active
R-2	$1,500^{cc}$ of 100 vol. % active
Average catalyst temp., °F	750 (both reactors)
Pressure, psig	2,500
Space velocity, hr^{-1} (1)	0.49
Hydrogen (total) to oil, SCF/bbl	5,000
Hydrogen consumed, SCF/bbl	1,470
Product fractionator feed, °F	331
reboiler, °F	635

Material balance,

Supplied wt.% fresh feed	
Feed	100.0
Hydrogen	3.35
Recovered, no-loss wt.% f.f.	
Fractionator overhead	43.85
Fractionator bottoms	56.56
High pressure gas	1.20
Low pressure gas	1.74
Closure wt.% total	96.1

Product Distribution, % f.f.	Wt.	Vol
Hydrogen	1.0	-
Methane	0.4	-
Ethane	0.5	-
Propane	0.5	1.0
i-Butane	0.2	0.3
n-Butane	0.2	0.3
i-Pentane	0.1	0.2
Liquid fractions (TBP cuts)		
120-490°F	19.9	22.9
490-650°F	47.2	50.8
>650°F	33.1	34.6

(1) Feed described in Table 14.

Hydrogen consumption for the design basis condition was 2.37 weight percent of fresh feed which is equivalent to 1,470 SCF/bbl. Quality of the hydrotreated liquid from the design basis run, as reflected by nitrogen and sulfur contents (5.4 ppmw and 54.7 ppmw, respectively), was much improved over operations in the process variable study preceding it. This is undoubtedly due to the inclusion of the R-2 reactor in the flow pattern, such that 80 percent of the catalyst in the system was relatively fresh.

d. Production run

The distillate hydrotreating production run was simply a continuation of the design basis run. During the run, attention focussed on defining and maintaining operating conditions for the fractionation section, to achieve the desired 490°F nominal cut point. In addition, nitrogen content of the still bottoms was measured periodically to determine the condition of the catalytic section.

Figure 12 presents trends in these two operational parameters over the course of the 16-day period of the production run. Both parameters display excursions, sometimes large ones, from the norms. The trends are addressed in the following description of operations during various time periods of the run:

Period #1 represents day 1 through day 7, with reactor operating conditions maintained at the same levels as the design basis runs. These included 0.5 hr^{-1} space velocity, 750°F catalyst temperature, 2500 psig pressure, and 5,000 SCF/bbl total hydrogen to oil rate. During this period, nitrogen content of the fractionator tower bottoms increased gradually from <2 ppmw to about 4 ppmw. Meanwhile, fractionating tower conditions -- primarily column feed and reboiler temperature-- were being adjusted to obtain the desired cut point. The adjustments caused some fluctuation in the nominal cut point (defined as the arithmetic mean of the 95 volume percent point of the column overhead and the 5 volume percent point of the column bottoms, both determined in an ASTM D86 distillation procedure), but had no noticeable effect on column bottoms quality. In general, operations were relatively smooth during period #1.

Conditions:

Ni-Mo-on-alumina catalyst
2,500 psig
750-760°F catalyst temperature
0.5-0.6 hr^{-1} space velocity
5,000 SCF H_2/bbl feed

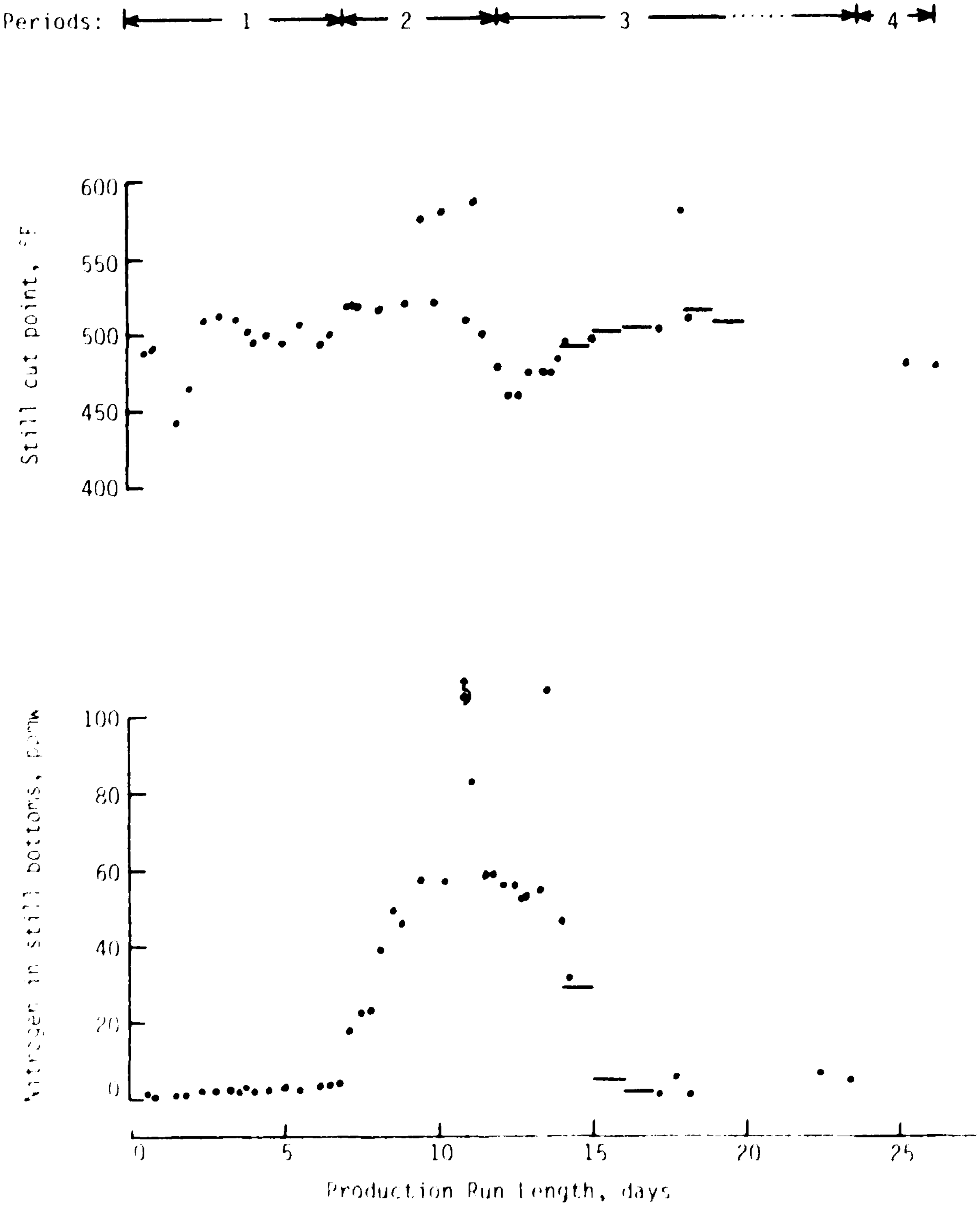


FIGURE 12 DISTILLATE HYDROTREATING PRODUCTION RUN

During this initial period, product quality was monitored fairly frequently. Other characteristics of the two liquid streams during this period included:

Characteristics	Stream Fractionator Overhead	 Bottoms
Yield, wt.%(1)	17	83
Sulfur, ppmw	56-131	1.1-3.2
Nitrogen, ppmw	0.3-0.6	1.4-3.6
Distillation range, °F		
95 vol.%(2)	448	---
5 vol.%(2)	---	540

(1) Average of 19 values; as percent of total liquid recovery

(2) Average of 16 values

Over the period, nominal cut point varied somewhat, as shown in Figure 12, but averaged 494°F.

Period #2 covers the span from days 7 through 12, where unsteady operations in both reactor and fractionation sections occurred, and large excursions from the relatively smooth trends of period #1 are evident. At the beginning of period #2, the fresh oil feed and total hydrogen rates were increased by 20 percent in order to accelerate the production run. The adjustment appeared feasible, since the bottoms nitrogen content was well below the target of 10 ppmw.

Rather than the modest increase in nitrogen content of the distillation tower bottoms that was anticipated, a major upward trend to the 40-60 ppmw range occurred. Simultaneously, operation of the product fractionator became very erratic, and product cut points cycled widely. We do not believe the two occurrences are related, although no definite reason for the still upset was determined (possibilities include column flooding, water carryover, and/or erratic operation of the liquid level controllers).

The cause of the high nitrogen quickly became apparent, when pressure drop across the R-1 reactor rose sharply to intolerable levels, forcing its shutdown. Undoubtedly, most of the feed was bypassing the catalyst in R-1 via channeling during the pressure build-up period, so the effective space velocity was probably more nearly 0.75 hr^{-1} immediately prior to the R-1 shutdown.

As prior discussion of the storage stability of the naphtha and distillate feeds has suggested, loss of the R-1 reactor was not totally unexpected. However, it did perform its intended function as a "trash basket" during the early part of the run, collecting deposits that might otherwise have fouled the fresh catalyst in R-2.

The operation at high effective space velocity was not entirely lost, as the products were isolated, redistilled to narrow the cut point spread, and set aside for use as a high nitrogen content feed during the hydrocracking process studies.

Period #3 encompasses operations from days 12 through 25, during which the unit was recovering from the upsets in period #2. Oil charge rate was adjusted downward to compensate for the shutdown of R-1 and to return to a nominal 0.5 hr^{-1} liquid space velocity. In addition, R-2 catalyst temperature was increased from 750 to 760°F to improve nitrogen removal. Fractionator operation also stabilized. The results were a return to the target cut point and to product nitrogen contents of $\lesssim$ 6 ppmw. These operations continued in a fairly stable fashion until the feedstock was exhausted, albeit interrupted for a 2-day shutdown at days 20 to 22 to repair a burned out heating circuit on the reactor salt bath.

Period #4 represents the 2-1/2 days prior to shutdown, during which previously hydroprocessed but off-spec distillate was rerun to increase the inventory of low nitrogen content material. The feed was a composite of products from the process variable studies and retains from various line-out periods. The material was processed at 1.0 hr^{-1} space velocity, 2500 psig and 750°F. Because the run was brief and the feed had no significance in the overall process concept, product testing during period #4 was minimal.

SECTION V

HYDROCRACKING

1. Introduction

Hydrocracking studies were performed in the same pilot plant facility used for both naphtha and distillate hydrotreating studies described in the preceding section. The hydrocracking program consisted of two elements: a series of scouting type runs in which the major operating parameters were varied to determine their effect on process results, and a pair of production runs designed to represent operations when the plant was producing either JP-4 type or JP-8 type fuel. Hydrocracker feed was the hydrotreated distillate prepared as described in the preceding section.

Scouting runs were carried out with liquid feed processed in a once-through operational mode. The production runs, which also yielded engineering design basis data, were made in a liquid recycle mode. The products accumulated during the production run were then used for blending prototype fuel samples, as described in Section VI.

2. Procedure

The pilot plant facility is described in Section IV-2. It includes an integral product fractionator, a necessity for carrying out liquid recycle-to-extinction type operations. During liquid recycle operation, all material in the reactor effluent which distills above a pre-selected temperature is segregated as fractionator bottoms and continuously recycled to the reactor inlet for further processing. Thus, the liquid feed to the reactor consists of a mixture of fresh feed and liquid recycle. That portion of the reactor effluent which distills at temperatures lower than the pre-selected cut point becomes fractionator overhead, and is recovered as net liquid product.

Generally, operating conditions are selected to achieve conversion levels of about 60 volume percent per pass, calculated on a total reactor feed basis. Representative recycle mode runs require extended operating time at a nominal set of conditions because the entire system, including all inventory in the liquid recycle loop, must reach equilibrium. Ideally, this occurs while net production of the recycle stream is exactly zero. In practice, true extinction recycle operation is difficult to achieve; the condition is approximated by operating as close as practicable to the desired conversion level while producing a very small surplus of recycle. This recycle drag stream is removed from the system as it accumulates. Operating on the other side of equilibrium, i.e., where more recycle oil is consumed than is being produced, is to be avoided because depletion of the unit inventory of recycle oil produces a major unit upset and the entire run must be restarted. Product distributions are adjusted mathematically to account for the small net make of recycle drag stream.

All hydrocracking work was performed with one reactor loading of catalyst. The catalyst was the same composition selected in the bench-scale activity tests performed during Phase II. It consisted of nickel and molybdenum oxides supported on a crystalline silica-alumina matrix, and was intended to represent the performance of current technology molecular sieve type hydrocracking catalysts. Nominal characteristics of the hydrocracking catalyst were:

Composition, wt. %	
NiO	7.3
MoO_3	13.0
Support	
	Crystalline silica-alumina
Form	
	1/8" x 3/8" cylindrical extrudate

Catalyst was loaded into R-1 reactor as a 25 volume percent active mixture: 300 cc of catalyst combined with 900 cc of inert Ottawa sand. The catalyst zone was supported on a bed of tabular alumina. Additional tabular alumina above the catalyst served as a pre-heat zone. The catalyst was pre-sulfided in-place, via the same procedure employed in preparing the hydrotreating catalyst. Following the sulfiding step, start-up and break-in operations with a refinery-derived dewaxed gas oil extended for ~ 4-1/2 days. Preliminary indications were that catalyst temperatures in the vicinity of 630°F would yield satisfactory conversion levels.

Two feedstocks, representing two different levels of total nitrogen content, had been prepared by severely hydrotreating a blend of San Ardo straight run middle distillate plus vacuum distillate from hydrovisbroken San Ardo residuum. Section IV-4-d contains a detailed description of the feedstock preparation work. Of the two feeds, the larger quantity was obtained from the more-or-less steady state operating periods of the distillate hydrotreating production run. It had a nitrogen content of 16.6 ppmw. A smaller quantity of feed was prepared by redistilling the pilot plant liquid product accumulated during operating period #2, when unsteady operations were occurring in both the reactor and separation sections of the pilot plant. The second feed had a nitrogen content of 55.4 ppmw and was used in a single experiment to determine if variation in feed nitrogen content had a significant effect on hydrocracking results.

Table 16 lists physical and chemical characteristics of the two hydrocracking feedstocks. The high nitrogen feed had a slightly lower API gravity, slightly higher distillation curve, and a somewhat higher aromatic content. The sulfur and nitrogen contents in the high nitrogen feed were both about 3-1/2 times those in the standard feed. Directionally, the property measurements reported in Table 16 were consistent with a somewhat lower level of hydroprocessing severity for the higher nitrogen feed

TABLE 16

PROPERTIES OF HYDROCRACKING FEEDSTOCKS

Feed type		Standard	High nitrogen
Physical properties			
Gravity, °API		28.0	26.5
Sp. gravity, 60/60°F		0.8871	0.8956
Distillation, °F(1)			
IBP	483	(439)	(466)
5%	522	(489)	(500)
10%	535	(509)	(518)
20%	557	(540)	(547)
30%	584	(570)	(578)
40%	610	(600)	(608)
50%	637	(629)	(638)
60%	667	(661)	(671)
70%	706	(699)	(711)
80%	756	(751)	(766)
90%	825	(828)	(844)
95%	894	(899)	(912)
FBP		(1036)	(1044)
Chemical Characteristics			
Elemental analysis,			
Carbon, wt %		87.0	87.0
Hydrogen, wt %		13.0	13.0
Sulfur, ppmw		5.0	18.2
Nitrogen, ppmw		16.6	55.4
Bromine No.		<0.5	0.81
Hydrocarbon type, wt % (by ASTM D2007)			
Saturates		77.1	70.9
Aromatics		20.6	28.4
Polars		2.3	0.7

(1) By ASTM D2887 if in parentheses; otherwise, by ASTM D1160.

3. Process Scouting Studies

Preliminary runs were made on a liquid once-through basis, to identify feasible combinations of operating conditions and to evaluate the effects of several operating parameters. Two of these scouting runs were performed after the two recycle production runs were made. Variables and levels investigated included:

Parameter	Levels
Average catalyst temperature, °F	610 to 690°F
Liquid space velocity, hr^{-1}	2.5 to 4.5
Reaction pressure, psig	1500 and 2000
Catalyst aging	after 449 hours
Feedstock nitrogen, ppmw	16.6 and 55.4

During catalyst break-in and conditioning operations with refinery gas oil, product yields suggested temperatures of 610 to 650°F would bracket the desired 60 volume percent conversion level. This was in agreement with Phase II results using the same catalyst. *However, at an average bed* temperature of 610°F, conversion of the standard San Ardo feed was consistently below 20 volume percent, even at a liquid space velocity as low as 2.5 hr^{-1}.

Additional combinations of temperature and space velocity were then examined to obtain increased conversion. Figure 13 summarizes the results of these trials. As noted, conversion levels at 610°F were relatively low, and were virtually unaffected by space velocity reductions from 4.5 to 2.5 hr^{-1}. However, with increasing temperature, not only did conversion increase, but it also became more responsive to space velocity variations. At the most severe combination, conversion was 74 percent. Throughout this series, pilot unit operating data moved in concert with feed conversion levels, e.g., specific gravity and production of low pressure flash gas increased, hydrogen consumption increased, recycle hydrogen purity decreased slightly, and liquid product API gravity increased.

Conditions

Ni-Mo-on-crystalline Si-Al
2,000 psig
Once-through liquid feed
5,000 SCF/bbl H_2/bbl feed

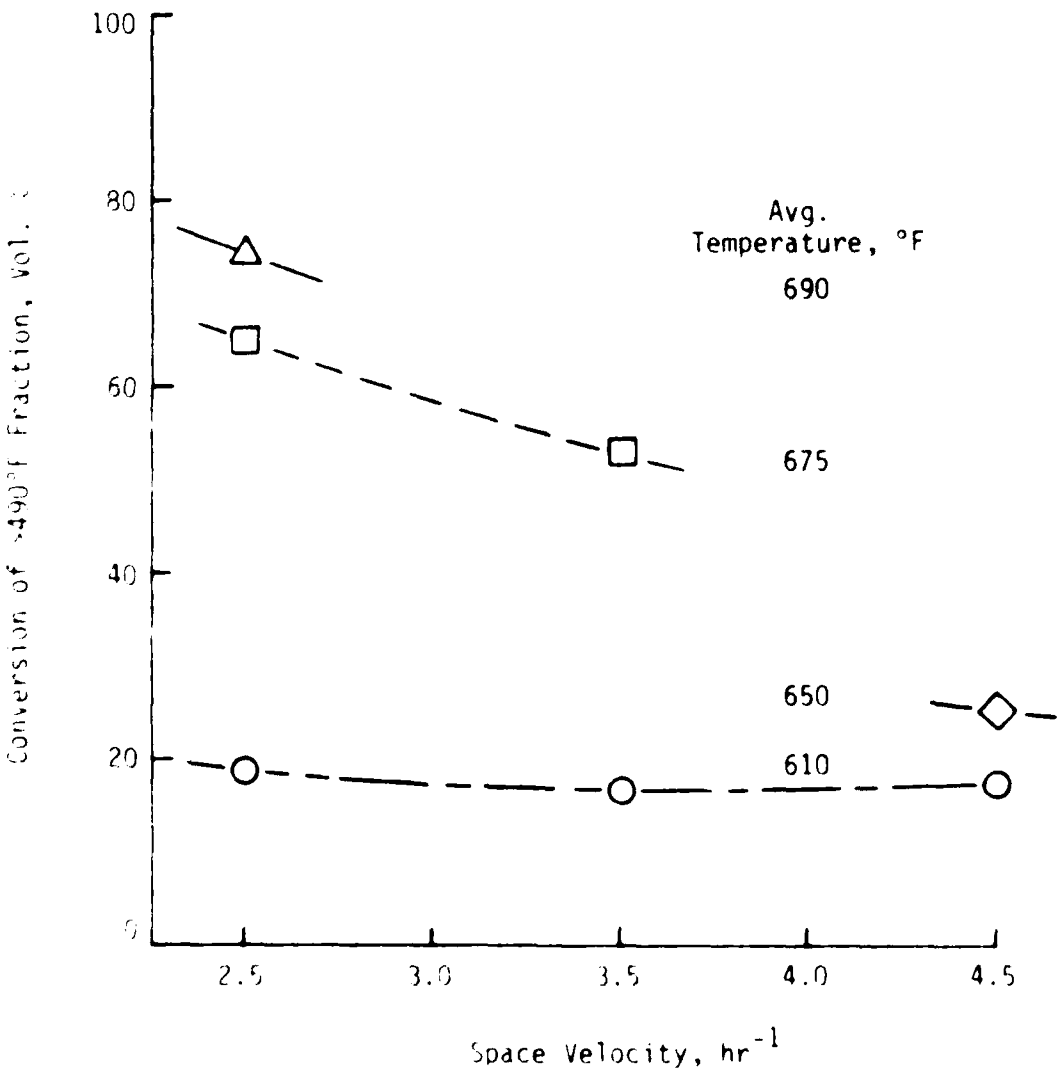


FIGURE 13 TEMPERATURE AND SPACE VELOCITY EFFECTS IN HYDROCRACKING

The above sequence defined combinations of catalyst temperature and liquid space velocity for achieving high fresh feed conversions at 2,000 psig reaction pressure. The feasibility of relaxing design pressure was examined at one of these conditions. When pressure was reduced from 2,000 to 1,500 psig at 675°F catalyst temperature and 2.5 hr^{-1} space velocity, feed conversion decreased from 64.9 volume percent to 58.0 percent. Therefore, we concluded that the hydrocracking plant should be designed for 2,000 psig operation. More comprehensive studies would obviously be of value in defining the cost/benefit relationships involved in changes in operating pressure.

Feedstock quality can also influence hydrocracking operations. In this case, our concern was the amount of nitrogen contained in the feed. We had originally aimed for a feed nitrogen content of 10 ppmw or less, but actually obtained 16.6 ppmw. This material, identified as our "standard" feed, was used for the major portion of these studies. In a pair of back-to-back runs, we compared the standard feed with another containing 55.4 ppmw nitrogen, or about 3-1/2 times that in the standard feed:

Feed	Standard	High Nitrogen
Nitrogen content, ppmw	16.6	55.4
Temperature, °F	← 6.75 →	
Space velocity, hr^{-1}	← 2.5 →	
Pressure, psig	← 2000 →	
Conversion, vol % feed	46.4	27.9

The effect was quite pronounced, and indicated the target feedstock nitrogen content should not be relaxed, at least not to the extent indicated here. Ramifications of hydrocracker feedstock quality are obviously more complex than this single trial. A significant loss in cracking activity was experienced after switching to the high nitrogen feed. Unfortunately, a low inventory of the standard feed prevented our studying how much of this loss was permanent, or what form the nitrogen content vs. activity relationship assumed. The subject merits additional study, in view of the relatively severe hydrotreating conditions required to produce the 16.6 ppmw feed nitrogen content used in these studies.

Although definition of expected catalyst life was not one of the objectives of these scouting studies, the above sequence afforded an opportunity to compare catalyst performance over time. The feed quality comparison was deferred until after the recycle production runs had been completed, to avoid possible deleterious effects on the production runs. This 19-day time interval allowed comparison of results from the "reference" run, made before and after the two extended recycle production runs. The results:

			Δ
Time on stream, hours	265	714	449
Temperature, °F	← 675 →		-
Space velocity, hr^{-1}	← 2.5 →		-
Pressure, psig	← 2000 →		-
Conversion, vol %	61.9	46.1	15.8

Thus, hydrocracking activity was considerably lower after the intervening JP-4 and JP-8 liquid recycle runs, as indicated by the reduction in conversion level from 62 to 46 volume percent. This is a much greater change than would be expected, based on both in-house and commercial plant experience, for that short a time.

At the conclusion of the hydrocracking work, it was discovered that the two production runs were made at a total hydrogen to oil ratio of 3000 to 3300 SCF/barrel, when both gas and oil rates take into account the recycle as well as the fresh feed streams. These rates are about 55 to 60 percent of the 5000 SCF per barrel of fresh feed rate that was maintained during the liquid once-through runs. Generally, higher hydrogen partial pressures help maintain catalyst activity by reducing the rate of coke-on-catalyst formation, but we would not have expected the above difference in gas rates to produce a significant effect.

We have also seen, in the 2000 vs. 1500 psig comparison above, a measurable short-term pressure effect. That study, incidentally, was performed within the 449-hour time span over which the two activity checks were made, and could also have contributed to the apparent activity loss. Additional studies of catalyst life and stability, particularly as they may be related to feedstock quality, would be fruitful endeavors.

4. Recycle Production Runs

Two extended liquid-recycle mode hydrocracking runs were made to generate engineering design bases and to provide hydrocracked product for blending prototype fuels. One run simulated operations for a refinery producing primarily JP-4; the other for a JP-8 based product slate. Both runs were made using the standard feed with 16.6 ppmw nitrogen. The principal difference between the two operational modes was the fractionator cut point target. For JP-4 type operations, the distillation cut point target was 490°F, with all material distilling higher than 490°F being recycled to extinction. For JP-8 type operations, the cut point target was raised to 550°F, which meant that the combined (fresh plus recycle) liquid feed for the JP-8 run would have slightly higher distillation temperatures than for the JP-4 run.

Each run lasted about 5 days, with the early portion of each devoted to making running adjustments in operating conditions to converge on the desired combination of total feed rate, total feed conversion, overhead cut point, and recycle drag stream production. This is particularly challenging when, as in this case, feedstock supply is limited. If recycle oil supply becomes inadequate, the unit upsets, cycles wildly, and the whole process must be begun again. Of the nominal five days operation at each condition, the final 100 hours of JP-4 operations and the final 88 hours of the JP-8 operations were included in the material balance calculations and the product composites.

Table 17 summarizes operating conditions for the stable portions of each production run. The JP-8 run was at a slightly higher catalyst temperature and space velocity than the JP-4 run. In both cases, conversions were somewhat shy of the nominal 60 volume percent. Net

TABLE 17

RECYCLE HYDROCRACKING RUNS

Production mode	JP-4	JP-8
Operating Conditions		
Catalyst	Co-Mo on Zeolite	
Pressure, psig	2000	
Average catalyst temp, °F	675	682
Liquid space velocity, hr^{-1}(1)	2.3	2.5
Hydrogen-to-oil ratio,		
SCF/bbl(1)	3300	3000
SCF/bbl FF(2)	5888	5000
Fractionator cut point, °F target (TBP)	490	550
Results		
Material balance closure, wt %	99.6	97.7
Conversion per pass, vol % feed(1)	54	51
Recycle drag stream, vol % feed(1)	1.5	7.6
Recycle oil/fresh feed, vol ratio(2)	1.3	1.5
Hydrogen consumption, SCF/bbl FF(2)	1822	1494
Fractionator cut point, °F actual, by ASTM D-86	480-516	518-559
Fractionator overhead, vol %(2) (no-loss basis)	93.8	85.4

(1) total feed (i.e., fresh plus recycle) basis
(2) fresh feed basis

production of recycle oil was a very low 1.5 volume percent for the JP-4 run, a bit higher, at 7.6 volume percent, for the JP-8 run. As a consequence, product yield was somewhat reduced for the latter. The actual fractionator cut point for the JP-8 run was generally somewhat less than the target of 550°F. Had the cut point been closer to the desired 550°F, the yield of fractionator overhead would have increased and the amount of recycle drag stream proportionally reduced.

The as-recorded yield data of Table 17 were adjusted to a no-loss basis, and to a no-excess-liquid-recycle basis, in order to define the design basis product distribution. These results are summarized in Table 18. Production of methane was nil, with a modest quantity of ethane and no ethylene. Significant production of higher light hydrocarbons was observed, with about 4 weight percent C_3's and from 12-16 weight percent of both C_4's and C_5's. The olefin proportion of the light hydrocarbons was generally less than 2 percent of the total. Light gas yields and hydrogen consumption were higher for the JP-4 operating mode, as expected for the more severe operations. Large amounts of light hydrocarbons remained in the condensed fractionator overheads, which accounts for the significant differences between the liquid yields reported in Table 17 and the stabilized liquid yields in Table 18.

Table 19 presents physical and chemical characteristics of the stabilized liquid products in each run. The TBP distillation end points of the respective overhead cuts were those nominally associated with the two major product types. Reflecting its higher end point, the C_6^+ liquid from the JP-8 operations contained slightly less hydrogen, more aromatics, and had a slightly higher density. For both products, nitrogen and sulfur contents were significantly reduced, compared to those of the fresh feed. Sulfur removal was about 93 percent, while nitrogen removal exceeded 99 percent. We emphasize that the properties listed in Table 19 are not those of finished turbine fuel products, but of C_6^+ hydrocrackate fractions that would find their way into the final blending/fractionation operation.

TABLE 18

PRODUCT DISTRIBUTIONS - HYDROCRACKING

Production mode	JP-4		JP-8	
Material balance(1)				
Supplied, wt % fresh feed				
Fresh feed	100.0		100.0	
Hydrogen	5.06		3.35	
Sub-total	105.06		103.35	
Recovered, % f.f.	wt	vol	wt	vol
Hydrogen (total)	1.94	-	0.80	-
Hydrogen (net)	(3.12)	-	(2.55)	-
Methane	0.02	-	0.01	-
Ethylene	-	-	-	-
Ethane	0.38	-	0.38	-
Propylene	0.05	0.1	0.18	0.3
Propane	4.21	7.3	3.61	6.3
Butylenes	0.21	0.3	0.24	0.4
i-Butane	11.71	18.4	9.51	15.0
n-Butane	4.35	6.6	4.21	6.4
Pentenes	0.13	0.2	0.10	0.1
i-Pentane	11.03	15.7	9.53	13.5
n-Pentane	1.59	2.2	1.62	2.3
C_6^+ liquid	69.44	81.1	73.16	85.0
Hydrogen consumed, SCF/bbl F.F.	1824		1490	

(1) No-loss basis; adjusted to zero production of liquid recycle

TABLE 19

PROPERTIES OF HYDROCRACKED LIQUIDS

Type operation	JP-4	JP-8
TBP cut points, °F	120-490	120-550
Physical properties		
Gravity, °API	54.8	53.9
Sp. gravity, 60/60°F	0.7594	0.7633
Distillation, °F (by ASTM D-2887)		
IBP	103	97
5%	141	123
10%	157	159
20%	175	186
30%	198	211
40%	214	237
50%	238	254
60%	252	286
70%	281	329
80%	314	412
90%	376	500
95%	423	524
EBP	490	571
Chemical characteristics		
Elemental analysis		
Carbon, wt %	85.6	85.9
Hydrogen, wt %	14.4	14.1
Sulfur, ppmw	0.34	0.32
Nitrogen, ppmw	0.09	0.09
Hydrocarbon type(FIA), vol %		
Saturates	93.4	90.0
Olefins	0.0	0.0
Aromatics	6.6	10.0

SECTION VI

FUEL SAMPLES

1. Introduction

Contract requirements included prototype samples made by the process scheme under study. We used liquid products from the various pilot plant operations previously described, obtained when the units were operating at design basis conditions. The various blend components were combined in yield proportions prior to a final fractionation.

Two specification type fuels were prepared in multi-gallon batches and compared with JP-4 and JP-8 aircraft turbine fuel requirements. In addition, two versions of variable quality fuel, for which no formal specifications exist, were prepared. The latter two fuels had higher distillation ranges than the former, which meant they could not be prepared from the hydrocrackate representing JP-4 or JP-8 production modes. Accordingly, the two variable quality fuels were formulated to represent an alternate processing scheme which did not include hydrocracking. However, the inventory of ingredients limited these samples to about 1-1/2 liters each.

2. Component Blending

Figure 14 illustrates how the process concept presented in Figure 1 was implemented in the ARD pilot plant facilities. The component streams used for blending the prototype fuels are labeled A through E in Figure 14.

The JP-4 type and JP-8 type fuel blends consisted of three components, viz. hydrotreated naphtha (stream A), the forecut from hydrotreated distillate (stream B), and hydrocracked distillate (stream C or stream D). Streams C and D differ in the nominal recycle oil cut points maintained during hydrocracking, simulating JP-4 or JP-8 operations, respectively.

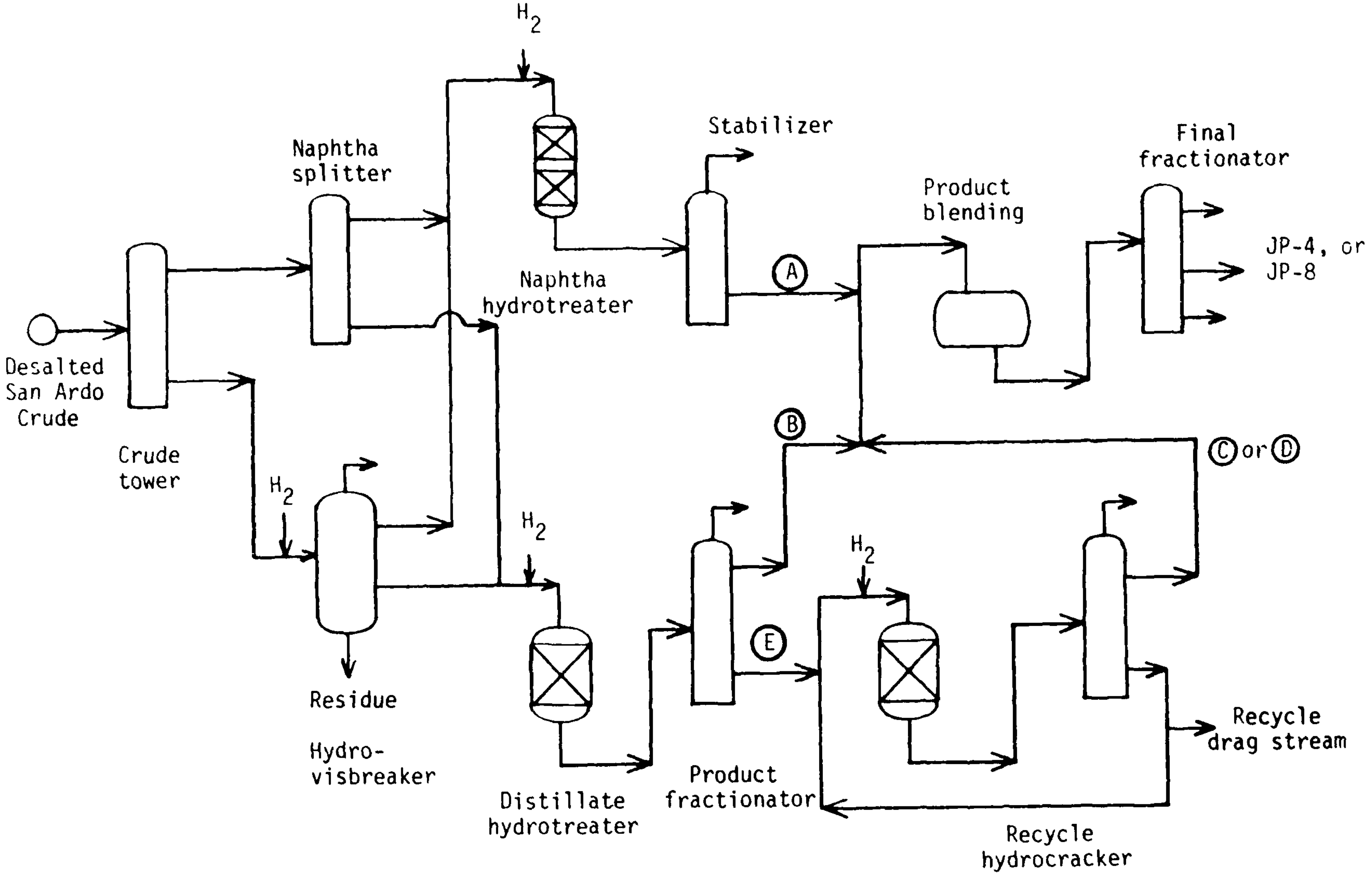


FIGURE 14 PROCESSING AND BLENDING PROTOTYPE SAMPLES

The component blending compositions for the two specification type fuels were:

Component	Stream Code	Volume % in blend for JP-4	Volume % in blend for JP-8
Hydrotreated naphtha	A	33.9	34.3
Naphtha forecut	B	13.9	14.1
Hydrocracked product			
490°F cut point	C	52.2	-
550°F cut point	D	-	51.6
Total		100.0	100.0

These proportions were derived from pilot plant or process simulation yields for each processing step, after adjusting the hydrocracker yields to equilibrium operation (i.e., no recycle drag stream).

Conceptually, turbine fuels with even higher distillation end points, such as the two variable quality fuels, could have been prepared merely by stepwise increases in the cut point of the hydrocracker recycle oil. This approach would have generated a series of fuels produced via the same process sequence but with increasing distillation limits. However, various program constraints rendered this approach not practicable, and an alternative process scheme was adopted. For the two variable quality turbine fuels, it was assumed that the distillate hydrocracking unit was bypassed, and fuels were blended only from hydrotreated components. We emphasize 1) the rationale for this approach was simply that the higher cut point hydrocracking production runs had not been made; it does not imply that either is the preferred route for the variable quality fuels, and 2) having been produced by an entirely different process, the two variable quality fuels do not lie on a continuum which includes the two specification type fuels. Specifically, the two lighter fuel blends contained over 50 volume percent hydrocracked distillate; the two variable quality fuels, none.

In lieu of hydrocracked distillate, the variable quality fuel blends contained hydrotreated distillate (stream E), actually the feed to the hydrocracker in the JP-4/JP-8 process concept. It was the only available stream with suitable distillation range and nitrogen content. The blend composition for both variable quality fuels was:

Component	Stream Code	Volume percent in blend
Hydrotreated naphtha	A	34.0
Naphtha forecut	B	13.9
Hydrotreated distillate	E	52.1
Total		100.0

3. Blend Fractionation

Each of the above blends was fractionated in a high resolution, true boiling point batch distillation. Still charges were 12 gallons for the specification type fuels and about 3 liters for the variable quality fuels. We collected several overhead fractions during the distillation. To prevent contamination or chemical change during storage, each still fraction was immediately transferred to an epoxy-lined steel can and maintained under an inert atmosphere during refrigerated storage. As soon as practicable, fractions were treated with 8.4 pounds per thousand barrels of a hindered phenol type antioxidant (di-tertiarybutyl-para-cresol). The nitrogen atmosphere was restored after each opening of the can.

For the two specification type fuels, small portions of the still cuts were re-blended in various combinations, to establish which could be included in the final fuel blend without exceeding the specification limits for front end volatility or freeze point. Compositions of the final, large blends were determined by these hand blend results.

The high density, variable quality fuels were defined solely by their distillation ranges. Therefore, the intermediate step of preparing hand blends to test against specification limits was unnecessary.

The component blend for the JP-4 prototype fuel was fractionated into the following overhead cuts, with yields as indicated:

TBP range of cut °F	Vol. % of still charge	In final blend?
Initial-to-90	9.5	-
90-to-120	1.1	Yes
120-to-450	76.4	Yes
450-to-475	6.8	Yes
>475	6.2	-
TOTAL	100.0	

Turbine fuel yield, % still charge 84.3

As indicated, TBP fractions from 90°F through 475°F, representing 84.3 volume percent of the still charge, were included in the final fuel blend. Preliminary tests of the 90 to 475°F blend showed fuel volatility was slightly under the Reid vapor pressure (RVP) requirement of 2.0 to 3.0 lb. Addition of 2 volume percent solvent grade isopentane increased RVP to the middle of that range. Isopentane was used because it was the predominant hydrocarbon (58 weight percent) in the initial to 90°F cut, while solvent grade material afforded a more reliable vapor pressure blending value than the mixed hydrocarbons in the initial cut.

After removal of the test samples, approximately 9-1/2 gallons of the prototype fuel sample remained for shipment to WPAFB.

The component blend for the JP-8 type fuel was fractionated into the following overhead cuts, with yields as indicated.

TBP range of cut, °F	Vol. % of still charge	In final blend?
Initial-to-120	9.0	-
120-to-275	36.7	-
275-to-300	5.9	Yes
300-to-475	39.9	Yes
475-to-500	3.9	Yes
>500	4.6	-
Total	100.0	

Turbine fuel yield, % still charge 49.7

The final fuel blend included the 275 to 500°F distillation range material, or a 49.7 volume percent yield on still charge. The reduced yield results from exclusion of material boiling below 275°F, nearly one-half the still charge, to meet the flash point minimum of 100°F.

After sampling, approximately 4-1/2 gallons of prototype blend remained for shipment to WPAFB.

The component blend for the two variable quality fuels was fractionated, in two separate still charges, into the following cuts, with yields as indicated:

TBP range	Variable quality fuel, vol. % still charge	
of cut, °F	300-to-575°F	300-to-675°F
Initial-to-120	0.3	0.3
120-to-300	14.4	14.6
300-to-575	51.2	-
300-to-675	-	67.6
575-to-675	17.9	-
>675	16.2	17.5
Totals	100.0	100.0

Since the fuels were defined solely by their TBP distillation range, there was no need to reblend still fractions to meet specification limits. Yields of the variable quality fuels, based on the charge to the still, were 51.2 volume percent for the 300 to 575°F fuel and 67.6 volume percent for the 300 to 675°F fuel.

After sampling for tests, approximately 1.2 liters of each sample were available for shipment to WPAFB.

4. Prototype Fuel Properties

Table 20 lists key properties of the JP-4 prototype fuel sample and compares the values with those in the JP-4 specification. In all categories

TABLE 20

PROPERTIES OF PROTOTYPE JP-4 FUEL

Identification	Prototype wide-cut gasoline	Specification limit MIL-T-5624L
Code	DRS 651	JP-4
Properties		
Color, Saybolt	29	(1)
Gravity, °API	51.1	45.0-57.0
Sp. gravity, 60/60°F	0.7749	(3)
Reid vapor pressure, lb.	2.5	2.0-3.0
Distillation, °F(2)		
IBP	138 (138)	(1)
10%	204 (165)	(1)
20%	225 (184)	293 (266) max.
50%	304 (242)	374 (365) max.
90%	427 (375)	473 (482) max.
FBP	447 (425)	518 (608) max.
Freezing point, °F	-72	-72 max.
Viscosity, cSt @ -20°F	2.26	(3)
Copper strip corrosion, 2 hrs @ 100°C	1b	1b max.
Total acid no., mg KOH/g	0.007	0.015 max.
Existent gum, mg/100 ml	1	7.0 max.
Thermal stability (JFTOT)		
change in Δp, mm Hg	0	25 max.
deposit rating	0	less than 3
Net heat of combustion, BTU/lb	18,608	18,400 min.
Hydrogen content, wt.%	14.0	13.6 min.
Aromatics, vol.%	8.8	25.0 max.
Olefins, vol.%	0.0	5.0 max.
Sulfur, total, wt.%	0.00017	0.40 max.
Nitrogen, ppmw	0.4	(3)

(1) To be reported - not limited
(2) By ASTM D-86 or, when in parentheses, by D2887
(3) Not listed in specification; for info only

tested, the prototype fuel was well within the specification limits. Reflecting the high degree of hydroprocessing, the fuel exhibited excellent thermal stability (JFTOT method). Heteroatom contents were in the parts-per-million range, and chemical composition (hydrogen content, aromatics content) indicates combustion properties should be acceptable. Low temperature properties appear adequate.

Table 21 lists key properties of the JP-8 prototype fuel sample and compares them with appropriate specification requirements. Again, all values readily satisfied the specification limits. Thermal stability was excellent, and heteroatom contents were extremely low. Fuel composition (hydrogen, aromatics contents) was consistent with the measured heat of combustion. The low temperature properties, in particular the freeze point, were very good. The measured freeze point of -80°F so exceeded the required -58°F that it suggests the hydrocracker operations might have safely been run for an even higher product cut point. This is supported by comparing the distillation curve with that of the JP-4 prototype; they have very similar distillation tail ends, which is the portion of the sample usually associated with freeze point behavior.

Table 22 list selected properties of the two variable quality prototype fuels. No specification or target limits are shown. The fuels were extremely clean (low carbon residue) with excellent low temperature properties. Freeze point increased modestly as fuel distillation range widened. The reporting of significant olefins in the heavier sample is questionable, and undoubtedly results from applying the FIA procedure to an unsuited sample, rather than representing actual composition. Elemental analysis suggests acceptable combustion characteristics, while heteroatom contents were not quite as low as observed in the prototype fuels containing hydrocracked distillate.

The two variable quality fuels have physical characteristics comparable to domestic No. 2 diesel fuels. Although sample size was inadequate for cetane number testing, other properties allowed calculation of cetane index numbers by ASTM method D976 --41.3 for the lighter fuel and 43.0 for the heavier. A method based only on aniline point (Reference 4) produced estimates of 43.6 and 47.4, respectively. While not to be taken too literally, since the validity of both methods for this type sample has not been established, the values suggest reasonable combustion quality fuels for compression ignition engines.

TABLE 21

PROPERTIES OF PROTOTYPE JP-8 FUEL

Identification	Prototype kerosene	Specification limit MIL-T-83133A
Code	DRS 650	JP-8
Properties		
Color, Saybolt	22	(1)
Gravity, °API	41.3	
Sp. gravity, 60/60°F	0.8187	37-51
Reid vapor pressure, lb.	110	100 min.
Distillation, °F(2)		
IBP	308 (310)	(1)
10%	335 (327)	401 (367) max.
20%	346 (342)	(1)
50%	386 (390)	(1)
90%	449 (465)	572 (626) max.
FBP	459 (465)	572 (626) max.
Freezing point, °F	-80	-58 max.
Viscosity, cSt @ -20°F	5.55	8.0 max.
Copper strip corrosion, 2 hrs @ 100°C	lb	lb max
Total acid no., mg KOH/g	0.0014	0.015 max.
Existent gum, mg/100 ml	1	7.0 max.
Thermal stability (JFTOT)		
change in Δp, mm Hg	0	25 max.
deposit rating	0	less than 3
Net heat of combustion, BTU/lb	18,532	18,400 min.
Hydrogen content, wt.%	13.7	13.5 min.
Aromatics, vol.%	16.9	25.0 max.
Olefins, vol.%	0.0	5.0 max.
Sulfur, total, wt.%	0.00026	0.3 max.
Nitrogen, ppmw	0.7	(3)

(1) To be reported - not limited.
(2) By ASTM D-86 or, when in parentheses, by D2887.
(3) Not listed in specification; for info only.

TABLE 22

PROPERTIES OF VARIABLE QUALITY FUELS

Fraction of blend(1)	300-to-575°F (TBP) cut		300-to-675°F (TBP) cut	
Code	DRS 647		DRS 648	
Physical properties				
Gravity, °API	36.8		34.5	
Sp. gravity, 60/60°F	0.8407		0.8525	
Flash point, °F	143			
Distillation, °F(2)				
IBP	343	(346)	344	(358)
5%	378	-	381	-
10%	389	(379)	394	(393)
20%	405	(401)	413	(417)
30%	419	(416)	443	(438)
50%	452	(437)	488	(475)
70%	485	(476)	546	(540)
80%	506	(496)	578	(570)
90%	533	(513)	609	(598)
95%	549	-	628	-
FBP	551	(544)	635	(630)
Freezing point, °F	-43		-37	
Viscosity, cSt °F				
-20°F	13.40		29.05	
100°F	2.00		2.74	
210°F	0.908		1.12	
Chemical characterization				
Elemental analysis,				
Carbon, wt.%	86.3		86.8	
Hydrogen, wt.%	13.7		13.3	
Sulfur, ppmw	1.3		8.5	
Nitrogen, ppmw	0.24		0.66	
Hydrocarbon type (D1319), vol.%				
Saturates	79.4		73.3	
Olefins	0.7		6.9	
Aromatics	19.9		19.8	
Aniline point, °F	138.7		146.4	
Carbon residue, wt.%	0.10		0.12	
Net heat of combustion, BTU/lb	18,506		18,461	

(1) Blend composition: 34.0 vol.% hydrotreated naphtha, 13.9 vol.% naphtha forecut, 52.1 vol.% hydrotreated distillate

(2) By ASTM D86 or, when in parentheses, by D2887

SECTION VII

ENGINEERING DESIGN AND COST ESTIMATE

1. Introduction

Experimental data from each pilot plant processing step generated appropriate process design bases. These bases became the foundation for the engineering design of a stand-alone refinery with a capacity to convert 50,000 BPSD of San Ardo heavy crude oil into turbine fuel products.

In view of the size and detail involved in a design project of this scope, this discussion is confined to an overview and summary. A supplemental engineering design package (Reference 5), containing individual process descriptions, equipment specifications, details of the capital costs, and components of refinery operating costs, has been issued as Volume II of this report. Copies of the design package were delivered to the Air Force Project Engineer at the conclusion of the program.

The refinery process concept was shown earlier in Figure 1, it having emerged from Phase I case studies and having been demonstrated in Phase II bench-scale work. The processing objective was the exclusive production of wide-cut gasoline, or JP-4 type, aviation turbine fuel. The configuration of processing units was arranged, however, to allow the production of kerosene, or JP-8 type fuel, with a minimum of equipment or operational changes. This effort was successful, and the resultant refinery scheme is capable of operating in a blocked out mode, i.e., switching from one product slate to the other, by changing only one primary control parameter. In addition, one fractionation column in the product separation train can be shut down during JP-8 production.

Economic assumptions upon which the following calculations and estimates are based were agreed to in January 1986, and are listed in Table 23. Significant changes have since occurred, notably in the tax structure and in crude costs. However, to retain comparability with other studies, the bases shown in Table 23 were retained for this assessment. Some effects, such as crude pricing, could be addressed in sensitivity studies; others would require more extensive re-structuring of the economic evaluation computer model.

2. Process Description

The refinery design includes not only those units directly associated with the conversion of heavy crude into turbine fuel, but also those auxiliary units required to support the processing side and to assure environmental compliance. The designs for the processing units originated in the experimental work described in the preceding sections of this report, details for which are included in the separate engineering design report. In general, the auxiliary units, e.g., hydrogen purification, sulfur recovery plant, etc., are vendor-supplied as complete packages, and design details are proprietary.

Figure 15 is a refinery block diagram illustrating the major operating units. Many of the inter-plant streams have been omitted from Figure 14, to improve clarity of the following discussion.

Crude oil, at 50,000 BPSD, is first charged to the crude unit, where it is diluted with recycled straight run naphtha, passes through 2-stage desalting, and then is fractionated into a straight run distillate fraction and a >650°F atmospheric reduced crude. The reduced crude, representing 79 volume percent of the whole crude, is charged to a hydrovisbreaking unit where it undergoes thermal hydrocracking. About 70 volume percent of the >975°F residuum contained in the reduced crude feed is converted to lower boiling products. The hydrovisbroken synthetic crude is separated into gaseous, naphtha, distillate and residuum streams. Feed sulfur conversion exceeds 60 percent; therefore, a high pressure amine scrubber is included to remove hydrogen sulfide from the recycled hydrogen stream. Recovered hydrogen sulfide is directed to the sulfur recovery plant.

TABLE 23

ECONOMIC BASES

CAPITAL INVESTMENT

Plant Location: Salt Lake City, Utah

Refinery Capacity: - 7,500 bbls/day for Tar Sands
- 50,000 bbls/day for Heavy Oil

Cost Base: 4th Quarter 1985

Plant Off-Sites: - 45% of plant on-sites minus cost of specified tankage for Heavy Oil refinery.

- 80% of plant on-sites minus cost of specified tankage for Tar Sands refinery.

Financing: - 100% Equity
- Three-year plant construction period
  25% 1st year
  50% 2nd year
  25% 3rd year

Investment Tax Credit: 10% 1st year

WORKING CAPITAL

Crude Inventory: 21 days storage capacity/14 day inventory.

Product Inventory: 14 days storage capacity/7 day inventory.

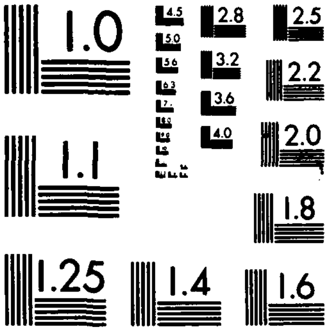
Crude Material: $20/bbl (tar sands bitumen or heavy oil).

Product Price: All liquid military transportation fuels, gasoline, JP-4, JP-5, JP-8, DF-2, valued at equal value as calculated for a 15% DCF rate of return

- Fuel Gas $20.00/FOE BBL
- Propane $16.00/BBL
- Iso Butane $31.00/BBL
- Normal Butane $29.00/BBL
- Ammonia, Anhydrous $210.00/Short Ton
- Sulfur $125.00/Long Ton
- Residual Fuel Oil $20.00/BBL

Debt Financing: 15% (including the cost of [illegible]

AD-A184 059 TURBINE FUELS FROM TAR SANDS BITUMEN AND HEAVY OIL 2/2
VOLUME 1 PHASE 3 PILOT (U) SUN REFINING AND MARKETING
CO MARCUS HOOK PA APPLIED RESEARCH A F TALBOT ET AL
UNCLASSIFIED AUG 87 AUG 87 AFWAL-TR-87-2043-VOL-1 F/G 21/4 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

TABLE 23 (continued)

CAPITAL RETURN

Discounted Cash Flow Rate: 15%

Plant Salvage Value: Zero

Plant Depreciation: 5 year accelerated cost recovery system.

OPERATING BASIS

Plant Life: 16 years

Plant Operating Factors: 50% Capacity 1st Year

Plant on Stream Factor: 90% after 1st Year

Startup Costs: 10% of estimated erected plant costs

OPERATING COST BASIS

Process Heat: $20.00/BBL FOE

Cooling Water: 7¢/1000 Gallons

Boiler Feed Water: 40¢/1000 Pounds

Electrical Power: 5¢/KWHR

Steam: Costed from the simple sum of enthalpy over 60°F Base @ FOE plus cost of boiler feed water.

Operator[1]: $16.00/manhour

Helpers[1]: $14.00/manhour

Supervision: 25% of direct labor

Overhead: 100% of direct labor

Taxes: Federal and state combined @ 50%

Maintenance, taxes, insurance: 4.5% of fixed investment

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[1] 4.2 shift positions plus 10% relief required for continuous plant operation.

Note: *Dotted line show products flow during JP-8 operation.*

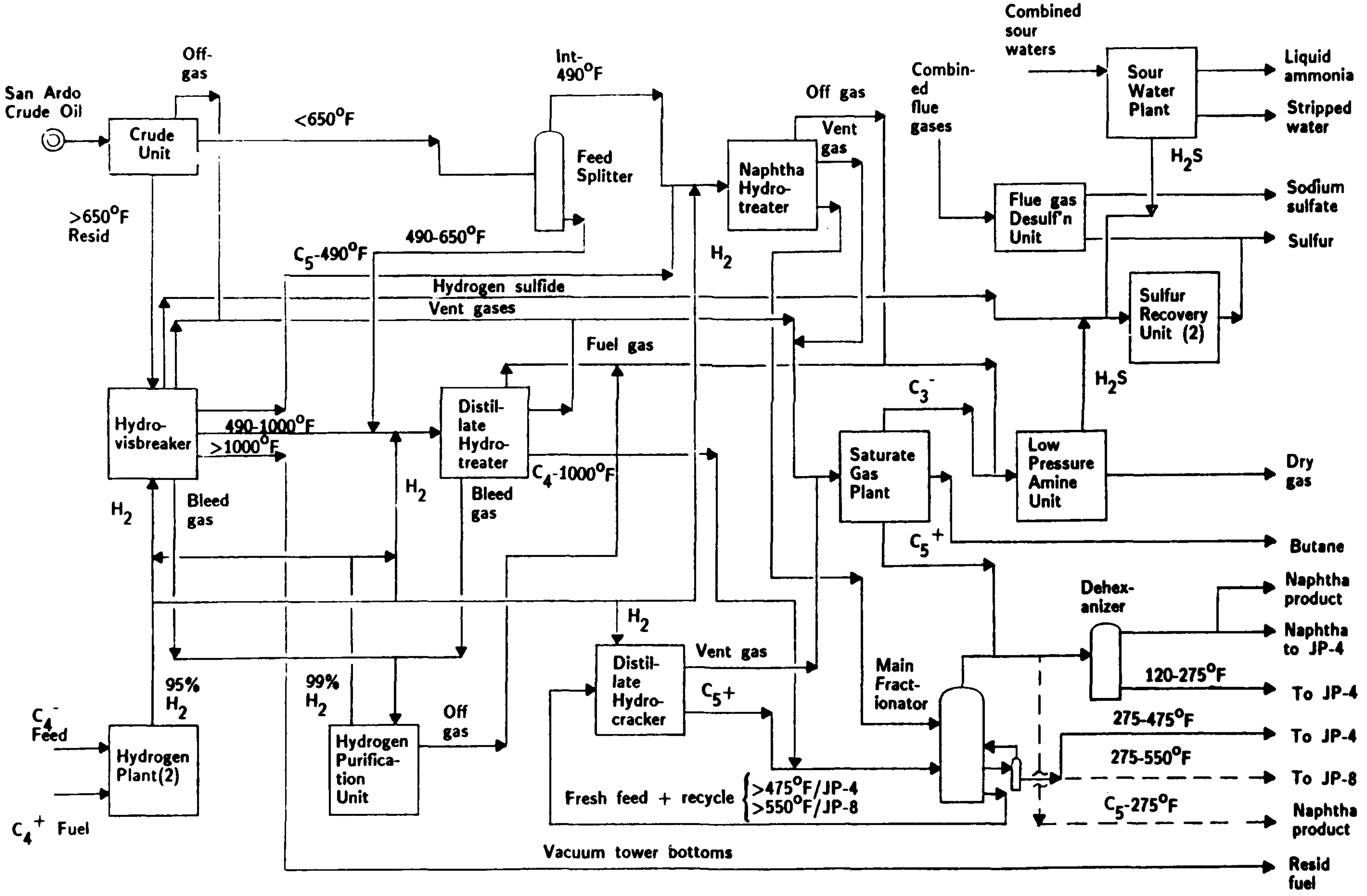

FIGURE 15 REFINERY BLOCK FLOW DIAGRAM

Straight run distillate from the crude unit is charged to the feed splitter of the naphtha hydrotreating plant, where it is fractionated into naphtha and middle distillate cuts. The higher boiling straight run middle distillate cut proceeds to the distillate hydrotreating unit; the straight run naphtha remains and is joined by the hydrovisbroken naphtha stream. The combined naphtha streams are catalytically hydroprocessed in the naphtha hydrotreater to reduce olefin, heteroatom, and aromatics to acceptable levels. The hydrotreated naphtha is stripped and stabilized, then charged to the main product fractionator.

Feed to the distillate hydrotreater consists of streams from two different plant areas: the straight run gas oil or splitter tower bottoms from the naphtha hydrotreater plant, and the vacuum distillate from the hydrovisbreaker syncrude fractionation unit. The combined distillates are also catalytically hydroprocessed to reduce olefin, heteroatom, and aromatics contents, producing acceptable quality hydrocracker feed. Hydrotreater processing conditions are relatively severe and considerable reduction in both feed molecular weight and distillation range occurs. It is therefore advantageous to direct the hydrotreater plant product, after preliminary stripping/stabilization, directly to the main product fractionator, rather than to the hydrocracking reactor.

In the main product fractionator, the hydrotreated distillate is freed of its naphtha boiling range components before proceeding, along with recycled hydrocracked liquid, to the hydrocracking reactor. Operating conditions within the hydrocracking reactor produce a total feed conversion of approximately 60 volume percent per pass. Reactor effluent enters the hydrocracker product separation system, which includes a prefractionator column to remove dissolved gases and light condensibles, a dehexanizer to split light naphtha, and the main fractionator which separates recycle oil from the kerosene range product. JP-4 type product is produced by appropriate blending of stripped main fractionator side draw with dehexanizer overhead and bottoms. For JP-8 operation, the dehaxanizer can be shut down, the recycle cut point increased about 60°F, and the main fractionator sidestream becomes the primary turbine fuel product.

Auxiliary plants shown in Figure 14 perform essential functions in support of the main processing units. Each primary processing unit produces some light ends, i.e., hydrogen plus methane through C_5 hydrocarbons. Off-gases from all three plants are collected and processed in the saturate gas plant. The gas plant includes absorber/stripper unit and debutanizing tower, and separates the feed gas into light naphtha, butane, refinery fuel gas, and dry gas (i.e., C_3 and lighter). The naphtha goes to product fractionation and the butane to storage.

Dry gas, which contains considerable hydrogen sulfide, is processed in the low pressure amine unit. Here, the circulating alkanolamine reagent contacts the dry gas to remove most of the hydrogen sulfide, which is driven off in the amine stripper. The hydrogen sulfide proceeds to the sulfur plant; the cleaned-up dry gas becomes hydrogen plant feed.

Two parallel hydrogen plants convert light hydrocarbon gases to hydrogen by the steam reforming process. By-product butane and light naphtha fuel this high temperature operation, which generates considerable high pressure steam for refinery use. The dry gas feed from the amine unit is further desulfurized and combined with water (plant condensate) before passing through the reformer furnace, high temperature shift, and low temperature shift reactors. A potassium carbonate absorber/stripper combination removes carbon dioxide and a methanation reactor removes residual carbon monoxide. The resultant 95 percent purity hydrogen is supplied to the hydrovisbreaking plant and both hydrotreating units.

This purity level is adequate for the naphtha hydrotreater and distillate hydrocracking plants, but not for the hydrovisbreaking or distillate hydrotreating plants. A hydrogen purification unit receives high pressure bleed gas from each of these two units, recovers some energy from the two streams via a turbo-expander, and processes the gas through a pressure swing adsorption unit. The solids-filled beds alternate between adsorption and depressurization cycles, to produce purified (99 percent) hydrogen and a tail gas which proceeds to the low pressure amine unit. Recompressed hydrogen returns to the two source units.

Sour process water, generated at the several operating units, requires treatment before reuse or disposal. Inorganic contaminants consist principally of ammonia, hydrogen sulfide, or chemical combinations of the two in various forms. The sour water stripping plant first strips the incoming water of residual combustible gases, then sequentially steam strips the water of hydrogen sulfide and ammonia. Plant products are stripped sour water available for re-use, liquid ammonia for sale, and hydrogen sulfide, which is supplied to the sulfur recovery unit.

Hydrogen sulfide from the three plant areas (hydrovisbreaker, waste water, and low pressure amine unit) supplies the sulfur plant, which includes a Claus sulfur unit and a tail gas clean-up unit. The Claus unit partially reacts hydrogen sulfide and oxygen (air) to produce molten elemental sulfur. The combustion gases from the Claus unit include low concentrations of sulfur oxides, preventing their direct release. The tail gas unit reduces the sulfur content to acceptable levels by catalytic reduction to hydrogen sulfide, followed by extraction of the hydrogen sulfide with alkanolamine. The hydrogen sulfide is returned to the front end of the Claus unit, and the scrubbed gases vented. The primary plant product is saleable molten sulfur.

Several process fired heaters operate on residual fuel, which is produced as syncrude vacuum tower bottoms in the hydrovisbreaking plant. Sulfur content of the resid fuel is high enough that the flue gas requires desulfurization before release to the stack. The Wellman Lord/Davy Powergas process was selected because it is regenerable, producing saleable molten sulfur plus a small amount of sodium sulfate by-product. It thus avoids the large waste disposal problems attending non-regenerable processes. In the FGD plant, flue gases are scrubbed with a sodium sulfite solution, which removes sulfur oxides while being converted to sodium bisulfite. The sulfur-free gases pass to the stack. The sodium bisulfite solution is heated to regenerate sodium sulfite, releasing sulfur dioxide-rich off gas. A small amount of sodium sulfate is a saleable by-product. The sulfur dioxide gas is catalytically reduced with natural gas to form molten elemental sulfur. Tail gas from the primary reduction zone passes through a two-stage secondary reduction zone where more sulfur is formed. Exhaust gas from this second zone is returned to the boiler house stack.

3. Refinery Material Balance

In Sections II through V, detailed material balance and product distribution data were presented for each of the pilot plant design basis operations. The summation of these individual operations required further adjustment, however, to arrive at an overall refinery material balance. The purpose of these adjustments was to maximize the utilization of those components or fractions unsuited for inclusion in the primary product, simultaneously satisfying each operating unit's non-feedstock requirements. These requirements included hydrogen, steam, and fuel, while the available components included methane through butane light hydrocarbons, and syncrude residue.

Total hydrogen requirements for the four major hydroprocessing units were satisfied by the twin hydrogen steam reforming plants, augmented by the hydrogen purification plant. The reforming units relish very clean feedstock, so refinery dry gas (hydrogen through propane) received priority for that application. High temperature reformer furnaces, meanwhile, were fueled by the butane and/or light naphtha fractions. Other refinery fired heaters and the boilerhouse requirements were met by use of hydrovisbreaker vacuum tower bottoms. These operations consumed some 85 percent of the available resid fuel, leaving about 700 BPSD for sale. Thus, the imposition of hydrogen and energy requirements resulted in a net refinery product slate that is impressively concentrated in aviation turbine fuel. Table 24 summarizes major stream flows of interest.

Primary refinery feed included 50,000 BPSD of crude oil, the deposit control additive, and hydrogen produced in the two hydrogen plants. All the dry gas produced in the process units was consumed in the production of that hydrogen, while all of the butane and a portion of the naphtha were required to fuel the hydrogen plants. The remaining naphtha, about 3300 BPSD, can be sold for gasoline blending, as it is predominantly isopentane. Most of the resid (85%) was used within the refinery; the excess, less than 1,000 BPSD, is sold. This hydrovisbroken VTB showed poor compatibility with a catalytic light cycle oil cutter stock in brief laboratory tests. Thus, it would have to be handled as a solid or molten liquid, somewhat limiting its

TABLE 24

REFINERY MATERIAL BALANCE

	Gross MSCFH	Gross lb/hr	Gross BPSD or TPSD	Net to Sales BPSD or TPSD
Feed(1)				
Crude oil	-	715,195	50,000	-
Additive	-	2,690	-	-
Hydrogen (95%)	-	43,336	-	-
		766,221		
Products				
Dry gas(2)	2,036	69,889	-	-
Butane(3)	-	55,820	6,726	0
Naphtha(4)	-	49,414	5,335	3,289
JP-4	-	499,126	44,294	44,294
Residuum(5)	-	74,128	4,688	681
Sulfur, lb or long tons	-	14,398	154.3	154.3
Ammonia, lb or short tons	-	8,367	100.4	100.4
Sodium sulfate, lb or short tons	---	272	3.3	3.3
		771,414		

(1) To process units.
(2) All consumed as hydrogen plant feed.
(3) All consumed as hydrogen plant feed (17%) or fuel (83%).
(4) Partly (38%) consumed as hydrogen plant fuel; remainder sold.
(5) Partly (85%) consumed as refinery fuel; remainder sold.

marketability. Since it is soluble in toluene, other cutter stocks may be more effective than the one tested here. Alternatively, a very slight increase in hydrovisbreaker severity could easily reduce the net resid to zero.

The far right column of Table 24 shows the net refinery products, and their quantities, for sale. The 44,292 BPSD of JP-4 represents a volumetric yield of 88.6 percent of the 50,000 BPSD crude charged. This compares favorably with the 92.2 volume percent which had been projected in the Phase I case studies made with a different heavy crude.

An energy balance around the outer bounds of the refinery would include auxiliaries and utilities (electricity, natural gas, boiler house). Including those requirements, the overall refinery thermal efficiency is calculated to be 84 percent.

Refinery yields for the JP-8 operational mode were estimated from pilot plant operations, coupled with the detailed process simulation computer models employed for the JP-4 analysis. It was also assumed that slightly lower process hydrogen requirement for JP-8 mode operation was in balance with the slightly lower dry gas make. The major difference between the two operations, then, is that much of the light naphtha contained in the front end of the JP-4 does not go into the final fuel blend, but is sold separately. Comparative fuel yields were:

	Est'd yield for indicated mode, Vol.% crude	
Product	JP-4	JP-8
JP-4	88.6	-
JP-8	-	50.7
>120°F Naphtha	-	37.3

As anticipated, turbine fuel yield is significantly reduced in the JP-8 operating mode. However, most of the volume shift is to a 120-275°F light naphtha, with compcsition and properties as shown in Table 25. The naphtha

TABLE 25

PROPERTIES OF NAPHTHA FROM JP-8 OPERATION

TBP fraction	120-275°F
Physical properties	
Gravity, °API	61.1
Sp. gravity, 60/60°F	0.7345
Distillation, °F (by ASTM D86)	
IBP	152
5%	177
10%	181
20%	188
30%	195
40%	201
50%	208
60%	217
70%	226
80%	234
90%	245
95%	255
FBP	270
Chemical characteristics	
Acid treat, vol. %	6.4
MS PONA	
Paraffins (n- plus iso-)	44.2 (est. 19.9 normal)
Olefins	0.0
Cycloparaffins, total	49.4
mono	48.8
di- and tri-	0.5
Aromatics, total	6.4
benzene	0.4
toluene	3.6
C_8	2.3

would be an excellent charge stock to a catalytic reformer for the production of either high octane unleaded gasoline component or for benzene/toluene/xylene petrochemicals. Figure 2A of the Appendix presents a yield-octane curve derived by computer model, for the catalytic reforming of this high quality naphtha. Excellent yields are obtained, even at clear research octane numbers approaching 100.

4. Plant Capital Cost

A capital cost estimate was generated for a grass-root refinery upgrading 50,000 BPSD San Ardo crude oil into ~44,000 BPSD JP-4 type aviation turbine fuel. The estimate applies to a Salt Lake City, Utah location in the fourth quarter of 1985. The estimate is of Phase 1 quality, suitable for comparison studies, economic evaluations, management review and budget appropriations, and is based on equipment lists, flow diagrams, vendor quotes and historical in-house equipment costs. Details of the cost estimate are included in the separate engineering design package; highlights are given here.

For the major processing units, equipment specification sheets were prepared based on computer simulation of each process flow sheet. Equipment sizes and operating environment were listed for each major item. Installed costs were developed from factored materials cost estimates. Additional factors applied to the summations of major equipment installed costs accounted for instrumentation, home office costs and contingencies, to arrive at total direct installed costs.

Several auxiliary units are available from vendors as packaged systems. In these cases, detailed equipment specification sheets were not generated, and total direct installed costs were by vendor estimate for the turnkey plant, based on performance specifications supplied by us.

Table 26 summarizes the refinery capital investment, breaking it down by operating plant areas. In the main processing units, major equipment items were defined and factored up to installed costs. Generally, auxiliary plants were by vendor quotes for the packaged plant. Total direct installed costs for the combined processing plus auxiliary plants and tankage was nearly $800 MM. Offsites, as specified by the Air Force, was another 45 percent of the total battery limits capital, excluding tankage. This added another one-third of a billion dollars. Total fixed capital, therefore was $1,124 MM.

TABLE 26

BREAKDOWN OF CAPITAL INVESTMENT

Plant/Unit	Major Equipment Items No.	Major Equipment Items Installed Cost ($000's)	Total Direct[1] Installed Cost ($000's)
Main Processes			
Crude unit	41	11,832	19,968
Naphtha hydrotreating	49	14,428	24,154
Hydrovisbreaking	89	100,608	168,119
Distillate hydrotreating	35	84,577	140,183
Distillate hydrocracking	60	56,649	94,724
Gas plant	32	5,684	9,380
Auxiliary processes			
Hydrogen manufacture (2)	NA	52,705	99,075
Hydrogen purification	NA	32,686	60,915
Low pressure amine	16	1,864	3,079
Sour water stripping	NA	18,994	33,091
Flue gas desulfurizing	NA	31,277	54,328
Sulfur recovery	NA	22,133	37,119
Sub-total		433,437	744,135
Other			
Tankage		22,823	45,061
Offsites			334,861
TOTAL			1,126,000[2]
Capital cost, $/bbl			22,520

(1) Includes contingency, instrumentation, home office costs
(2) Includes spare parts and rounding of $1.94 MM.

Refinery fixed capital investments were also projected during the Phase I case studies, including one case (Case X4) similar to that addressed here. The current estimate of $1,124 billion is considerably higher (~55%, excluding working capital) than the earlier one:

Component	Total fixed capital, $MM Phase I	 Phase III
Battery limits	457.3	744.1
Off-sites	205.8	334.9
Tankage	62.7	45.1
Total	725.8	1124.1
Timing	3Q/1983	4Q/1985
Refinery construction index (1956=100)	1030.6	1075.0

As indicated by the refinery construction indices, inflation would have only accounted for 4.3 percent cost escalation.

Table 27 compares the distribution of capital among various plant areas for the X4 case study of Phase I and this work. Large differences arose in the hydrovisbreaker and the refining units, some of which is attributable to differences in crude and/or process yield patterns. In the Phase III upgrading of San Ardo crude, distillate yield was relatively high and naphtha yield was relatively low, compared to the earlier projections. This directly impacted the hydrovisbreaker unit, since a very much larger syncrude vacuum tower was required. Downstream, naphtha hydrotreating, which operated at a reasonably moderate severity but on a relatively smaller volume, absorbed much less capital. On the other hand, the high nitrogen content distillate requires very high severity plus two-stage processing, and it was by far the larger volume stream. An additional factor impacting the hydrovisbreaker was the relatively low conversion of nitrogen in the feed, compared to sulfur conversion. If the two conversions were in better balance, the resultant hydrogen sulfide could have been removed from the system in the sour water stream, rather than via the high

TABLE 27

COMPARISON OF CAPITAL DISTRIBUTIONS

Reposition

	$MM	
Source	Phase I Case X4(1)	This Study
Crude unit	17.5	20.0
Upgrading unit	70.2	168.1
Refining units		
Naphtha hydrotreater	79.6	24.2
Distillate hydrotreater	}94.2	140.2
Distillate hydrocracker		94.7
Gas plant	35.4	9.4
Auxiliary plants		
Hydrogen plant	54.4	99.1
Hydrogen purification	-	60.9
Flue gas desulfurizer	35.4	54.3
Sulfur plant	70.6	37.1
Low pressure amine		3.1
Sour water stripper		33.1
Tankage	62.7	45.1
Battery limits	457.3	744.2
Off-sites	205.8	334.9
Spares, rounding	-	1.9
Total fixed capital	725.8	1126.0

(1) ex Reference 1

pressure gas scrubbing system. The former is clearly the lower capital approach. Thus, the low nitrogen conversion during upgrading exerts its effect twice, once in the hydrovisbreaker and again in high severity hydroprocessing of the syncrude distillate.

The Phase I case studies did not anticipate the extensive management of hydrogen that became part of the Phase III design. Hydrogen facilities represent over 20 percent of the Phase III process plant capital. Accordingly, thorough evaluation of hydrogen partial pressure effects in both upgrading and distillate refining sections of the plant could produce significant economics. Investment for environmental control type operations was also higher in Phase III, partly due to installation of two separate and independent sulfur recovery plants. Conceptually, the flue gas and hydrogen sulfide plants could have been integrated to varying degrees, but the consequences of such interdependency were considered not worth the risk.

In both Phase I and Phase III estimates, off-sites capital investment was defined as 45 percent of plant on-sites, excluding tankage. Thus, in Phase III, off-sites amount to nearly one-third billion dollars, an immense sum even for a grass roots refinery. In the absence of recent new refinery construction, however, historical data are lacking. For perspective, several textbook approaches to estimating off-sites are noted:

- Ulrich (Reference 6) suggests, for predesign accuracy levels in estimating grass roots facilities, use of a 30 percent factor, based on total module installed cost prior to adjustment for exotic materials or extreme operating conditions. The reasoning here is that auxiliaries (site preparation, buildings, utilities) are minimally affected by the severity of the process operating conditions.

- Valle-Riestra (Reference 7) proposes use of equipment bare purchased cost factors of 40 to 140 percent for grass-roots plants. Since installed cost can range from 3 to 4 times purchased cost, off-sites factors could range from 11 to 40 percent of installed cost.

Thus, use of the 45 percent off-sites factor may be overly conservative. Obviously, at higher design and estimating levels, site-specific estimates of individual off-site components (boilers, power generators, cooling towers, stacks, flares, fire protection, yard lighting, sidings, change house, etc.) would be carried out.

The total fixed capital of $1,124 billion for a 50,000 BPSD refinery results in a very sizeable $22,500 per barrel of installed capacity. Evaluation of this factor is also hampered by the absence of new refinery construction activity in the U.S. Recent brief news announcements mention a proposed new refinery for Valdez, Alaska to supply exports to Pacific rim countries (Reference 8). Few process details have been released, yet, although a 100,000 B/D capacity and $750 MM have been cited. This would result in a capital cost of $7,500 per barrel of installed capacity, if maintained.

The Valero Refining plant in Corpus Christi is perhaps the closest to a new, operating, U.S. heavy oil refinery, processing about 46,000 BPSD of atmospheric resid. It is an upgrade of a small topping plant, and started up in 1983/1984. Literature references to the cost range from $350 MM to $535 MM (References 9 and 10). The latter figure results in a cost of $12,100 per barrel of capacity (in 1985 dollars).

Modernization of the existing Tenneco refinery in Chalmette, LA reportedly cost $559 MM, increasing crude capacity from 100,000 to 145,000 BPD, and sour crude capability from 33,000 to 52,000 BPD (Reference 11). Based only on the incremental capacity, that works out to $12,400 per barrel.

In the three instances cited, the multi-fueled product slates included, in addition to motor gasoline and middle distillate fuels, several lower quality streams such as resid fuel, cutter stock or slurry oil. Although the available data are sparse, the figures indicate the process concept employed here in an effort to maximize production of JP-4 carries a significant capital burden. This should not surprise, given that each of the major plants operates in moderate to high hydrogen partial pressure environment.

5. Operating Costs

Direct refinery operating costs include raw materials, utilities, labor, catalyts and chemicals, maintenance, supplies. For some categories, these costs are derived as factors which were defined in the economic bases established at the start of Phase III and presented in Table 23.

Table 28 summarizes the utilization rates and equivalent dollar values for the major direct operating costs. Crude costs are by far the largest element. Excluding federal income tax and capital recovery, levelized processing costs amount to about $8 per barrel of crude.

One noteworthy item in the operating cost schedule is the cost of chemicals, at 13 percent of feed cost. Essentially all (99.5 percent) of the chemicals cost is represented by the 367 ppm Mo added as deposit control additive. This is clearly another area where the potential for significant economies could justify an extensive research effort into a more cost-effective approach.

6. Fuel Cost

Plant capital and operating costs from the two preceding subsections were input to a corporate economic evaluation computer model to project fuel manufacturing costs for the base case conditions set forth in Table 23. The base case parameters included a crude oil cost of $20 per barrel, 100 percent equity financing, 15 percent interest rate, 16 year project life, 50 percent plant capacity during the start-up year, and 90 percent on-stream factor for subsequent years. The recently abolished 5-year accelerated cost recovery system was assumed to have still been in effect for this analysis, as was a 50 percent combined Federal and state income tax rate. After-tax discounted cash flow rate of return for the base case was 15 percent.

TABLE 28

REFINERY OPERATING COSTS

	Rate	$ MM (1) per year
Purchases		
Crude (2)	50,000 BPSD	328.5
Labor		
Operating	24 per shift	3.55
Supervision	25% direct labor	0.89
Overhead	100% direct labor	3.55
Sub-total		7.99
Materials		
Catalyst (process, hydrogen units) (3)	---	1.85
Chemical (molybdenum, caustic, carbonates)	---	42.65
Royalties (running-sour water) (4)	---	0.10
Sub-total		44.60
Utilities		
Natural gas	920 M SCF/SD	1.02
Cooling water	142 MM Gal/SD	3.26
Boiler feed water	21.1 MM lb/SD	2.78
Electricity	53.15 MW	20.95
Sub-total		28.01
Maintenance, taxes, insurance	4.5% fixed capital	50.58
TOTAL		459.68

(1) Excluding start-up year
(2) For base case $20 per bbl crude
(3) Levelized; actual costs fluctuate
(4) Excludes up-front royalties

Table 29 summarizes the base case parameters, refinery total capital costs and levelized refinery operating costs (i.e. after the start-up year). Revenues from JP-4 and by-product (i.e. ammonia, sulfur, naphtha and resid) sales required to provide the target 15 percent after-tax discounted cash flow return on equity result in a JP-4 manufacturing cost of $51.97 per barrel, or $1.24 per gallon.

The projected cost of nearly $52/bbl is about 17 percent higher than the $44.5 per barrel derived in the Phase I case studies for a comparable process scheme, in spite of a lower assumed feed cost ($20/bbl in Phase III; $25/bbl in Phase I). As noted earlier, the higher capital costs associated with the Phase III results (high nitrogen feed, but low nitrogen conversion during hydrovisbreaking; low naphtha/distillate ratio in hydrovisbroken product) accounted for much of this difference.

The sensitivity of fuel manufacturing cost to several economic parameters was tested:

	Levels Tested		
Parameter	Low Level	Base Case	High Level
Feedstock,$/bbl	10	20	30
Fixed capital, % base	90	100	120
Return on equity, %	10	15	20
Debt financing, % total capital	-	3.6	75

The results of the sensitivity tests are summarized in Table 30, and illustrated in Figure 16. Halving the feedstock cost to $10 per barrel reduced fuel cost by about the same increment, $10.57 per barrel. By comparison, a 10 percent shift in fixed capital impacted fuel cost by only one fourth that amount, or about $2.60 per barrel. A change in expected return of 5 percent (to 10 percent or 20 percent ROE, from 15 percent) moved fuel cost about $7.00 per gallon. At otherwise base case assumptions, debt funding of 75 percent of total capital reduced fuel cost about $4.50 per barrel.

TABLE 29

BASE CASE FUEL COST

Basis	50,000 BPSD San Ardo crude oil 44,294 BPSD JP-4 product
Refinery scheme	
Upgrading	Hydrovisbreaking
Refining	Naphtha hydrotreating Distillate hydrotreating Distillate hydrocracking
Parameters	
Crude cost, $/bbl	20
DCF rate of return, %	15
Equity financing, %(1)	100
Plant capital, $MM	
Battery limits	744.1
Off-sites	334.9
Tankage	45.1
Total fixed capital(2)	1126.5
Working capital	42.4
TOTAL CAPITAL	1168.9
Operating costs, $MM/yr(3)	
Feedstock,	328.5
Chemical, catalyst	44.5
Labor, supervision, overhead	8.0
Utilities	28.0
Other (royalties, taxes, insurance, maintenance)	48.1
TOTAL	457.1
Fuel cost	
$/bbl	51.97
¢/gal	124

(1) Excludes working capital (borrowed)
(2) Includes up-front royalties, spares
(3) Excludes start-up year

TABLE 30

SENSITIVITY OF FUEL COST

Case	Base	B-1	B-2	B-3	B-4	B-5	B-6	B-7
Parameters								
Feedstock, $/bbl	20	10	30					
Capital, $MM								
Fixed	1126.5			1013.9	1351.7			
Working	42.4	31.4	53.56					
TOTAL	1168.9	1157.9	1180.1	1056.3	1394.1			
Return on equity	15					10	20	
Financing, %(2)								
Debt	3.6							75
Equity	96.4							25
Interest rate, %	15							
Fuel cost								
$/bbl	51.97	41.40	62.58	49.35	57.21	45.17	60.51	47.49
¢/gal	123.7	98.6	149.0	117.5	136.2	107.6	144.1	113.1

(1) Same as Base Case, if no alternate value shown
(2) Base Case of 3.6% represents financing of working capital

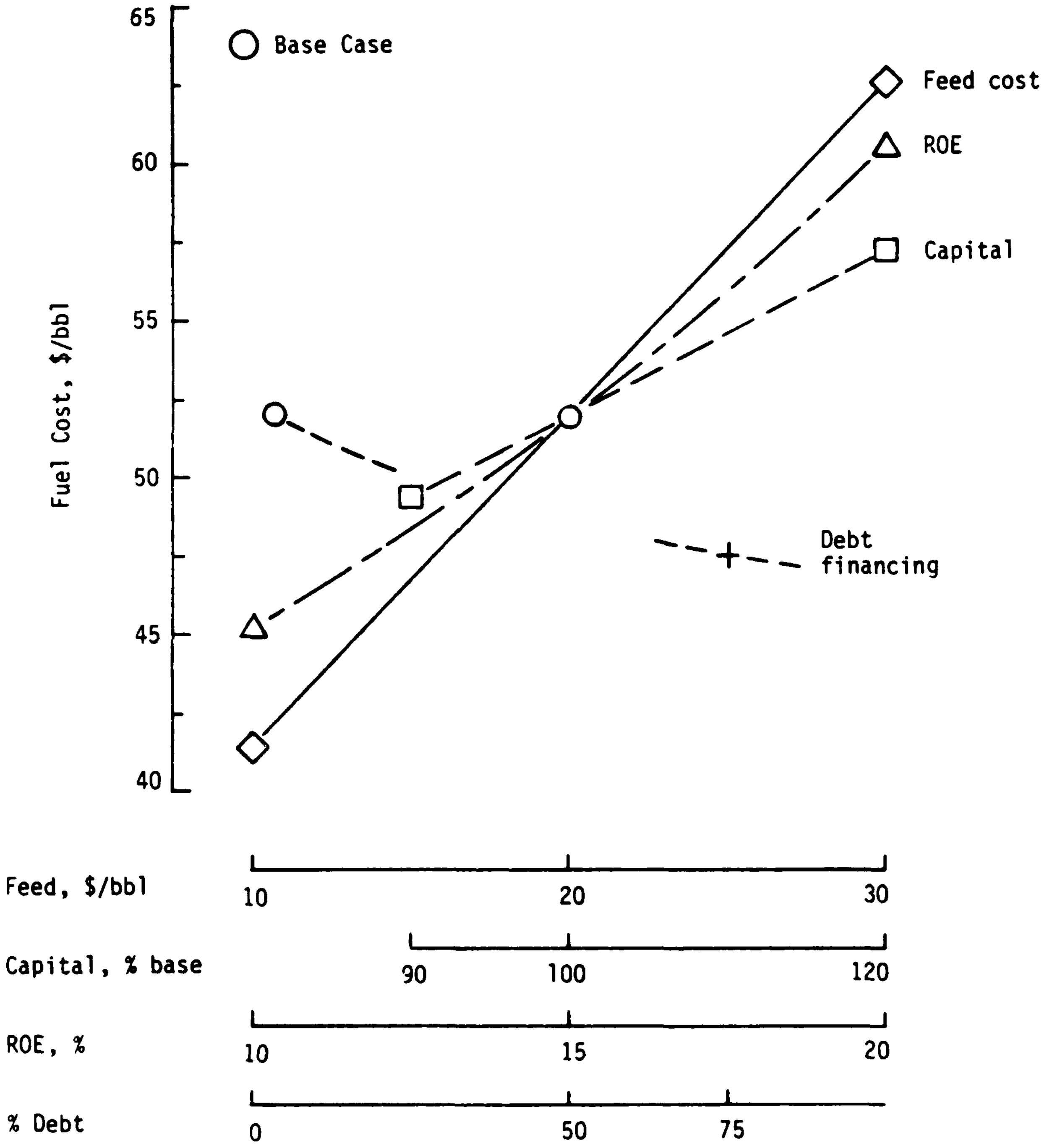

FIGURE 16 SENSITIVITY OF FUEL COST TO ECONOMIC PARAMETERS

SECTION VIII

CONCLUSIONS

1. Low-grade domestic fossil resources represent a potentially significant source of aviation turbine fuels for military use.

2. The conversion of these resources into specification quality fuels is achievable employing current technology.

3. This conversion can be accomplished in high yield, at moderately high efficiency, and with minimal by-product make, by the process sequence examined in this program.

4. The process sequence selected is capable of producing a lesser volume of kerosene type (JP-8) turbine fuel, with minimal adjustments. The decrease in volume is accounted for as a high quality gasoline reforming charge stock.

5. Capital investment for applying this process technology is very high, compared to approaches which use less extensive hydroprocessing to produce a wider mix of transportation fuels.

6. The concept of upgrading residua by hydrovisbreaking is valid. Zero net residual fuel production appears attainable, while the process appears relatively insensitive to feedstock.

7. Numerous opportunities for potential cost reduction arose during this study which could enhance the appeal of the approach taken.

8. Mastering the conversion of feed-bound nitrogen appears to be one key to controlling processing costs. It directly and significantly impacts plant capital.

9. Excellent quality prototype fuels, representing both aviation turbine fuel and diesel types, can be produced when applying this technology.

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GLOSSARY OF TERMS

API Gravity	an arbitrary specific gravity scale, applied to petroleum crudes and products, defined as: °API = (141.5/specific gravity @ 60°F) - 131.5
ASTM distillation	empirical procedure for vaporizing a liquid under conditions which provide a low degree of separation between successive fractions. Method ASTM D86 is performed on lower boiling materials, at atmospheric pressure (cf. TBP distillation); Method ASTM D1160 is performed on higher boiling materials at sub-atmospheric pressure to prevent thermal decomposition.
barrel	for petroleum usage, 42 U.S. liquid gallons.
bitumen	a naturally-occurring hydrocarbon which is too viscous to flow at the reservoir conditions.
bottoms	see residue
catalytic light cycle oil	a highly aromatic distillate fraction produced during the fluid catalytic cracking of heavy feedstocks. It may be recycled for further cracking, or withdrawn for use in blending fuel oils.
catalytic reforming	process for dehydrogenating naphtha to produce aromatics or high octane gasoline.
centipoise (cp)	a measure of the absolute viscosity, or resistive flow, of a fluid. One poise (P) equals one dyne-second per centimeter squared.
centistoke (cSt)	a measure of the kinematic viscosity of a fluid flowing under the force of gravity. It is related to the absolute viscosity by cp = cSt x density when both kinematic viscosity and density are measured at the same temperature.
desalting	process of removing entrained water, inorganic salts and sediment from a crude oil by contacting it with water at elevated temperature and allowing the two phases to separate. Imposition of electric charge and use of demulsifier additive may aid settling/coalescing.

GLOSSARY OF TERMS (continued)

design basis	that set of process operating criteria upon which the design of a commercial-scale operating unit is based.
distillate	a distillable petroleum fraction with a boiling range higher than that of naphtha and excluding vacuum residue. The term middle distillate implies an atmospheric fraction, containing no vacuum distillate.
dry gas	mixture of light hydrocarbon gases, which may also include hydrogen, from which C_4 and higher condensible hydrocarbons have been removed.
factorial design	a set of experiments in which pre-selected levels of independent variables are maintained while system response is being determined. In a 2^3 design, three variables are examined at two levels each.
fuel oil equivalent	used to define quantity of fuel gas in terms of heating value of fuel oil, which is 6.05 million BTU's per barrel.
heavy crude oil	crude oil which has specific gravity less than 20° API and is mobile at reservoir conditions.
heteroatoms	used to denote atoms other than carbon and hydrogen contained in organic compounds or structures; applied principally to sulfur, nitrogen and oxygen atoms.
hydrodenitrogenation	reduction in the amount of nitrogen in a feedstock by processing in a hydrogen-containing atmosphere, usually with aid of a catalyst.
hydrodesulfurization	hydrogenative processing of a material to reduce its sulfur content.
hydrovisbreaking	reduction in viscosity of a feedstock under the action of heat and hydrogen.
JP-4	wide cut, gasoline type aviation turbine fuel defined by specification MIL-T-5624L.
JP-8	kercsene type aviation turbine fuel defined by specification MIL-T-83133A.

GLOSSARY OF TERMS (continued)

light pyrolysis fuel oil	a highly aromatic liquid fraction, boiling in the 300 to 700°F range, produced during the manufacture of ethylene by steam cracking of gas oil feeds.
naphtha	a distillable petroleum fraction the boiling range of which falls between those of pentane and gas oil or distillate.
refining	in this study, refers to the secondary processing steps which follow upgrading, to produce marketable products from refinery intermediates.
residue	synonymous with resid, residua, residuum; the higher boiling portion of a crude or intermediate which is not distillable without degradation; a long resid refers to tower bottoms from distillation at atmospheric pressure; a short resid to bottoms from vacuum distillation.
residuum	see residue
simulated distillation	a determination of the boiling range distribution of a hydrocarbon product by application of gas chromatographic methodology; formalized as ASTM Method D2887.
space velocity	an expression of reaction severity, referring to volume of reactant(s) per volume of reactor volume per unit time; usual units are reciprocal hours (hr^{-1}).
specific gravity	mass per unit volume of a material, compared to that of a reference material (often water) at standard conditions (e.g. 60°F).
straight run	refers to a distillate fraction obtained from a crude oil not previously exposed to conditions which would produce appreciable change in chemical structure.
syncrude	see synthetic crude
synthetic crude	a wide boiling range product stream that has been subjected to conditions which brought about an appreciable change in the original chemical structure, in one or a combination of processing steps; also referred to as "syncrude"

GLOSSARY OF TERMS (concluded)

TBP distillation	an empirical procedure for vaporizing a liquid under conditions which provide a high degree of separation between successive fractions. May be performed at atmospheric or sub-atmospheric pressure, depending on boiling range of the material.
tar sands	deposits of mineral, whether consolidated (rock-like) or unconsolidated (sand-like), which have intimately associated with them a significant amount of bitumen.
tower bottoms	the bottom fraction produced from a distillation column; depending on its boiling range, it may or may not be non-distillable, i.e., a residuum.
upgrading	in this study, refers to the primary conversion step in a sequence of processing steps converting very low quality feedstocks to marketable products; generally excludes those operations which do not result in an appreciable change in chemical structure, such as fractionation, desalting.

LIST OF SYMBOLS AND ABBREVIATIONS

Symbols

@	at
°API	degrees API
°F	degrees Fahrenheit
>650°F	exceeds 650°F (as in a fraction boiling above 650°F)
<500°F	less than 500°F (as in a fraction boiling below 500°F)
>>	very much greater than
<	less than
C_n	where n is an integer from 1 to 6, represents hydrocarbons containing n carbon atoms
H_2	hydrogen
H_2S	hydrogen sulfide
H/C	hydrogen to carbon ratio
%	percent
#	pounds
R-1	reactor number one
R-2	reactor number two
hr^{-1}	reciprocal hours (i.e. 1/hours)
v/hr/v	volumes per hour per volume, as in space velocity
~	approximately

Abbreviations

API	American Petroleum Institute
ARD	Sun Co.'s Applied Research and Development Department
ASTM	American Society of Testing and Materials
bbl	barrel
BPD	barrels per day
BPSD	barrels per stream day
BTU	British thermal unit
C	Centigrade
cSt	centistokes

LIST OF SYMBOLS AND ABBREVIATIONS (concluded)

EP	end point
F	Fahrenheit
FBP	final boiling point
FOE	fuel oil equivalent
gal.	gallons
gr	gram
IBP	initial boiling point
init.	initial (as in initial boiling point)
M	thousands
mg	milligrams
ml	milliliter
MM	millions
MMM	billions
ppm	parts per million
ppmw	parts per million by weight
lb.	pounds
PSA	pressure swing adsorption
psig	pounds per square inch gauge
RVP	Reid vapor pressure
SD	stream day
sp. gr.	specific gravity
SCF	standard cubic feet
SCF/bbl	standard cubic feet per barrel
TBP	true boiling point
VTB	vacuum tower bottoms
vol.	volume
wt.	weight

Appendix A

Heavy Oil Pilot Plant Facility

The heavy oil pilot plant was designed, built, and placed in service during the calendar period April 1985 through March 1986 by ARD's Facilities and Design Section of the Process Development Division. The initial application for the unit, the study of residuum hydrovisbreaking, was the upgrading route to be studied under US Air Force Contract F33615-83-C-2352. However, flexibility in the design concept allows, by interchanging reactor configurations, its application to other heavy oil processes such as visbreaking, expanded bed hydrocracking, or delayed coking.

Figure 1A illustrates the heavy oil pilot unit process flow. In the hydrovisbreaking configuration, the reaction zone of the unit consists of three stirred tank reactors, manifolded in series so that one to three reactors can be employed. The combination provides considerable versatility with respect to overall residence time, throughputs, or temperature sequencing.

Charge stock is transferred from heated drums by air-operated drum pumps into one of two charge tanks. The tanks are heated and insulated, with nitrogen pressure adequate to move the charge through heated filters and transfer lines to the heavy oil charge pump. The amount charged from either tank is determined from load cell readouts. A smaller capacity liquid feed system allows charging a low viscosity liquid or slurry additive stream. In this program, an oil soluble molybdenum compound (molybdenum octoate) was diluted three volumes to one with kerosene, for easier metering control.

Fresh heavy oil charge is combined with the additive stream and hydrogen (fresh make-up mixed with recycle) prior to passing through the first of two coil type sand bath preheaters. The gas stream from the hydrogen compressor consists of recycle gas, which had been previously scrubbed with caustic solution, and fresh hydrogen from the main supply.

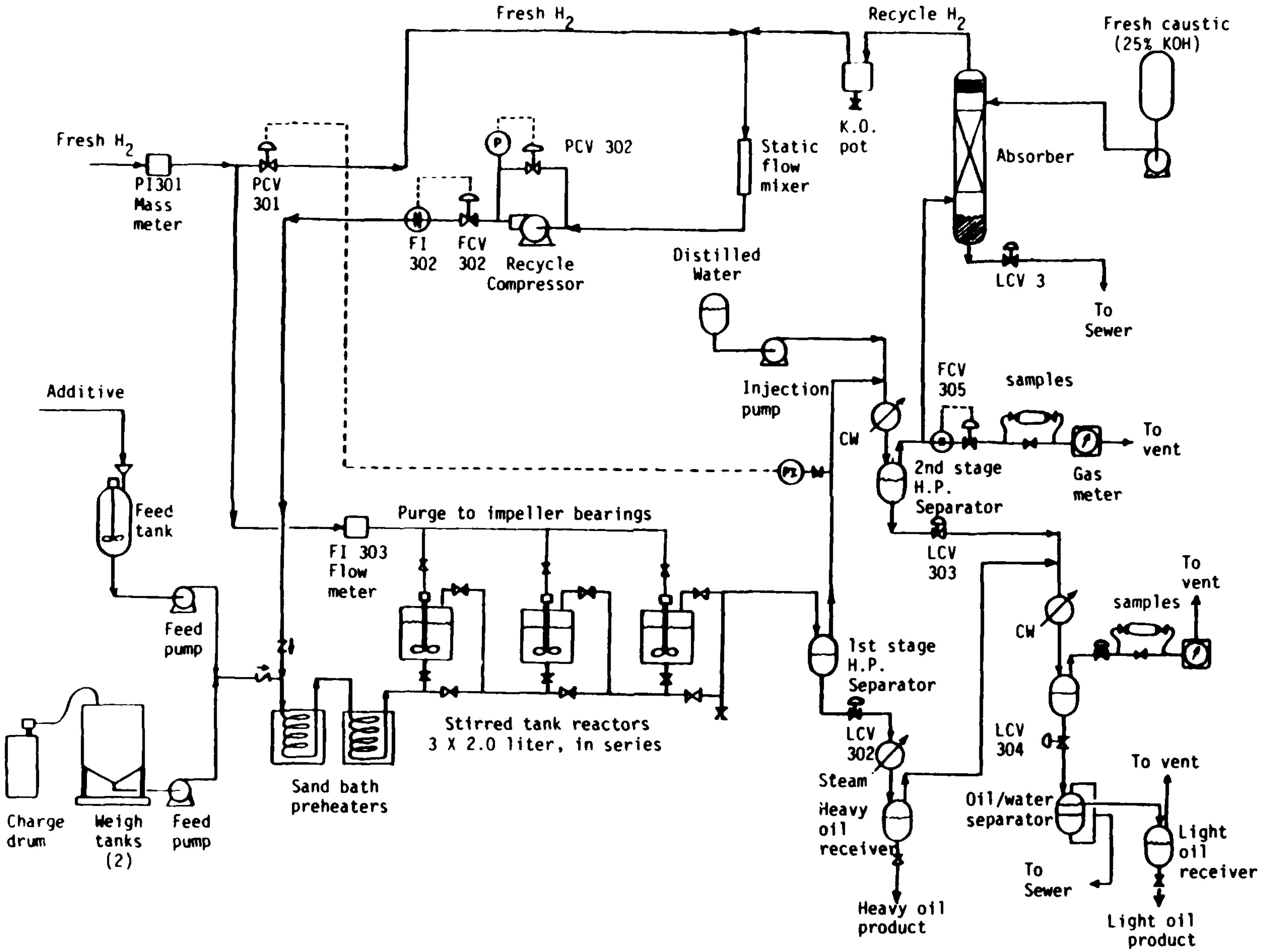

FIGURE 1A HEAVY OIL PILOT UNIT

The proportion of fresh to recycle hydrogen is determined by the type operations being carried out. The amount of hydrogen admitted to the system is that required to maintain designated system pressure at the first-stage high pressure separator. More fresh hydrogen is introduced when chemical consumption of hydrogen is high, or when the high pressure bleed gas is set at high rates, e.g. to increase recycle gas hydrogen purity. A slip stream of fresh hydrogen is admitted to each reactor to purge the impeller shaft bearings during operations. Fresh hydrogen rate is determined by mass flow meter.

The mixed gas-liquid feed stream passes, via heated and insulated transfer line, from the outlet of the second sand bath preheater coil to the bottom of the first reactor. Feed enters the reactor at the bottom center, and exits at the top, close to the reactor wall. The reactor is equipped with a turbine type impeller, powered by magnetic drive. Hollow rotor shafts are designed to promote internal recirculation of gas from top to bottom of the reactor, providing more intimate contacting of gas and liquid. Internal baffling, a series of four vertical vanes positioned around the reactor perimeter, provides high turbulence mixing of the contents. Each reactor is heavily insulated and resides within a circumferential shell heater. Suitably placed thermocouples supply reactor inlet, skin, and internal temperatures and provide the means for maintaining any two of these temperatures via appropriate control circuitry.

Effluent from the final reactor in the series is cooled to about 600°F in a temperature controlled transfer line before entering the first stage, or high temperature, vapor-liquid separator. Heavy oil accumulates in the first stage separator and passes through a series of in-line filters, through a high pressure level control valve, partial cooler, and into the heated and insulated heavy oil product receiver, from which it is periodically drained. Gas which is flashed off during depressuring joins a similar stream from the second stage separator before entering the gas metering/sampling system, and thence the vent.

Lower boiling components in the gas stream from the first stage separator are quenched by distilled water injection, further cooled to room temperature, and accumulated in the second stage separator. Uncondensed high pressure gas leaving the top of the second stage separator either 1) is depressured and passes through the gas metering/sampling system to the vent, or 2) enters the bottom of the absorber where it is scrubbed of residual acid gases by a countercurrent flow of caustic (25% KOH) solution. Recycle gas exits the top of the caustic scrubber and passes through a knockout pot before joining the make-up fresh hydrogen upstream of an in-line static mixing device. The mixed gas stream is boosted in pressure by the unit recycle compressor before returning to the charge preheater inlet. Flow is controlled by a throttling valve which picks up flow rate signals from a downstream orifice meter.

Light oil plus quench water which collect in the second stage or low temperature separator also pass through in-line filters and let-down valve, before entering the oil-water separator. The sour water lower layer drains to the chemical sewer; the hydrocarbon layer passes to the light oil receiver for periodic draining.

NOTE: Projections, based on naphtha properties from Table 25, derived from reforming kinetic model.

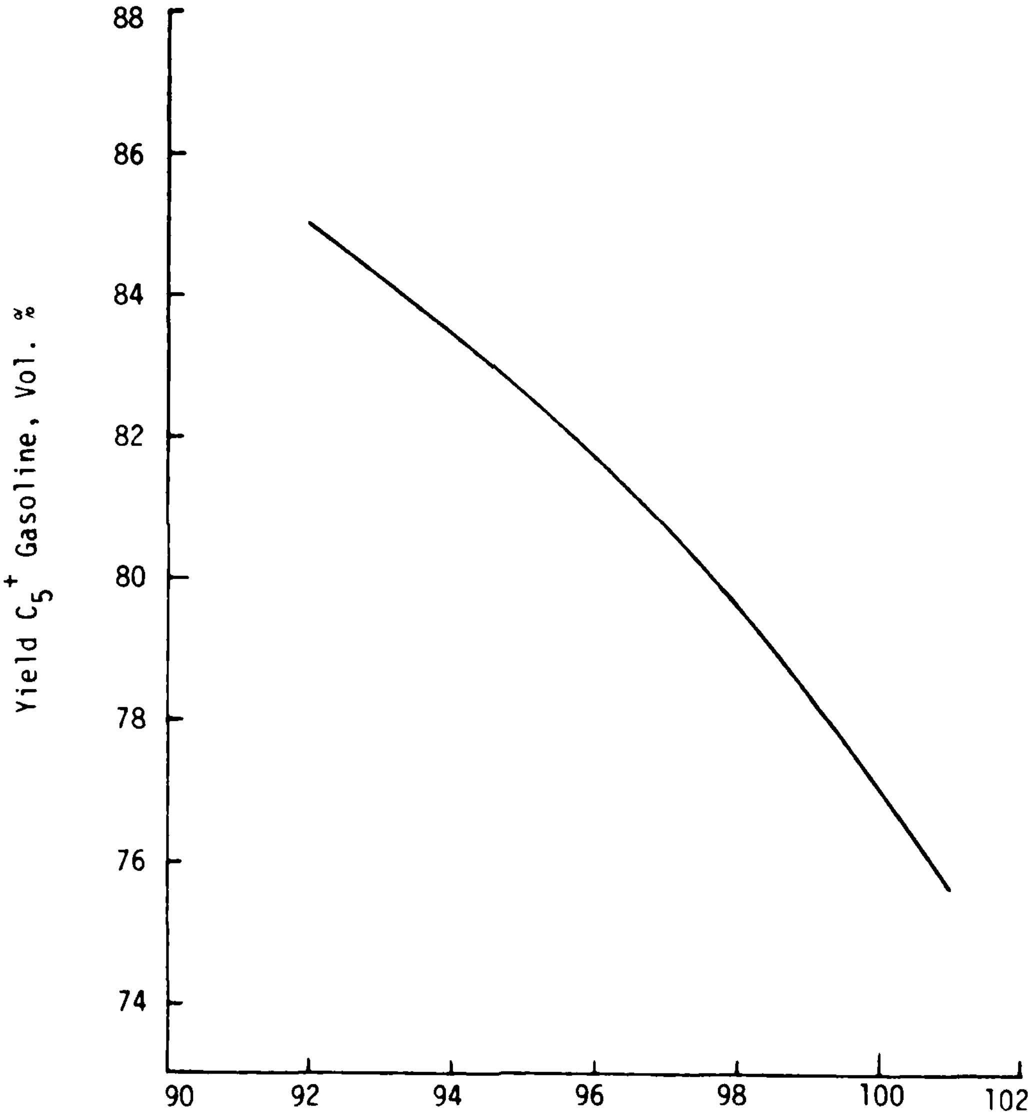

FIGURE 2A YIELD-OCTANE CURVE FOR NAPHTHA CO-PRODUCT FROM JP-8 OPERATION

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