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UNCLASSIFIED S/W-PROC-111579 AFWAL-TR-80-2012 NL

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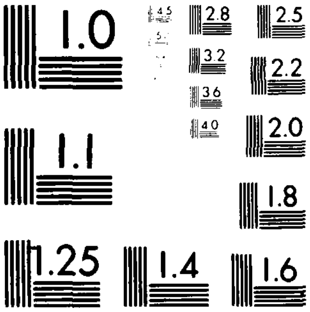

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NATIONAL BUREAU OF STANDARDS-1963-A

AFWAL-TR-80-2012 LEVEL II

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HYDROPROCESSING OF LIGHT PYROLYSIS FUEL OIL FOR KEROSINE TYPE JET FUEL

ALEXANDER KOROSI
J. N. RUBIN
STONE & WEBSTER ENGINEERING CORPORATION
P. O. BOX 2325
BOSTON, MASSACHUSETTS 02107

FEBRUARY 1980

TECHNICAL REPORT AFWAL-TR-80-2012
Final Report for period 1 October 1978 — 31 October 1979

Approved for public release; distribution unlimited.

AERO-PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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

Edward N Coppola

Edward N. Coppola, 2/Lt, USAF
Fuels Branch
Fuels and Lubrication Division
Aero Propulsion Laboratory

Arthur V. Churchill

Arthur V. Churchill
Chief, Fuels Branch
Fuels and Lubrication Division
Aero Propulsion Laboratory

FOR THE COMMANDER

Robert D. Sherrill

Robert D. Sherrill
Chief
Fuels and Lubrication Division
Aero Propulsion Laboratory

AIR FORCE/56780/8 August 1980 — 200

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
AFWAL-TR-80-2012

2. GOVT ACCESSION NO.
AD-A089101

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
HYDROPROCESSING OF LIGHT PYROLYSIS FUEL OIL FOR KEROSINE TYPE JET FUEL

5. TYPE OF REPORT & PERIOD COVERED
Final Report, Oct. 1, 1978 to Oct. 1979

6. PERFORMING ORG. REPORT NUMBER
S&W Proc. 111579

7. AUTHOR(s)
Alexander Korosi
J. N. Rubin

8. CONTRACT OR GRANT NUMBER(s)
F 33615-78-C-2074

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Stone & Webster Engineering Corporation
P. O. Box 2325
Boston, MA 02107

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
69

11. CONTROLLING OFFICE NAME AND ADDRESS
Aero-Propulsion Lab.
Air Force Wright Aeronautical Labs., Air Force Systems Command, Wright Patterson Air Force Base, Ohio, 45433

12. ~~REPORT DATE~~
February 1980

13. NUMBER OF PAGES
67

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
14 S/W-

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Jet Fuel
Synthetic JP5
Pyrolysis Fuel Oil
Ethylene
Steam Cracking
Hydroprocessing
Hydrogenation
Aromatic Fuels
Naphthenic Fuels

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

The feasibility of converting light pyrolysis fuel oil (a steam cracking by-product) into jet fuel was assessed. The raw aromatic fuel oil was hydrostabilized and converted into naphthenic products by hydrogenation in pilot plant operation. The fully hydrogenated fuel showed excellent cold properties, high heat of combustion values on volume basis and met nearly all specifications on kerosine-type fuels. Conceptual process design and related economics indicated the product cost was competitive with other petroleum products. This fuel is a new potential source for JP5 or JP8 kerosine type jet fuel.

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

PREFACE

This report was prepared by Stone & Webster Engineering Corporation Boston, Massachusetts 02107, under Contract F33615-78-C-2074. The award was given on the basis of a proposal submitted by Stone & Webster July 7, 1978 to the Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio. The Air Force assigned E. N. Coppola, 2LT, USAF, as project engineer.

The report covers the results of the experimental and process design work undertaken by Stone & Webster. Pilot plant hydrogenation work was provided by the Institut Francais du Petrole, Rueil-Malmaison, France, as subcontractor.

The content of this report has been reviewed and is approved for release.

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SUMMARY/RECOMMENDATIONS

Results of pilot plant work performed on behalf of the US Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio are reported on the conversion of aromatic light pyrolysis fuel oil to various experimental jet fuel candidates. Six hundred liters of each, hydrostabilized, partially hydrogenated and nearly fully saturated jet fuel products were prepared for further test purposes by Stone & Webster in cooperation with the Institut Français du Petrole as subcontractor.

Properties of the fully hydrogenated test fuel matched all essential specifications prescribed for JP5/8 kerosine-type jet fuel. This product exhibited outstanding low temperature properties and showed about 8-10 percent higher than normal heat of combustion on volume basis. Being such, the fuel is a potential source to supplement current kerosene type jet fuel supplies, and also could serve as a diluent for high-density missile fuel, test liquid for broadened jet fuel specifications and an ingredient for carbon slurries.

The raw fuel is a low-grade by-product from olefins manufactured by steam cracking. Estimates included in this report indicate that from current commercial operation, sufficient quantities of product could be obtained to cover about 30 percent of the military's kerosine type jet fuel requirements. A growing supply of the material is also anticipated in the future due to the rising use of heavier feedstocks in ethylene production.

Process design and economics prepared and reported herein on a 100,000 tons per annum hydroprocessing plant showed that the production cost of fuel is competitive with other sources.

Based on these findings, it is recommended:

1. Multiple combustion rig studies should be carried out to establish the behavior of the various test fuels in turbo combustion.

2. A larger quantity of fully and partially hydrogenated fuel, on the order of 100,000 gallons should be prepared in a suitable smaller commercial plant, with the processing technology and catalysts described in this report. These fuels used in an engine and system test program could model future naphthenic/aromatic jet fuels and offer a new source for kerosene type jet fuel in their routine and special application territories.

SECTION I

INTRODUCTION

Late in 1976 and again in May of 1977, Stone & Webster Engineering Corporation contacted the Air Force Aero Propulsion Laboratory and transmitted results of an in-house experimental program covering hydroprocessing of pyrolysis fuel oil for aviation turbine fuel. The raw fuel obtained from steam cracking of gas oil was shown to be completely aromatic with distinct similarities in structure to coal liquids in the same boiling range. By conventional hydrotreating, the aromatic constituents were converted to cycloalkanes and the saturated naphthenic fuel was characterized. For all practical considerations, the fuel met the kerosine type jet fuel specifications, and exhibited high value for specific gravity, as expected.

The thought of using this fuel as a modelling candidate for alternative fuels was incorporated in a proposal submitted to APL by S&W on June 7, 1978. In addition, several other potential applications of the hydrotreated light pyrolysis oil were mentioned, such as diluent fluid for high-density missiles and ramjet fuels, carrier for carbon slurry fuels, and test liquid for broadened specification turbine fuels.

The pyrolysis fuel oil is a by-product from commercial steam cracking. Projections indicate a growing use of heavier liquid feedstocks for olefins, thus the availability of pyrolysis fuel along with the pressure to find profitable end uses will increase. This potentially high volume by-product represents a commercially significant new source for various aviation fuels, especially in the application categories outlined above.

The subject matter presented in the S&W proposal was accepted for support and an award covering a nine-month R&D effort was given by the USAF Air Force Systems Command, Wright-Patterson AFB, September 1978. Results of this investigation are presented in this report.

SECTION II

SCOPE OF WORK

Major target achievements in fulfillment of S&W's contractual obligations were as follows:

a. Three 165-gallon combustor rig test fuel samples with 90(+), 30 and 5 percent aromatics content were prepared and delivered to Wright-Patterson AFB and Shell Research Center, Thornton, England.

b. Characterization of the fuels by routine quality acceptance procedures and by mass spectrometry (MS) and nuclear magnetic resonance (NMR) techniques along with the interpretation of results was accomplished.

c. Process development and conceptual plant design for hydrotreating 100,000 metric tons per annum (MTA) light pyrolysis fuel oil for jet fuel manufacture was completed.

d. Process economics and projections for market availability of the light pyrolysis fuel were prepared.

SECTION III

BACKGROUND

1. Alternative Fuels

In response to anticipated future shifts in the traditional supply of the petroleum based aviation turbine fuels, a number of investigations were supported by the U.S. Air Force and other organizations to explore the use of alternative fuels (1, 2, 3). The list of the turbine fuel candidates tested, included both synthetic petroleum mixtures, and syncrude based products such as shale oils, tar sands and coal liquids.

The conclusion emerged from these studies that shale oils are most amenable to conventional refinery treatment and the refined products with predominantly paraffinic features, would conform even to current aviation turbine fuel specifications. In contrast, processed coal liquids represent a new generation of turbine fuels. The production and upgrading of coal liquids differs from routine petroleum refining operations and these future product streams are expected to be highly aromatic and naphthenic in nature. Process economics dictate the mildest treating conditions and minimum hydrogen consumption.

At best, as a compromise, the advent of the alternative fuels signals the need for the acceptance of reduced hydrogen content and the accommodation of aromatic/naphthenic types of fuels. These changes may impact on the design of the combustor, turbine, and the fuel delivery system of the aircraft, and could alter the structure of the entire air frame. To investigate the effect of changing fuel quality on the engine several series of combustion tests were undertaken.

2. Combustion Tests with Alternative Fuels

Results of recent combustor rig studies universally confirmed the adverse effects of reduced hydrogen content both in the conventional and alternative fuels. Moses and Naegeli of Southwest Research Institute, Friswell from Shell Research, Thornton (4, 5) in good agreement with Martel and Angello's findings (6), showed diminishing hydrogen content to be responsible for increased radiation, liner temperature and smoke formation in the engine. These combustion phenomena were best correlated by hydrogen content rather than the hydrocarbon types of fuels.

The extreme pernicious effects of luminous flames in a stationary turbine simulating test rig were brought out in an EPRI study (7). When SRC and H-Coal derived fuel products with less than 11 weight percent hydrogen were fired, large coke deposits were found and segments of the combustor wall burned through.

The ominous combustion performance of some of the test fuels with reduced hydrogen confirmed the need for continued efforts to find the right conditions under which satisfactory firing can be achieved. Although combustion behavior is the most important criterion in judging the fuel quality, aviation turbine fuels must also function as service fluids with well defined properties. In this role they must remain stable, in homogeneous liquid phase even under the extremities of flight conditions. Consequently, in the fuel selection procedure both criteria ought to be met and an a priori elimination based solely on the expediency of a hydrogen correlation would be highly imprudent. Pyrolysis fuel-oil-derived naphthenic/aromatic aviation turbine fuels can <u>now</u> be obtained in significant quantities and their introductory use could establish the extent of a three-way compromise that is required for fuel quality, availability and aircraft design. This step is a necessary preparation for the future, when a group of products of similar nature will appear in large quantities as alternative aviation turbine fuel.

SECTION IV

EXPERIMENTAL

1. Raw Light Pyrolysis Fuel Oil

Four metric tons of light pyrolysis fuel oil, LPFO, (sometimes also referred to as "cracked gas oil") was purchased from a European fuel supplier in September, 1978. The oil represented a nominal 205-310C (ASTM D-86) boiling range cut of the PFO, a by-product obtained from steam cracking of various petroleum feedstocks for olefins. This particular sample was an approximate 90:10 mixture of LPFO, originating from gas oil and naphtha cracking, respectively.

The fresh oil, in twenty 55-gallon drums was delivered to the pilot plant of the Institut Francais du Petrole located in Solaize, near Lyon, France.

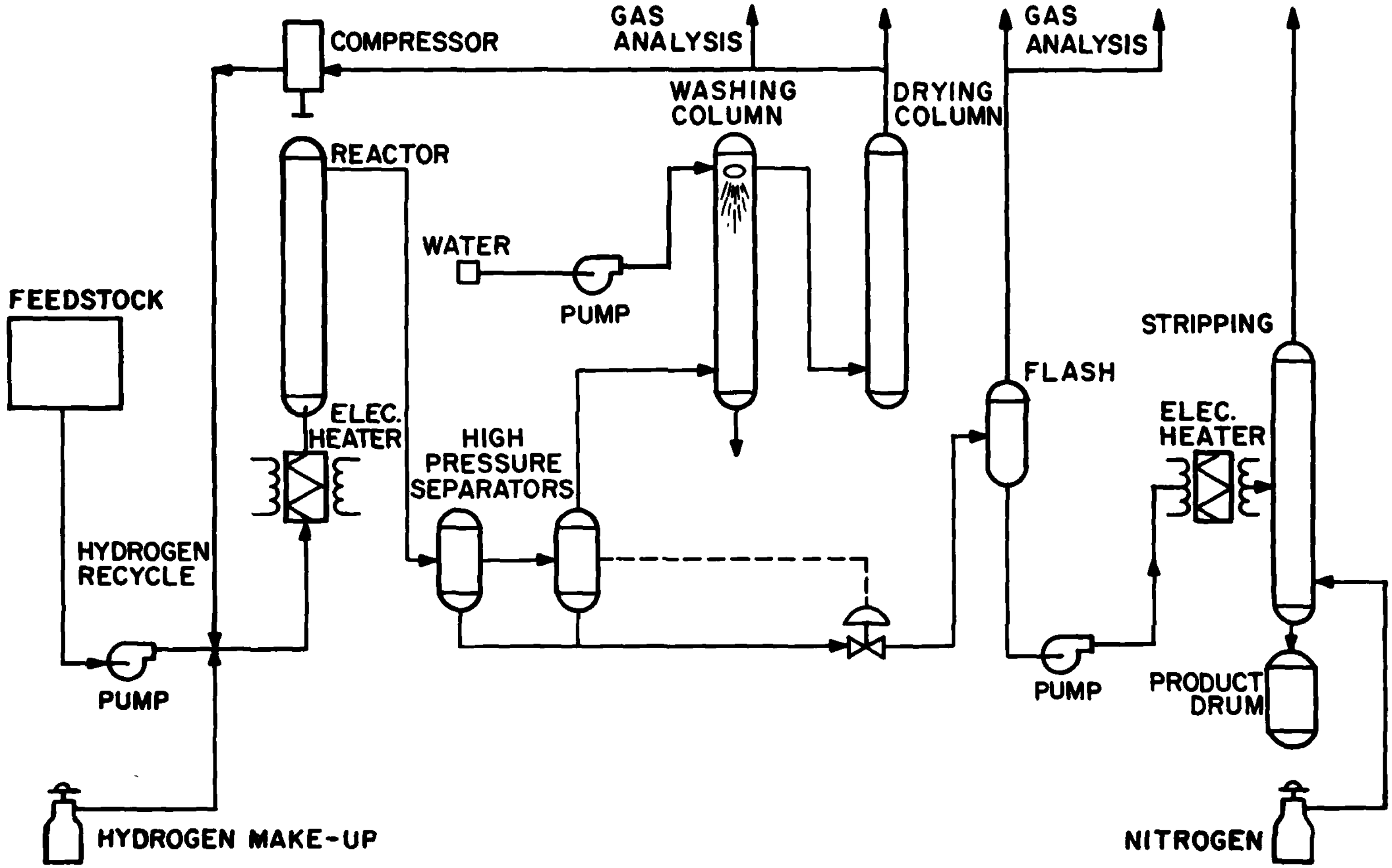
Approximately 2000 ppm anti-oxidant "bisoxol," 2,4-dimethyl, 6 tertiary butyl phenol was added to the fuel at the time of the drum filling. The unusual high level of dosage was a precautionary measure for prolonged storage.

2. Description of Hydrogenation Pilot Plant Unit

The stepwise hydrogenation of the raw PFO was carried out at Solaize in one of IFP's intermediate size continuous operation hydrogenation unit. Figure 1 is a schematic diagram of the hydrogenation assembly used, whereas in Figure 2, a photographic view of the related segment of the IFP hydrogenation pilot facility is presented. The hydrogenation unit shown in Figure 1 is divided into two major portions - a high and low-pressure section, each providing simulation of the operation of its industrial counterpart.

The high pressure section comprised the following major components:

- feed tank
- feed pump



HYDROGENATION PILOT PLANT

FIGURE 1

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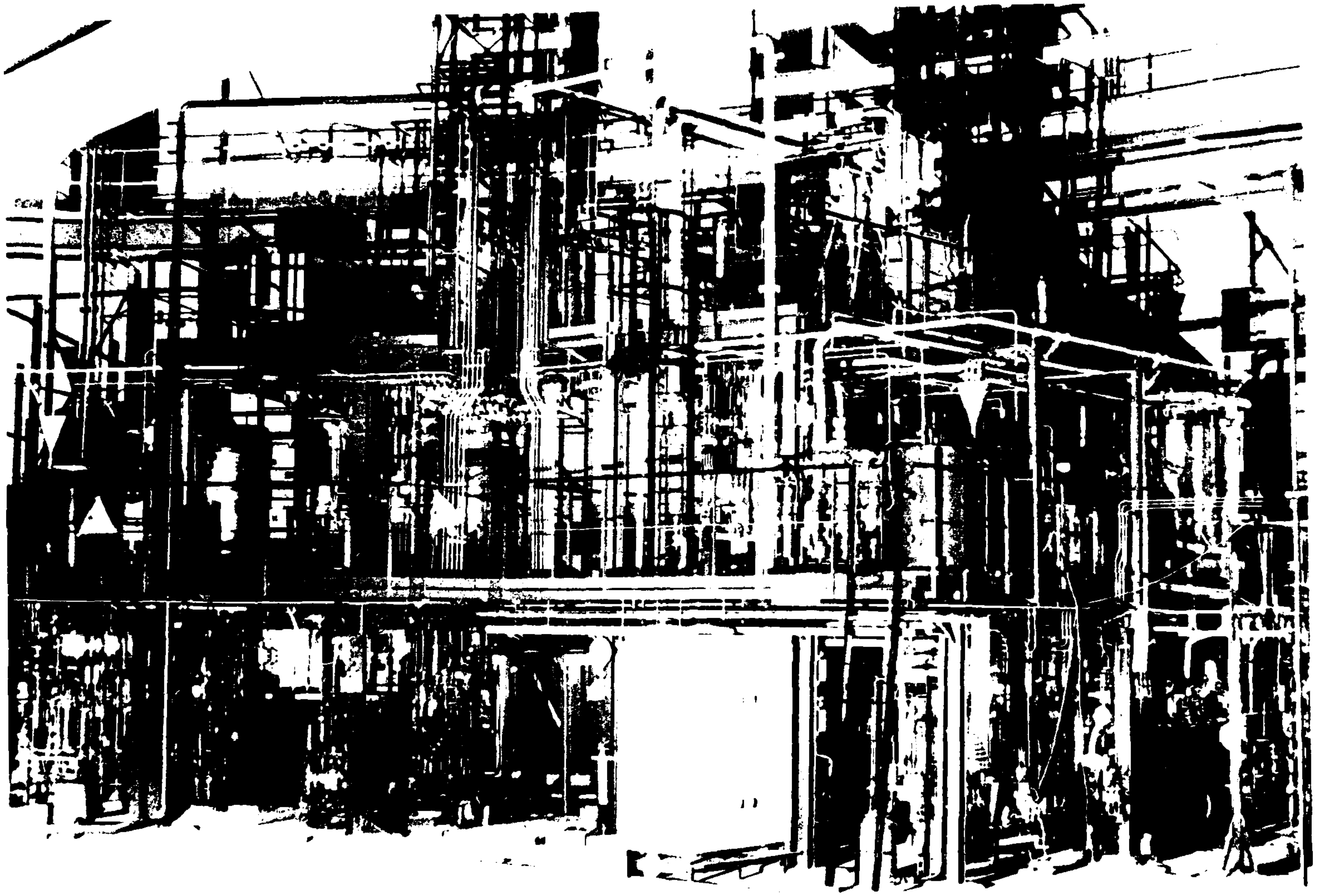


IFP HYDROGENATION PILOT PLANT

FIGURE 2

- feed preheater make-up hydrogen reservoir
- reactor
- drum for gas/liquid separation
- hydrogen purification and recycle system with washing and drying columns
- a compressor

A 3.5 liter capacity (catalyst volume) reactor was assigned to carry out the present LPFO hydrogenation work. The unit on automatic control at LHSV = 1 had about a 20-22 gallon per day production capacity.

Liquid products from the high pressure separator entered the second low pressure section of the unit via a pressure regulator valve. This section contained an atmospheric flash drum and a stripping and stabilizing column. For convenience, a small flow of nitrogen provided the stripping. Liquid products were collected and weighed. Gaseous effluents from both the high and low pressure segments of the unit were metered and analyzed, for the purpose of material balances.

3. Hydrogenation Schemes

In setting up the experimental procedure at IFP and selecting the catalyst for the production of LPFO based jet fuels, results of several earlier investigations were utilized. These hydrogenation tests were carried out on behalf of S&W and also in IFP supported in-house projects. Some of the related results were incorporated in the proposal submitted to the Air Force by S&W in June 1978 and other results were published by J. P. Franck of IFP (8). Preparation of hydroprocessed "Synthoil" (USBM) coal liquid feedstocks for petrochemicals in a nearly identical scheme were reported by A. Körosi et al. (9).

Experimental conditions for the present test series were chosen to satisfy the overall requirements of the contract, namely:

a. To hydrostabilize and deliver three drums of raw light pyrolysis fuel oil with 90 (+) percent aromatics content, and

b. To produce the same quantity of intermediate and fully hydrogenated jet fuel candidates with aromatic contents below 50 and 10 percent, respectively.

Additional criteria influencing the selection of experimental conditions included constraints on product quality and those of process considerations. Contract requirements prescribed that the fully hydrogenated product must comply with JP-8 fuel specifications and the related process conditions should constitute the basis of a commercial plant design. To achieve favorable process economics, the goals for minimum hydrogen consumption and maximum yields for jet fuel range products were fixed, therefore no considerations were given to treatments resulting in significant hydrocracking.

At the outset of the work it was decided to hydrostabilize 2500 liters of the raw LPFO, a common preparatory step required for all subsequent processing. This was performed at low pressure and low temperature, on a palladium-on-alumina, commercially available (LD 265) catalyst. The objective of this treatment was to saturate the reactive gum-forming olefinic and diolefinic compounds of the feed. Details of the processing conditions used are presented in Table 1. As a general rule, product stability is reached at bromine numbers at ten or below. This had been achieved in our case, along with a significant drop in the maleic anhydride value. Maleic anhydride value is a measure for conjugated diolefinic bonds, however, not entirely specific. Accordingly, the residual MAV and bromine consumption by the hydrostabilized product could have been caused by other reactions. Mild reaction conditions

TABLE 1

OPERATING CONDITIONS
HYDROPROCESSING PILOT PLANT

(Reactor Capacity: 3.5 liters)

PROCESS STEP	HYDROSTABILIZ	INTERM HYDROG	FULL HYDROG	FULL HYDROG	DESULFURIZATION	FULL HYDROG
Run Type	Production	Production	Exploratory	Production	Exploratory	Exploratory
PRODUCT DESIGNATION	AFLPF-1	AFLPF-2	AFLPF-3	AFLPF-3(Final)	AFLPF-5	AFLPF-4
Number S -	1545	1548	1550	1550	1558	1563
FEED DESIGNATION	AFLPF	AFLPF-1	AFLPF-1	AFLPF-1	AFLPF-1	AFLPF-5
Number S -	1528	1545	1545	1545	1545	1558
OPERATION						
Catalyst*	LD 265	HR 354	HR 354	HR 354	HR 354	LD 402
Temperature, C	170	335	335	335	335	285
F	338	635	635	635	635	545
Pressure (total) bars	50	130	130	130	70	70
psi	725	1885	1885	1885	1015	1015
LHSV 1/1/h	1	1	0.5	0.5	2	2
H Recycle, (H/feed) 1/1	200	900	900	900	450	1000
H CONSUMPTION (Chemical)						
kg H_2/100 kg raw LPFO	0.36	4.41	5.45	5.76	nd	5.71
kg H_2/100 kg hydrostabl feed	-	4.03	5.07	5.38	nd	5.32
SCF H_2/BBL LPFO Feed	230	2850	3530	3720	nd	3700

* LD-265, -402 Pd/alumina; HR 354 Ni-W/alumina

were maintained throughout the hydrostabilization tests without affecting the activity of the otherwise sulfur sensitive catalyst. Only negligible quantities of aromatics were saturated.

The next hydroprocessing step was devoted to the partial saturation of aromatic constituents. It provided the intermediate quality jet fuel. Here, 600 liters of hydrostabilized feed were further processed at high temperature, pressure and relatively high space velocity, on a commercial nickel-tungsten catalyst. (HR 354). Using the process conditions listed for the preparation of this intermediate product in Table 1, the aromatic content was reduced to about 30 percent.

Two different processing options were considered in the next phase for the preparation of fully hydrogenated jet fuel products: Under the first option, the use of the above described nickel-tungsten - under the second, a noble metal catalyst was suggested.

Experimentation was required in the planning stage to find answers to the following questions:

a. Could the low aromatic final jet fuel be produced directly from the hydrostabilized LPFO, or must an intermediate hydrogenation step precede it?

b. What level of feed purification (mainly desulfurization) on the nickel-tungsten catalyst is required prior to the use of the sulfur-sensitive noble-metal catalyst in the production of the final product?

Exploratory runs were made in both categories under the conditions listed in Table 1. Based on the test results, the decision was made to proceed with the nickel-tungsten route, since it became evident that at reduced space velocity, the final product could be easily prepared in one step directly from the hydrostabilized product. Initially 30 liters of fully hydrogenated fuel were prepared. The results were submitted to the Air Force for approval, then the full quantity of fuel was produced under matching conditions. In Tables 2 and 3, the characterization of products obtained in the noble metal hydrogenation, exploratory runs are shown. Hydrodesulfurization was accomplished with the HR 354 catalyst at intermediate pressure and high space velocity, followed by hydrogenation at relatively mild conditions on a noble metal catalyst. The selection of the hydrogenation scheme for the current work, however, does not preclude the future use of the noble metal route. It has attractive features - being capable of producing a nearly equal quality fuel at much lower temperatures and pressure, and at double space velocity, which merit is offset by the higher price of the catalyst and by an extra step in the process scheme.

4. Catalysts

Catalysts used in the pilot plant hydrogenation work are commercially available, manufactured by Procatalyse, a subsidiary of Rhone-Poulenc and IFP. In the production runs, LD 265 a high-purity alumina with palladium active agent and HR 354, a nickel-tungsten on alumina catalyst, were used - whereas in the exploratory run, a noble metal catalyst with LD 402 designation was used.

Literature provided by the manufacturer claims LD 265 to be especially suitable for the saturation of olefinic and acetylenic bonds. Application territories include selective hydrogenation of olefins and acetylenes in C_4 - C_9 streams from steam cracking. In our case, the same function provided the hydrostabilization of the raw fuel. Because of the sulfur-sensitive nature of the catalyst, low temperature operation was required to avoid sulfur poisoning. Physical properties of the catalyst LD 265 are shown in Table 4.

TABLE 2

CHARACTERISTICS OF RAW AND HYDROTREATED JET FUEL CANDIDATES

PRODUCT	ASTM D	RAW PFO	HYDRO-STABIL	INTER-MEDIATE	FULLY HYDROG	FULLY HYDROG
No. Steps in Hydrotreatment		0	1	2	2	3
Designation		AFLPF	AFLPF-1	AFLPF-2	AFLPF-3	AFLPF-4
Sample No. (S-)		1528	1545	1548	1550(Final)	1563
I HEATING VALUE						
Specific Gravity 60/60F	1298	0.983	0.978	0.896	0.874	0.878
100/100F		0.974		0.887	0.864	
210/210F		0.971		0.878	0.854	
Net Heat of Combustion Btu/lb	2382	16,881		18,141	18,374	18,354
Btu/gal		138,060		135,647	134,016	134,483
II COMPOSITION, BURNING QUALITY						
Aromatics, Vol. % FIA	1319	100	100	32.0	4.0	7.5
Aromatics, Vol. % (Sulfonation)	1019		95	30.0	2.3	6.0
Carbon, Wt %		91.57	91.26		86.67	86.72
Hydrogen, Wt %		8.33	8.66	12.20	13.32	13.28
Sulfur, Wt %	1552	0.08	0.06			
Sulfur, (Microcoulomtr.), ppm				0.5	0.5	bel. 0.5
Nitrogen (Kjeldahl) Wt %		0.016	0.018			
Nitrogen (Microcoulomtr), ppm				0.2	bel. 0.2	
Mercaptan S, ppm	1323	3		bel. 1	0	
Smoke Point, mm	1322	4	5	11	20	19
Naphthalenes, Vol. %	1840				0.01	
Luminometer No.	1740	-10	-10	18	46	37
Aniline Point, F	611	bel. 12	bel. 12	82	127	123
Cetane No.	613			33.3		
Viscosity (See IV)						
III VOLATILITY						
Flash Point (Tag CC) F	56	175(+)	175(+)	150	142	
Distillation, F	86					
IBP		392	412	365	360	372
5 Vol %		436	444	401	390	398
10		448	452	408	398	405
20		461	462	418	406	412
30		468	469	425	412	418
40		472	475	430	420	424
50		478	483	436	426	430
60		484	490	444	432	437
70		492	499	453	442	447
80		502	510	466	456	460
90		516	528	488	482	484
95		534	554	505	506	507
EP		562	579	560	562	560
Simulated TBP, F	2887					
IBP, %		289		289	267	
5		381		356	366	
10		395		270	379	
20		429		393	400	
30		446		411	411	
50		481		449	437	
70		512		487	468	
90		550		529	520	
95		569		544	544	
EP		609		568	637	
IV COLD HANDLING						
Freezing Point, F	2386		-45	bel. -76	bel. -76	bel. -76
Pour Point, F	97	-76	bel. -98	bel. -65	bel. -65	bel. -98
Viscosity, cSt -65F	445				57.2	
-40F		74.0	61.0	26.2	21.15	24.45
-30F		41.9	19.14	17.17		
- 4F		9.6		9.65	9.26	9.79
100F		2.26	2.20	2.12	2.17	2.05
200F		0.93	1.0	0.94	0.96	0.96
V THERMAL STABILITY (JFTOT) (@ 500F, 500 psig, 3 ml/min)	3241					
Test Duration (min)			36	150	150	
Heater Tube Rating			2	2	0	
TDR Max Spun Rating			12.0	17.0	5.0	
Max Diff Press mm Hg			254	2.5	2.5	
VI STORAGE/CORROSION						
Existent Gum, mg/100 ml	381	520	400*	44**	1	
Potential Gum mg/100 ml (@212F,16H)	873	3290		77	34 (oily)	
Precipitate				bel. 1.0	bel. 0.1	
Total Acidity mg KOH/g	3242	0.03		0.01	0.003	
Copper Corrosion (3hrs, 212F)	130	1a	1a	1a	1a	1a
VII OTHER PROPERTIES						
Refractive Index	1218	1.5794	1.5731	1.4880	1.4698	1.4730
Molecular Weight	2503	158	162	172	164	
Bromine Number	1159	31	10.4	0.4	0.06	0.10
Maleic Anhydride Value	UOP	22	3.7	0.85	0.75	
Color, Saybolt	156	7.5		+8	+29	

* after heptane washing 10 mg
** after heptane washing 2 mg

TABLE 3

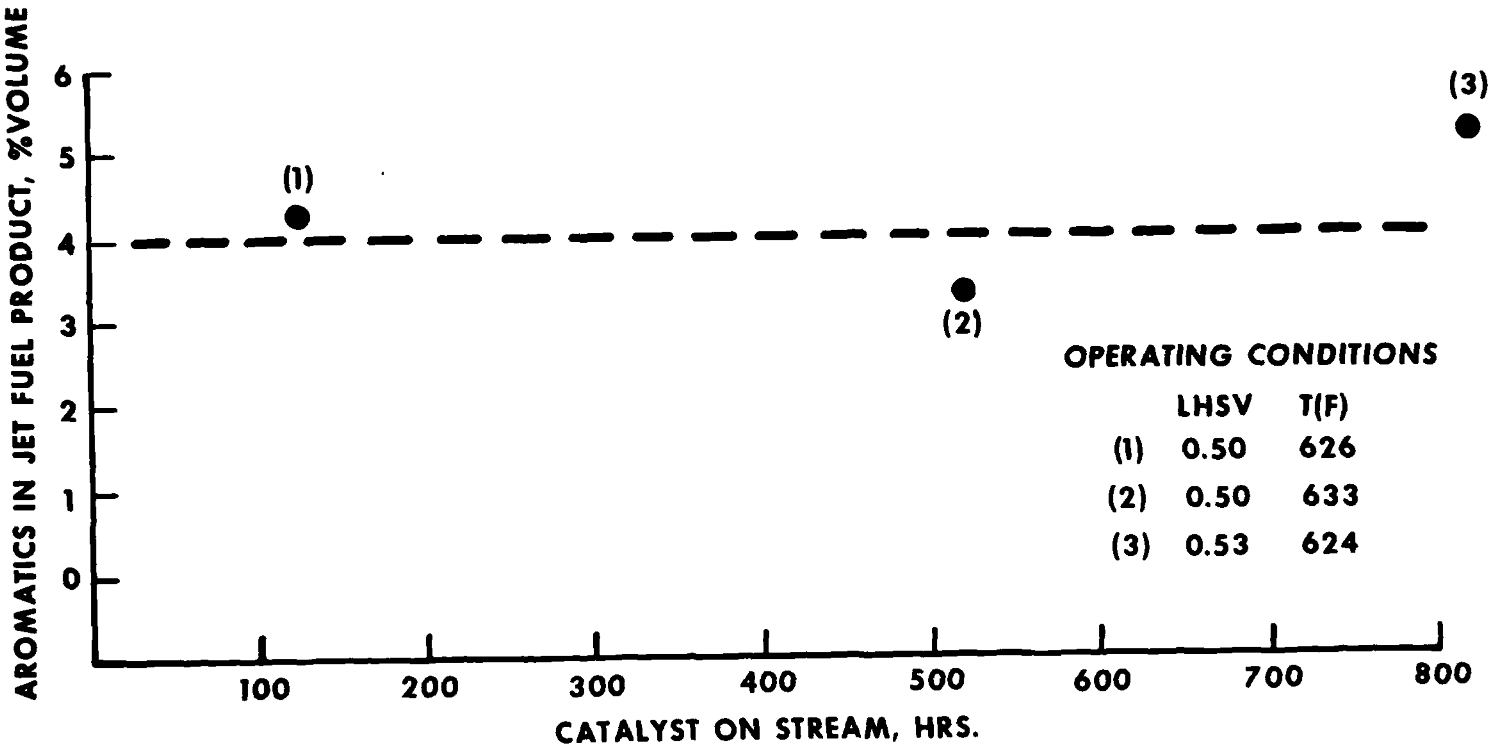
CHARACTERISTICS OF JET FUEL SAMPLES FROM PREPARATORY RUNS

PRODUCT		HDS PURIFIED	FULLY HYDROG
No. Steps in Treatment		2	2
Designation		AFLPF-5(HDS)	AFLPF-4
Sample No. (S-)		1558	1550 (Exploratory)
PROPERTIES	**ASTM-D**		
I HEATING VALUE			
Specific Gravity 60/60F	1298		0.875
68/68F		0.924	
Net Heat of Combustion Btu/lb	3338		18,370
II COMPOSITION, BURNING QUALITY			
Aromatics, Vol % FIA	1319		6.0
Aromatics, Vol %, Sulfonation	1019	69.7	
Carbon, Wt %			86.93
Hydrogen, Wt %			13.07
Sulfur, (Microcoulomtr.) ppm		20	0.5
Nitrogen, ppm		10	
Smoke Point, mm	1322		18
Naphthalenes, Vol %	1840		0.09
Luminometer No.	1740		36
Aniline Point, F	611		120
III VOLATILITY			
Flash Point (Tag CC) F	56		143
Distillation, F	86		
IBP			372
5			399
10			406
20			413
30			418
50			429
70			445
90			482
EP			560
IV COLD HANDLING			
Freezing Point, F	2386	bel. -98	bel. -76
Pour Point, F	97	bel -98	
Viscosity, cSt, -65F	445		60.7
-30F			17.56
- 4F			9.38
V OTHER PROPERTIES			
Refractive Index	1218	1.5163	
Maleic Anhydride Value	UOP	1.70	

TABLE 4
PROPERTIES OF CATALYSTS USED

	LD 265	HR 354
Source	Procatalyse	Procatalyse
Type	Pd on Alumina	Ni/W on Alumina
Function	Hydrostabilization	Hydrogenation
Form	Balls, 2-4mm 0	Extrudates, 1.2 mm 0
Surface area m^2/g	60	170
Pore Volume, cm^3/g	0.60	0.37
Bulk Density, g/cm^3	0.67	0.80
lb/cu ft	43.7	55.5
Ave Crush Strength kg/cm^2	7	10

HR 354, an alumina-supported nickel tungsten catalyst with high metal content belongs to the large family of sulfur insensitive catalysts which require presulfiding. It is recommended by the manufacturer for the deep hydrogenation of sulfur-containing feedstocks, and to improve the smoke point of kerosines. Other application territories include: diesel index improvement, manufacture of white oils, paraffin oils, etc. Total porous volume of the catalyst is about 40-50 cm^3/100g, and only less than 10 cm^3 of the pore volume is distributed in the 0.1 - 1.0 micron range; the balance is finer. It can be operated at high temperature with several years lifetime. The use of dimethyl sulfide is recommended to provide pre-sulfidation. Physical characteristics of HR 354 are given in Table 4 - and activities of both catalysts vs time are shown in Figures 3 and 4. In this relatively short time of use (1000 hrs) in these experiments, no sign of changing activities was detected. The slight scatter of results for HR 354 was caused by fluctuations in reactor temperature.

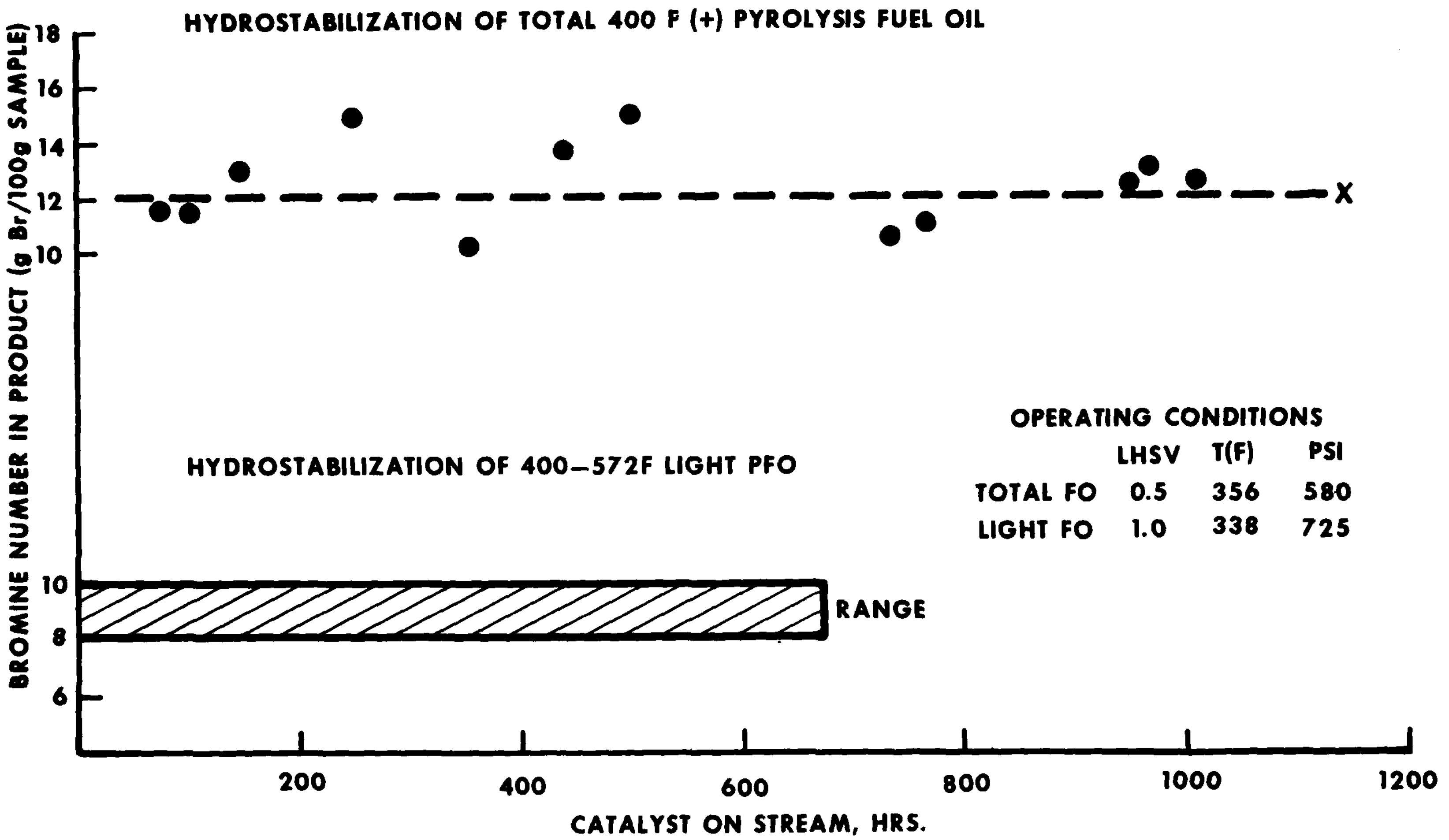


ACTIVITY OF CATALYST HR 354 vs TIME

(Ni, W ON ALUMINA BY PROCATALYSE)

FIGURE 3

79-15,527



79-15, 228

ACTIVITY OF CATALYST LD 265 vs TIME

(0.3% Pd ON γ ALUMINA BY PROCATALYSE)

FIGURE 4

5. Results

Properties of the raw fuel oil and those of the hydrotreated products established by standard characterization tests are shown in Tables 2 and 3. In Table 2, the first four columns pertain to the 600 liters production samples. In the order of listing, starting from AFLPF raw fuel, each consecutive column represents a hydrotreating of increased severity; thus moving from left to right, the effect of hydrogenation can be studied. In the last column of Table 2, the properties of the fully hydrogenated, AFLPF-4 exploratory sample were entered, for comparison. This sample was obtained in the described three-step noble metal hydrogenation scheme.

In Table 3, characteristics of two exploratory samples are listed. AFLPF-5 is an intermediate hydrodesulfurized product used for the production of AFLPF-4, whereas AFLPF-3 represents the initial 30 liters run of the fully hydrogenated final product in Table 2. The sample was prepared for the purpose of product approval by the Air Force.

To facilitate the evaluation of the jet fuel candidates produced, the measured properties of these fuels were grouped by service requirements. The same, somewhat arbitrary grouping was also applied in Table 5. This table lists the essential service requirements of selected jet fuels, as prescribed by various ASTM and military specifications.

Tables 6 and 7 summarize the effect of hydrotreatment on the hydrocarbon types present in the various jet fuel candidates as established by mass spectrometer. Table 8 presents the characterization of the aromatic hydrocarbon fractions by proton and carbon-13 NMR analyses. The tables reveal the molecular structural changes of the fuels induced by the hydrotreating. These changes, in turn, were responsible for the shifts in service properties as detected by the results of the routine tests. The interpretation of the

TABLE 5

ESSENTIAL PROPERTIES OF US COMMERCIAL AND MILITARY JET FUELS

FUEL		WIDE CUT		KEROSINE TYPE			
SPECIFICATION	ASTM TEST, D	JET B D-1655	JP - 4 MILT 5624	JET A, A-1 D-1655	JP - 5 MILT 5624	JP - 7 MILT 38219	JP - 8 MILT 83133
P R O P E R T I E S							
I **HEATING VALUE**							
Specific Gravity 60/60F	1298	.751-.802	.751-.802	.775-.840	.788-.845	.779-.806	.775-.840
Net Heat of Combustion Btu/lb, min	2382 or 1405	18,400	18,400	18,400	18,300	18,700	18,400
II **COMPOSITION, BURNING BEHAVIOR**							
Aromatics, Vol %, max	1319	20(22)	25	20(25)	25	5	25
Hydrogen, Wt %, min	1018 or 3343	-	13.6	-	13.5	-	13.6
Sulfur, wt %, max	1266 or 1522	0.3	0.4	0.3	0.4	0.1	0.4
Smoke Point, mm, min	1322	25	20	25	19	-	25
Smoke Point, mm and} min	1322	19	-	18	-	-	20
Naphthalenes, Vol %} max	1840	3	-	3	-	-	3.0
Luminometer No., min	1740	45	60	45	50	75	-
III **VOLATILITY**							
Flash Point, F, min	56 or 93	-	-	100	140	140	100
Vapor Pressure, lb	323	3 max	2-3	-	-	-	-
Distillation, F	86						
IBP/EP		-	-	-/572	-/550	360/550	-/572
10/20 %		-/290	-/290	400/-	400/-	385/403	400/-
50/90 %		370/470	370/470	-	-	-/500	-
IV **COLD HANDLING**							
Freezing Point, F, max	2386	-58	-72	-40;-58/A-1)	-51	-46	-58
Viscosity, cSt @ -4F, max	445	-	-	8	-	-	8
@ -30F, max		-	-	-	16.5	15	-
V **THERMAL STABILITY (JFTOT)**							
Heater Tube Rating	3241	< 3	< 3	< 3	< 3	Res.)	< 3
Pressure Drop, mm Hg, max	3241	25	25	25	25	Coker)	25
VI **STORAGE/CORROSION**							
Existent gum, mg/100 ml, max	381	7	7.0	7	7.0	5.0	7.0
Potential Residue mg/100 ml 16 hours, max	873	-	-	-	-	10.0	-
Acidity mg KOH/g, max	3241	-	0.015	0.1	0.015	-	0.015
Copper Strip Corrosion, 2 hr 212 F, max	130	No. 1	No. 1b	No. 1	No. 1b	No. 1b	No. 1b

TABLE 6

EFFECT OF HYDROTREATMENT ON HYDROCARBON TYPES DISTRIBUTION

PRODUCT	RAW PFO			HYDROSTABILIZED			INTERMEDIATE			FULLY HYDROG			FULLY HYDROG		
No. Steps in Hydrotreatment	0			1			2			2			3		
Designation	AFLPF			AFLPF-1			AFLPF-2			AFLPF-3			AFLPF-4		
HYDROCARBON TYPES, Wt%															
Normal Paraffins) Isoparaffins)	5.0			5.0			0.4			0			0.1		
CYCLOPARAFFINS	5.6			6.8			67.7			94.4			89.3		
Mono-cyclic								28.6			41.9			36.5	
Di-cyclic (Condensed)								34.6			47.6			47.7	
Tri-cyclic (Condensed)								4.5			4.9			5.1	
AROMATICS	89.4			88.2			29.8			2.4			6.9		
Monoaromatics		26.1			29.2			28.6			2.1			6.2	
Alkylbenzenes			4.5			8.6			7.5			1.6			2.5
Indanes/Tetralins			7.2			14.3			20.6			0.5			3.4
Indenes			14.4			6.3			0.5			0			0.3
Diaromatics		62.1			57.7			1.1			0.3			0.6	
Naphthalene			4.3			3.4			0						0
Alkylnaphthalenes			48.6			45.8			0.4						0.2
Acenaphthenes			7.7			7.3			0.4						0.1
Fluorenes			1.5			1.2			0.3			0.3			0.3
Triaromatics		1.2			1.3			0.1						0.1	
VOLATILES (Loss in FIA Separation)	0			0			2.1			3.2			3.7		
TOTAL	100.0			100.0			100.0			100.0			100.0		

TABLE 7

COMPARISON OF AROMATICS DISTRIBUTION BY LOW AND HIGH VOLTAGE MASS SPECTROMETER

PRODUCT DESIGNATION	RAW PFO AFLPF									
Mass Spec. Ionization	High		Low Voltage							
No. Carbon Atoms			7	8	9	10	11	12	13	14
MONOAROMATICS, Wt %										
Alkylbenzenes	4.5	4	1	1	1	1	1	0	0	0
Indenes/Tetralins	7.2	7	0	0	1	1	2	2	1	0
Indenes	14.4	21	0	0	1	4	10	5	2	0
Total Mono-	26.1	32								
DIAROMATICS, Wt %										
Naphthalene	4.3	48	0	0	0	5	18	16	7	2
Alkylnaphthalenes	48.6									
Acenaphthenes	7.7	7	0	0	0	0	0	2	3	2
Fluorenes	1.5	2	0	0	0	0	0	0	1	1
Total Di-	62.1	57								
TRIAROMATICS, Wt %										
Phenanthrenes	1.2	1								
Total Tri-	1.2	1								
Aromatics Total, Wt %	89.4	90								

PRODUCT DESIGNATION	HYDROSTABILIZED AFLPF-1									
Mass Spec. Ionization	High		Low Voltage							
No. Carbon Atoms			7	8	9	10	11	12	13	14
MONOAROMATICS, Wt %										
Alkylbenzenes	8.6	6	0	0	1	2	2	1	1	0
Indenes/Tetralins	14.3	14	0	0	1	2	6	3	2	0
Indenes	6.3	7	0	0	1	3	2	1	0	0
Total Mono-	29.2	27								
DIAROMATICS, Wt %										
Naphthalene	3.4	51	0	0	0	5	20	19	8	2
Alkylnaphthalenes	45.8									
Acenaphthenes	7.3	7	0	0	0	0	0	2	3	2
Fluorenes	1.2	2	0	0	0	0	0	0	1	1
Total Di-	57.7	60								
TRIAROMATICS, Wt %										
Phenanthrenes	1.3	1								
Total Tri-	1.3	1								
Aromatics Total, Wt %	88.2	88								

PRODUCT DESIGNATION	INTERMEDIATE HYDROG AFLPF-2									
Mass Spec. Ionization	High		Low Voltage							
No. Carbon Atoms			7	8	9	10	11	12	13	14
MONOAROMATICS, Wt %										
Alkylbenzenes	7.5	5	0	1	1	1	1	1	0	0
Indenes/Tetralins	20.6	23	0	0	2	2	8	8	4	0
Indenes	0.5	2	0	0	0	0	0	0	0	0
Total Mono-	28.6	30								
DIAROMATICS, Wt %										
Naphthalene	0									
Alkylnaphthalenes	0.4									
Acenaphthenes	0.4									
Fluorenes	0.3									
Total Di-	1.1									
TRIAROMATICS, Wt %										
Phenanthrenes	0.1									
Total Tri-	0.1									
Aromatics Total, Wt %	29.8	30								

Accuracy of low voltage MS is about ± 2% absolute data in both measurement categories will be provided in Section V.

TABLE 8
FUEL CHARACTERIZATION BY NUCLEAR MAGNETIC RESONANCE ANALYSES

SAMPLE	AFLPF		AFLPF-1		AFLPF-2	
NMR	Proton	C13	Proton	C13	Proton	C13
Avg Molecular Weight *	169	158	174	162	198	
Aromaticity	0.73	0.78	0.70	0.71	0.49	0.50
Aromatic Rings/Molecule	1.9	1.6	1.8	1.5	1.3	
No. Carbon in Arom. Ring/Molecule	9.4	9.3	9.3	8.7	7.3	
Percent Saturate Carbon	27.5	22.2	30.1	29.0	51.0	
Alkyl Substituent/Molecule	2.2	2.3	2.2	2.2	3.5	
No. Carbon/Alkyl Substituents	1.6	1.3	1.8	1.7	2.2	

* MW Proton NMR: by calculation
C13 NMR: experimental value

6. Sample Delivery

Three 55-gallon drums each of AFLPF-1 hydrostabilized, AFLPF-2 intermediate, and AFLPF-3 fully-hydrogenated jet fuel candidates were produced in the pilot plant. A commercially used antioxidant, "Topanol A" (6-tertiary butyl 2-4 dimethylphenol) was added to the products in 20 ppm quantities. One drum of each product was shipped to Shell, Thornton Labs., Chester, England, and 2 drums of each were airfreighted to Wright Patterson AFB, May 1979.

SECTION V

DISCUSSION OF RESULTS

1. Interpretation of Data

The fundamental concern of the raw fuel processing was to impart properties by hydrogenation which would qualify the upgraded product for use in turbo propulsion combustion. As a result of this hydroprocessing, the hydrogen content of the fully hydrogenated product has increased by five percentage points over that of the raw fuel, accompanied by other changes as listed below.

The calorific value, on weight basis, has increased by about 9 percent; sulfur, nitrogen and naphthalenes were practically eliminated, and the smoke point reached the required 20mm level. The specific gravity has significantly dropped, causing the volumetric heat of combustion to decrease; however, it was still about 10 percent higher than most of the commercial and military jet fuels listed in Table 5. There was a small increase in the front light ends of the processed fuel coupled with some drop in the flash point, as expected. Cold temperature viscosity of the hydrogenated product has significantly improved along with a dramatic improvement in its thermal stability, (JFTOT), and storage stability, (existent and potential gum). The high residual gum values reported in Table 2 may not be representative at all, partly because of the interference of non-volatile antioxidant additives and partly due to the presence of oily, difficult to evaporate hydrocarbons. (Indeed, after heptane washing, the oily components were dissolved and the gum formers remained below acceptable levels.)

Among the changes introduced by the hydrogenation, the largest was the reduction of aromatics from 100 percent in the raw fuel to 4 percent volume in the fully hydrogenated product, as measured by ASTM D 1319 FIA determination. By observing the results of Tables 6 to 8, an insight can be gained on the nature of the changes caused by hydrogenation, and a quantitative assessment is offered for the disappearance and transformation of various groups of molecular species. However, before discussing the subject, some clarification concerning the aromatic content appears to be in order.

The raw fuel was found to be 100 percent aromatic by FIA determination, but only about 90 percent by mass spectrometer. This difference was caused by the inability of the silica gel column used in the FIA method to separate the small amount of saturates in the presence of overwhelming quantities of aromatics, whereas the mass spectrometer detected those. Since FIA is the method specified for the determination of aromatics in jet fuels, those figures generated by FIA were retained in Table 2, even though they are somewhat conflicting with results of Tables 6 and 7.

The breakdown of the aromatics in the raw fuel as entered in Table 6 shows that these were predominantly diaromatics, consisting mainly of naphthalenes and alkylnaphthalenes. Triaromatics were present only in negligible quantities and the saturates most likely originated from the unconverted portion of the feedstock used in the production of olefins. Approximately one quarter of the raw fuel consisted of various monoaromatics. The low voltage MS results are in reasonable agreement with the breakdown on aromatics and in addition, they provide the distribution of the aromatic types by carbon numbers. (The discrepancy, showing some small quantities of C-7, 8, 9 alkylbenzenes present in our higher boiling kerosines could mainly be ignored.)

Examining the effect of hydrostabilization, it is clear that this treatment has not reduced significantly the total aromatics, but reactive species such as indenes were hydrogenated to indans, and probably some naphthalenes to tetralins. As the severity of hydrogenation increased, first the triaromatics were eliminated and the group of diaromatics converted into monoaromatics. In the case of full hydrogenation, small quantities of monoaromatics were the only survivors and the loss of paraffins was probably due to an analytical error.

Assuming that the originally present cycloparaffins in the raw fuel were predominantly noncondensed and adding these to the monoaromatics there, one can conclude that the condensed cycloparaffins in the fully hydrogenated sample exceeded by 9-10 percentage points their potentially available quantities. This increase of monocyclics has occurred at the expense of the dicyclic compounds. The onset of the phenomenon observed signals - some degradation, ring openings and possibly mild cracking. Since only negligible quantities of light hydrocarbons were produced during the treatment, one can also conclude that the hydroprocessing pursued still remained in the realm of hydrogenation vs that of extensive hydrocracking.

NMR measurements by proton and C13 techniques in Table 8 show the changes in the average aromatic structures as a result of progressing hydrogenation. The percent of saturate carbon has increased and the aromaticity decreased.

The aromaticity is calculated by the following equation:

$$f_a = C_a/(C_a + n_s\ C_s)$$

where C_a = number of aromatic carbons

C_s = number of alkyl substituents

n_s = chain length per substituents

in an average assumed hypothetical aromatic molecule.

In the case of C13 NMR, the aromaticity is directly established experimentally versus the proton NMR, where the carbon atoms are assigned to the protons found in their respective environments. The measurements reported in Table 8 were performed on the pre-separated aromatic fraction of the samples obtained via FIA silica gel treatments. Since the residual quantity of aromatics in the fully hydrogenated sample was 2.1 percent, NMR measurements on AFLPF-3 product were omitted. In the case of AFLPF-2, the C13 analysis was directly performed on the entire sample without pre-separation, thus the measured aromaticity had to be adjusted by taking into consideration that the sample contained only 30 percent aromatics.

As an overall conclusion we may summarize that the hydrotreating introduced significant improvement in the quality of the products and these changes were mainly attributable to the transformation of an aromatic fuel to its naphthenic analogue.

2. Service Requirements vs Properties

The primary purpose of setting up fuel specifications is to assure that fuel would meet average service requirements and not fail even under extreme flight conditions. Unduly tight quality specifications could hurt supply and limit fuel availability.

From the engine's point of view alone, the calorific value is the most important quality criterion. Along with it, however, the importance of the density of fuel is also to be considered. Apart from price considerations, (the fuel is usually purchased on volume basis, hence it pays to buy higher density fuel), the aircraft could be weight or volume limited. Under weight limited conditions, changing to low density fuel, the payload can be increased due to the higher Btu/lb heat content of the lighter fuels, whereas by changing to dense fuels in case of volume limitations, the mission range can be extended. Usually, the advantage gained in the second category is more significant. Other areas, where the knowledge or limitations on specific gravity may be important are: controlling fuel dosage to the engine, and calculating fuel load to the aircraft.

The use of the fuel in the tank of the aircraft is not limited to combustion alone; it also serves as a utility fluid and a heat sink. The most important requirement imposed on the fuel while performing in this capacity is that it must remain in liquid state under wide fluctuations of temperature and pressure.

Limitations built into fuel specifications covering initial boiling - and flash point - are to prevent vaporization or boiling losses of the fuel while exposed to reduced pressure in a high altitude flight. Distillation end point, freezing point, pour point limitations - on the other hand - are introduced to prevent the formation of solids in the fuel system. The onset of partial solidification could plug up fuel lines, filters and decrease pumpability, leading to excessive wear in the booster and main fuel pump or in case of severe freeze-up could cut off the fuel supply to the engine. Extremes in temperatures under which the fuel must remain liquid could range from -80C outside and -50C fuel tank temperatures in subsonic flights. In contrast, up to 85C recorded fuel tank temperatures were measured at Mach 2 supersonic level. The high temperature encountered in supersonic flights is due to the adiabatic compression of air. At 35,000 feet, the pressure drops to about 4 psi, obviously disqualifying the use of wide-cut kerosines in supersonic flights, or requiring tank pressurization for the others because of fuel boiling. Set minimum values are required for fuel viscosities at low temperatures to maintain pumpability and lubrication and at high temperature to ensure the proper atomization of the fuel entering the combustor.

Among procedures used for establishing the combustion characteristics of fuels, smoke point has a frequent application.

Although smoke point is not a fundamental property of the fuel, it has found wide application in anticipating the tendency of the fuel to smoke in the engine. Paraffinic fuels smoke less; naphthenic and aromatic fuels exhibit increasing tendencies to smoke more. Since in our case interest focussed around the naphthenic alternative fuels, we measured the smoke point of decalin. Under standard conditions, it was found to be 23 mm.

The use of fuel in heat exchangers, cabin air conditioning, and the hot zone of the engine area, requires the fluid to exhibit sufficient thermal stability and a resistance toward thermal breakdown. In the presence of trace metals and oxygen, the fuel may become unstable and its degradation could occur at elevated temperatures. In this process, solid particles are formed which would deposit on exchanger surfaces and block filters. To predict the behavior of the fuel under simulated aircraft use, a test procedure (JFTOT), was designed to examine its propensity for degradation under accelerated laboratory conditions. The deposit formed on the "exchanger" tube is rated and the amount of solids formed is quantified by measuring the pressure increase across a filter.

The purpose of writing this brief survey on essential properties of the aviation turbine fuels was to indicate that in the preparation of the jet fuel candidates, serious consideration must be given to meet service requirements. In pursuing the present project, the philosophy was adopted that regardless of economics and arguments over the soundness of some overly tight specification values in fuel standards, at least one of the processed LPFO product must have matched the properties prescribed for a conventional jet fuel. An examination of the values entered in Table 5 for JP-8 and Table 2 for AFLF-3 product, confirms that this goal has been achieved. It also shows that a fuel equivalent to JP-8 can be commercially produced from LPFO.

However, in the near future, with the help of some pending combustion tests on AFLPF-3 and other "off-spec" products knowledge will be obtained as to what level of "laxity" can be tolerated in the fuel properties without affecting the engine performance. Any relaxation in quality is a step towards less hydrogen consumption and cheaper fuel. But, prior to moving in this direction, the response of the entire fuel system must be assessed in terms of service requirements as briefly outlined above.

3. Tailoring Properties of Intermediate Density Fuel

Componential breakdown on the LPFO in Tables 6 and 7 shows that over 60 percent of the raw fuel was diaromatic and the amount of naphthalenes exceeded 50 percent. However, because of distillation end point limitations at around 560F, triaromatics such a phenanthrenes were cut off and probably a portion of fluorenes eliminated. Phenanthrene boils at 609F and fluorene at 570F. The excellent cold temperature properties of naphthenic compounds especially those of dicyclic alkanes are well known. Fabuss (10) under an Air Force contract has also found that decalins and some alkyl decalins exhibited the highest thermal stability. However, if a fuel of higher density is to be produced, consideration should be given to extend the boiling range for the inclusion of some triaromatics. After hydrogenation, the resulting perhydrophenanthrenes and fluorenes could significantly increase the density of the fuel as reported by Schneider (11), and also a biased cis hydrogenation could have the same effect on the density.

SECTION VI

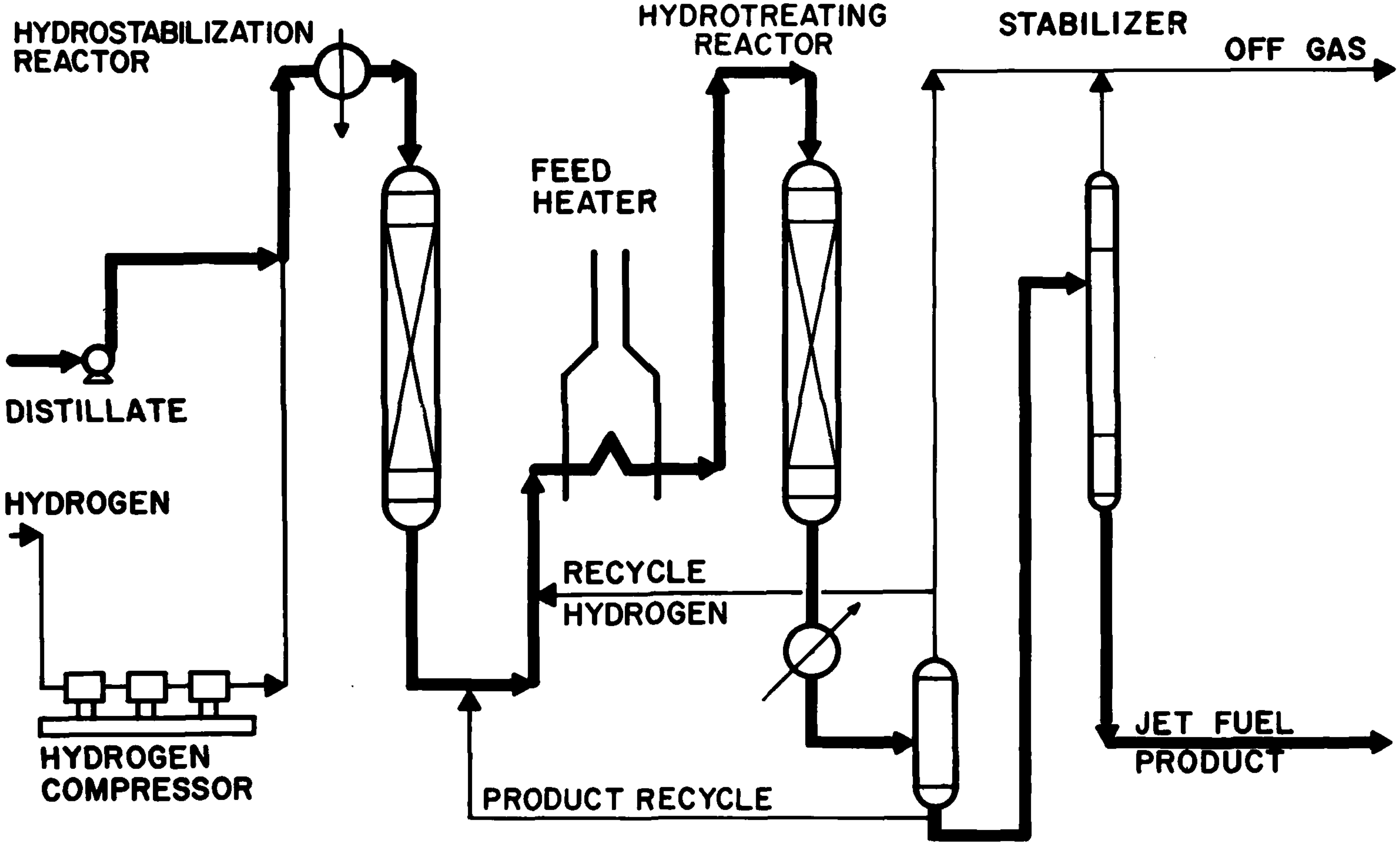
IFP/SWEC JET FUEL PROCESS

1. Process Description

The design of this plant to convert light pyrolysis fuel oil into a premium jet fuel product as shown in the schematic diagram, Figure 5, incorporates several important features. Both hydrotreater reactors are operated at high pressure, about 2600 psig, thereby reducing the recycle compression horsepower requirements and avoiding the use of an intermediate compressor. The plant is designed to use 95 mol% hydrogen, which is readily available as a by-product of an ethylene plant. Extensive utilization of heat exchange results in an energy efficient design.

Referring to the detailed process flow diagram in Figure 6, and the accompanying Equipment List in Table 9, the hydrogen make-up feed, assumed to enter the battery limits at 400 psia, is compressed to reactor pressure by a motor-driven three-stage reciprocating compressor. Light fuel oil feed is pumped from atmospheric pressure to reactor conditions in feed pump P-103. Fuel oil and hydrogen are mixed and heated to the first stage reactor inlet conditions against hot effluent from the second stage reactor in T-101. A start-up heater (T-102) which is heated by medium pressure steam, is also provided. The first stage hydrotreater reactor, Figure 7, consists of two beds of IFP catalyst LD-265, a commercially proven palladium catalyst. Temperature control is provided by a hydrogen quench stream injected between the beds. The feed enters the reactor at 320F and leaves the reactor at 428F (start of run conditions).

First-stage reactor effluent is mixed with recycle liquid from the second stage by P-101, and some additional hydrogen, from Hydrogen Recycle Compressor R-102.



JET FUEL PROCESS SCHEME

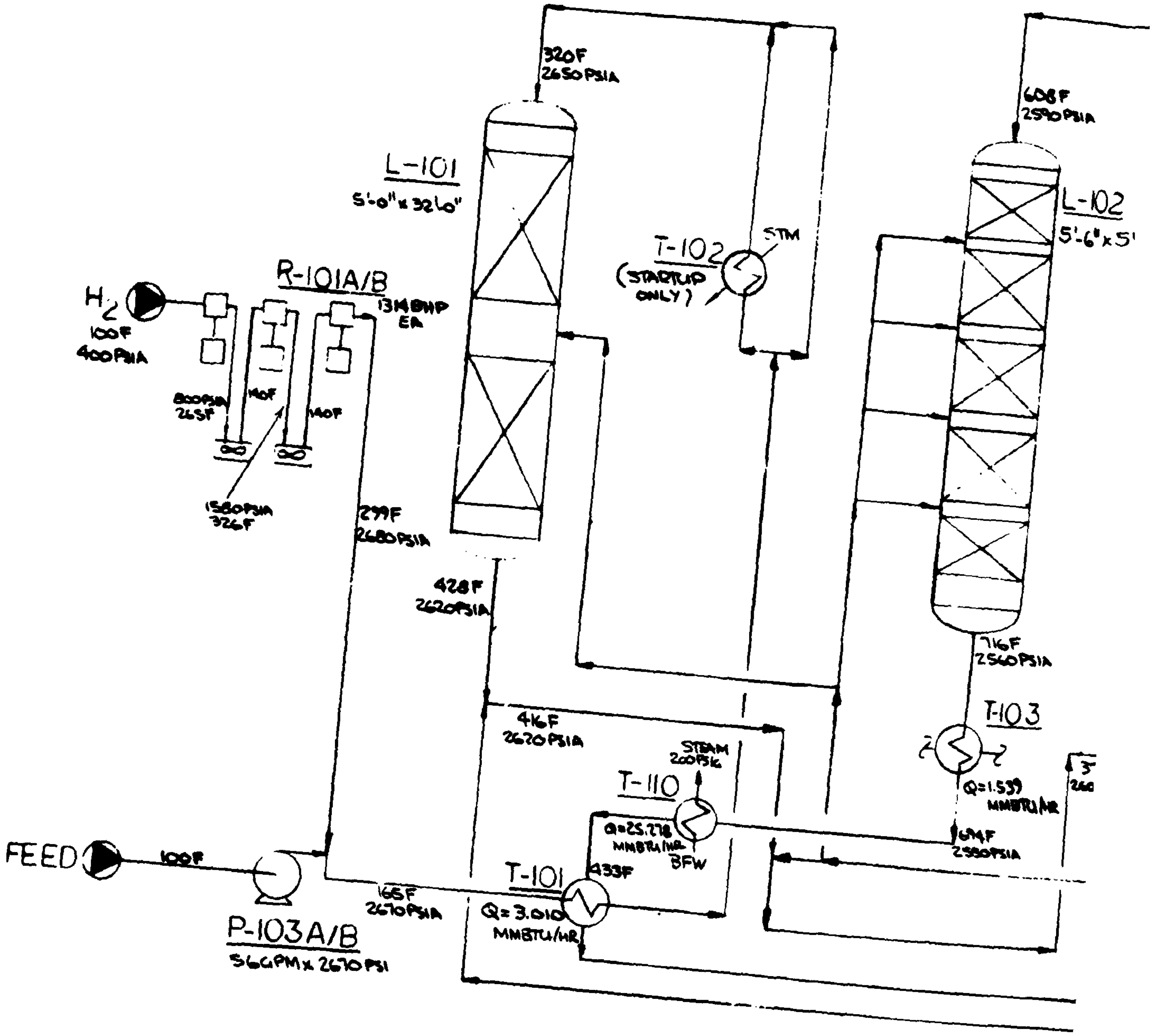
FIGURE 5

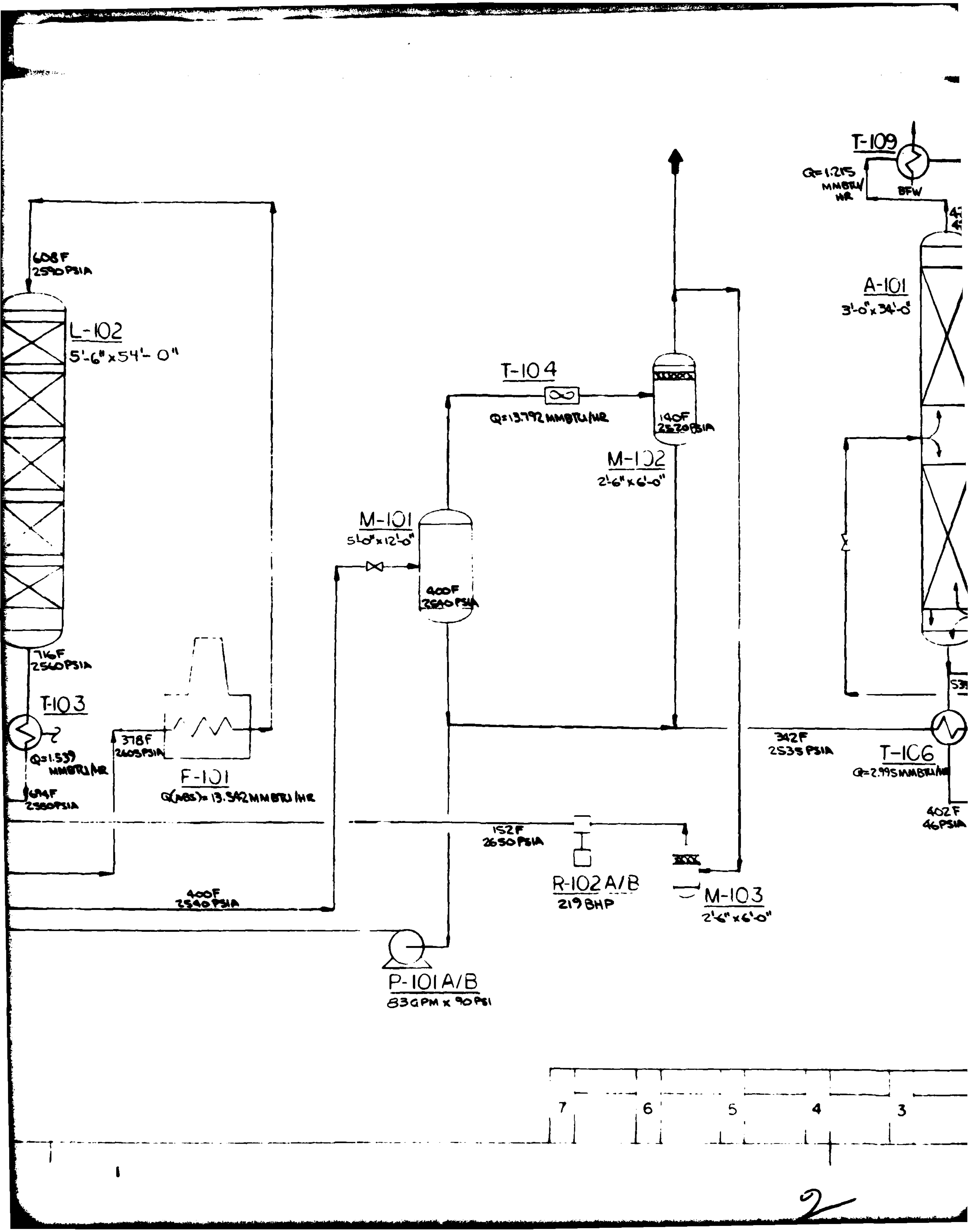
79-14.832

TABLE 9

EQUIPMENT LIST FOR PROCESS FLOW DIAGRAM, JET FUEL

ITEM	DESCRIPTION
A-101	TOWERS (A)
	Stabilizer
F-101	FIRED HEATERS (F)
	Hydrotreater No. 2 Feed Heater
	REACTORS (L)
L-101	Hydrotreater No. 1
L-102A/B	Hydrotreater No. 2
	DRUMS (M)
M-101	High Pressure Separator
M-102	Recycle Hydrogen Separator
M-103	Recycle Hydrogen Compressor Knockout Drum
M-104	Stabilizer Reflux Drum
	PUMPS (P)
P-101A/B	Product Recycle Pump
P-102A/B	Stabilizer Reflux Pump
P-103A/B	Feed Pump
	COMPRESSORS (R)
R-101A/B	Hydrogen Compressor
R-102A/B	Recycle Hydrogen Compressor
	EXCHANGERS (T)
T-101	Reactor No. F/E Feed Heater
T-102	Reactor No. 1 Startup Heater
T-103	Stabilizer Reboiler
T-104	Flash Vapor Condenser
T-105	Product Air Cooler
T-106	Stabilizer F/E Exchanger
T-107	Stabilizer Condenser (Air Cooled)
T-108	Product Water Cooler
T-109	Stabilizer Condenser/BFW Heater
T-110	Reactor No. Effluent Cooler


320F
2650PSIA
L-101
5'-0" x 32'-0"
T-102
(STARTUP ONLY)
STM
608F
2590PSIA
L-102
5'-6" x 5'
H2
100F
400PSIA
R-101A/B
1314BHP EA
800PSIA
265F
140F
140F
1580PSIA
326F
299F
2680PSIA
428F
2620PSIA
716F
2560PSIA
T-103
Q=1.539 MMBTU/HR
416F
2620PSIA
STEAM 200PSIG
T-110
Q=25.278 MMBTU/HR
BFW
694F
2580PSIA
FEED
100F
P-103A/B
56GPM x 2670PSI
165F
2670PSIA
T-101
433F
Q=3.010 MMBTU/HR


T-109
Q=1.215 MMBTU/HR
BFW
A-101
3'-0"x34'-0"
608F
2590PSIA
L-102
5'-6"x54'-0"
T-104
Q=13.792 MMBTU/HR
140F
2570PSIA
M-102
2'-6"x6'-0"
M-101
5'-0"x12'-0"
400F
2540PSIA
716F
2560PSIA
T-103
Q=1.539 MMBTU/HR
378F
2605PSIA
F-101
Q(ABS)=13.542MMBTU/HR
694F
2580PSIA
342F
2535PSIA
T-106
Q=2.995MMBTU/HR
402F
46PSIA
152F
2650PSIA
R-102A/B
219BHP
M-103
2'-6"x6'-0"
400F
2540PSIA
P-101A/B
83GPM x 90PSI
7
6
5
4
3
1
2

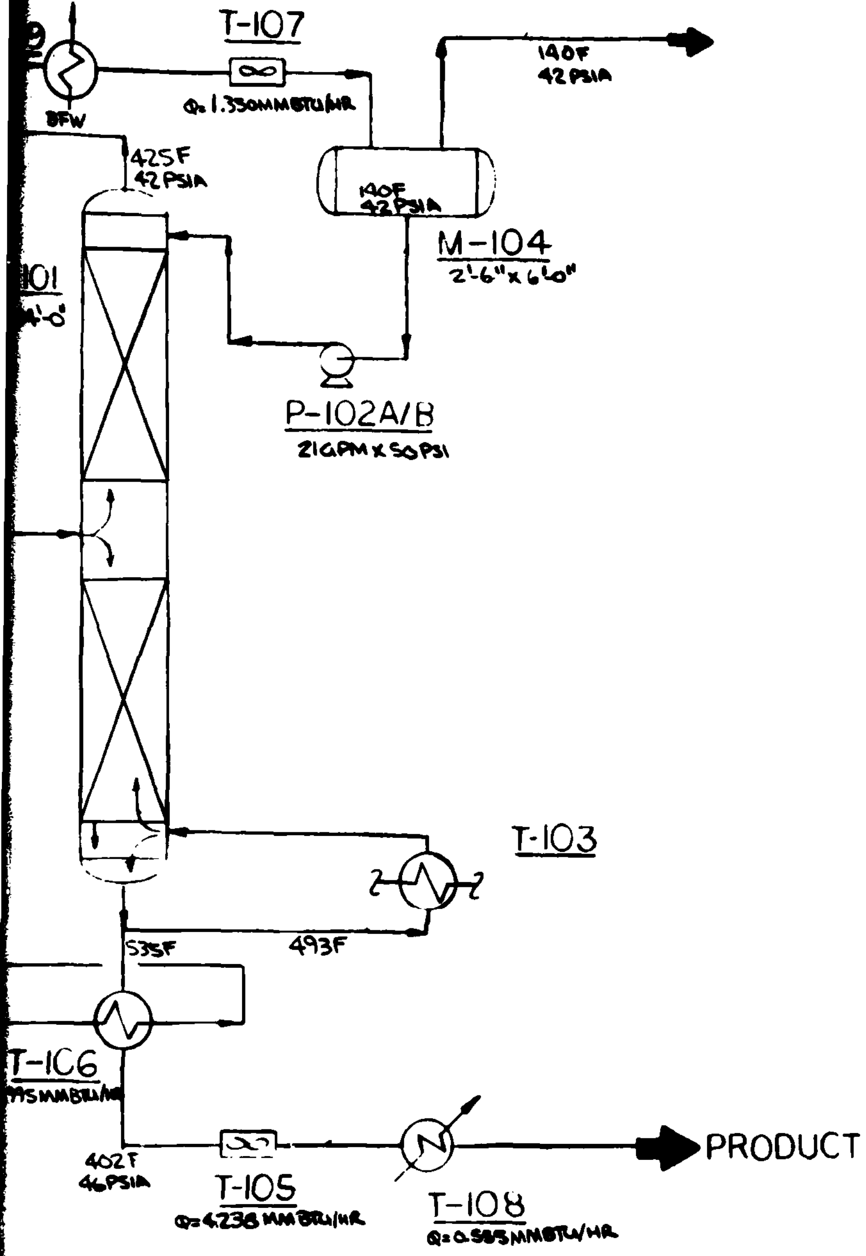


FIGURE 6

USAF

PROCESS FLOW DIAGRAM-JET FUEL

95% HYDROGEN CASE

		JNR		JMD	STONE & WEBSTER ENGINEERING CORPORATION
3	2	8.15.79	1	8.1.79	13248-SK-01

46037 18

DESIGN DATA

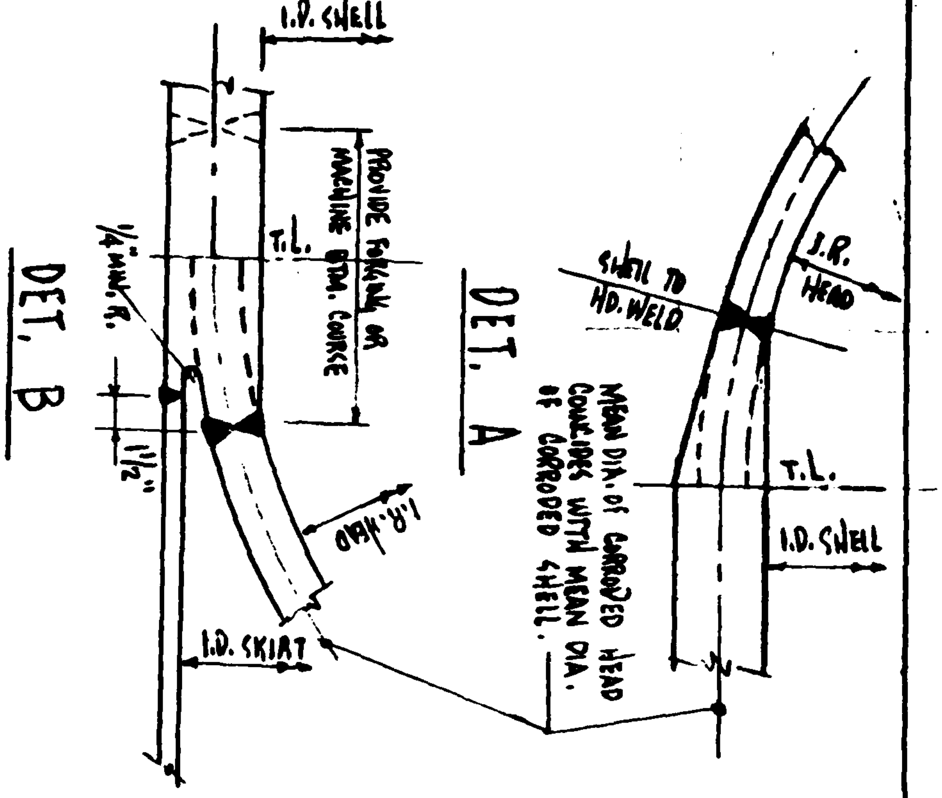
OPERATING PRESSURE	2620	PSIG	DESIGN PRESSURE	2751	PSIG
OPERATING TEMPERATURE	428	F	DESIGN TEMPERATURE	428	F
EMERGENCY VACUUM (7.5 PSIG AT F)			YES	[✓ NO]	
LONG. JOINT EFFICIENCY	100%				
CODE	ASME SECT VIII, DIV. 2				
CODE STAMP			[✓ YES]	NO	
RADIOGRAPHY	[✓ 100% FULL]		FULL LONG. PARTIAL GIRTH	SPOT	
POSTWELD HEAT TREATMENT REQ'D.			[✓ YES]	NO	
CORROSION ALLOWANCE	1/8	IN.			
ALLOW STRESS AT DESIGN METAL TEMP.			21,364 PSI		
HYDRO TEST HORIZ. LIMITED BY					
PAINTING					
INSULATION (BY OTHERS) HOT COLD			INSULATION THICKNESS (NOTE 41)		IN.
SKIRT FIREPROOFED (BY OTHERS)			FIREPROOF THICKNESS (NOTE 43)		IN.
EMPTY WEIGHT (EXCLUDES TRAYS)			131,000		LB.
OPERATING WEIGHT (INCLUDES TRAYS)					LB.
WEIGHT OF TRAYS					LB.
MAX. LOAD ON FOUNDATION (FULL OF WATER)					LB.
ERECTION MOMENT AT BASE					FT. LB.
MAX. MOMENT AT BASE INCL. MOMENT DUE TO PIPE THRUST					FT. LB.
MAX. SHEAR AT BASE					LB.
TYPE OF TRAYS & LIQUID FLOW					

MATERIALS

VESSEL MAT'L CLASS (ESA-A02) PI-C (SA515 GR 70)

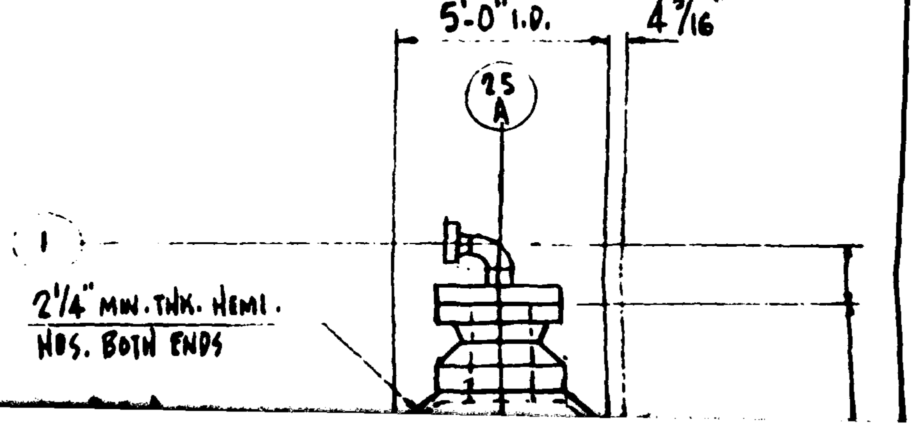
NOZZLES & MANHOLES

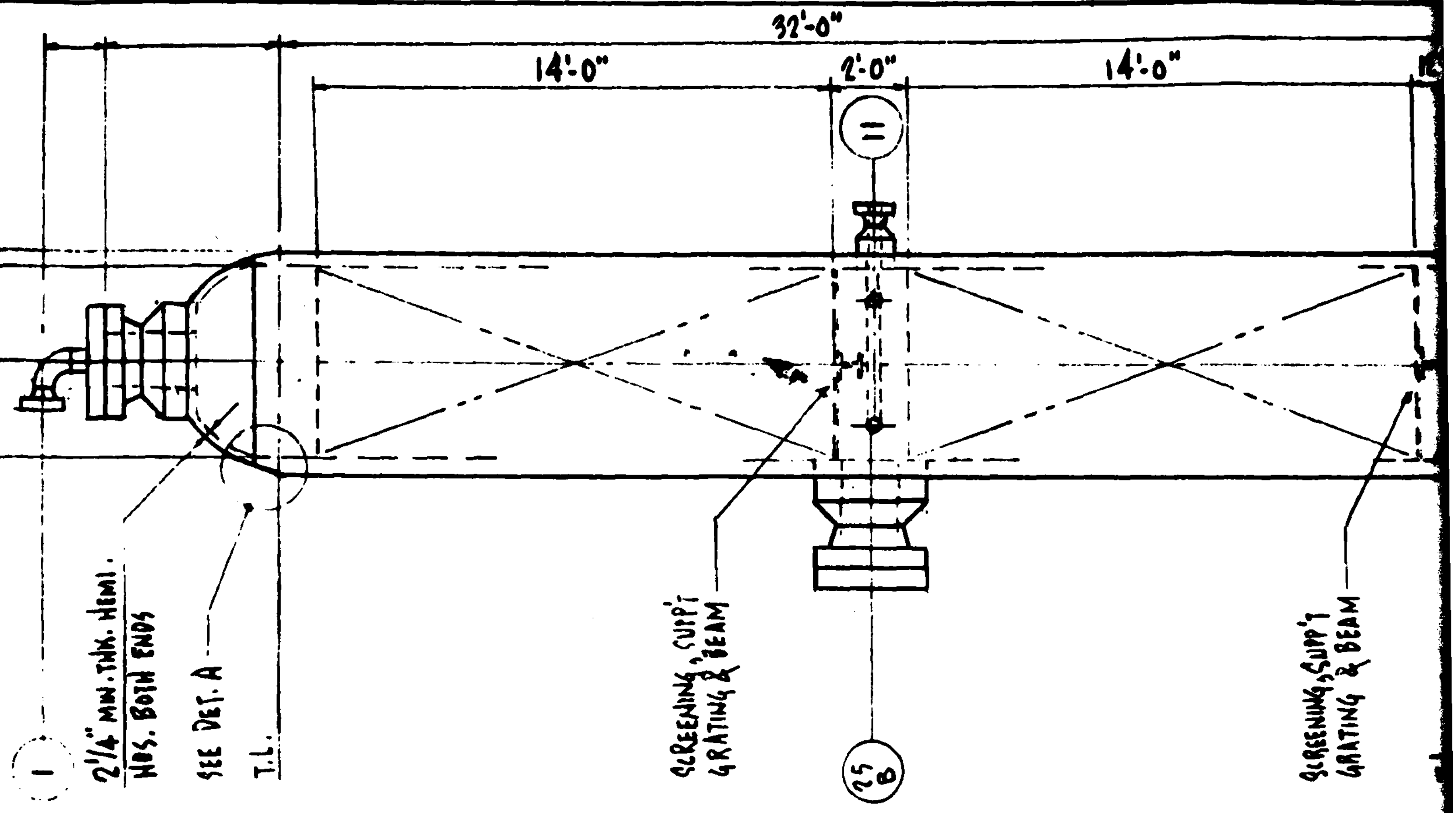
SERVICE	MARK	SIZE	RATING	FAC-ING	ORIENT	TAIL DIM OR ELEV	NOTES AND REMARKS (NOTE A)
INLET	1		1500#	RTJ			
VAPOR OUT	2		1500#	RTJ			
QUENCH	11		1500#				SEE NOTE K
MANHOLE	25A	18"	1500#	RTJ			
MANHOLE	25B	18"	1500#	RTJ			



DET. B

DET. A





MANHOLE	25A	18"	1500# RTJ
MANHOLE	25B	18"	1500# RTJ
ACCESS OPNG.	01	18"	

GENERAL NOTES

A ALL GENERAL NOTES LISTED APPLY TO THIS VESSEL. NUMBERED NOT
ESA A-03 SHOWN IN SQUARES (☐) APPLY ONLY IF CALLED FOR ELSEW
SKETCHES OR DRAWINGS

B TAIL DIMENSIONS ARE MEASURED FROM THIS TANGENT LINE.

C THE POSITION OF ALL NOZZLES, MANHOLES, CLIPS, ETC. IS DIAGRA
THE TRUE LOCATION IS SHOWN IN THE PLANS AND TABLES.

D UNLESS OTHERWISE NOTED, NOZZLE (OR MANHOLE) PROJECTIONS FR
OF VESSEL SHALL BE AS FOLLOWS FOR THE NOMINAL NOZZLE (MA
GIVEN
3 IN. DIA. AND LESS ____________ 12 IN. TO 16 IN. DIA. ____
4 IN TO 10 IN. DIA. ____________ 18 IN. TO 24 IN. DIA. ____

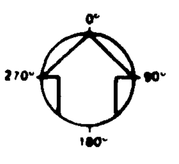
E ALL FLANGE PROJECTIONS AND DIMENSIONS ARE TO THE GASKET C
EXCEPT FOR RING JOINT FLANGES WHICH ARE TO CENTER RAISED FAC

F UNLESS OTHERWISE NOTED ANCHOR BOLTS FOR VERTICAL VESSELS
SPACED AND STRADDLE 0°-180°, 90°-270° CENTERLINES.

G DRAWING AND REFERENCES ARE NOT COMPLETE UNTIL ALL NOTES
TIONS ARE REMOVED

H. FATIGUE ANALYSIS NOT REQ'D

J. ALL NOZZLES & MANWAYS TO BE OF THE INTEGRA
REINFORCED TYPE (FIG. AD-610.1 g).



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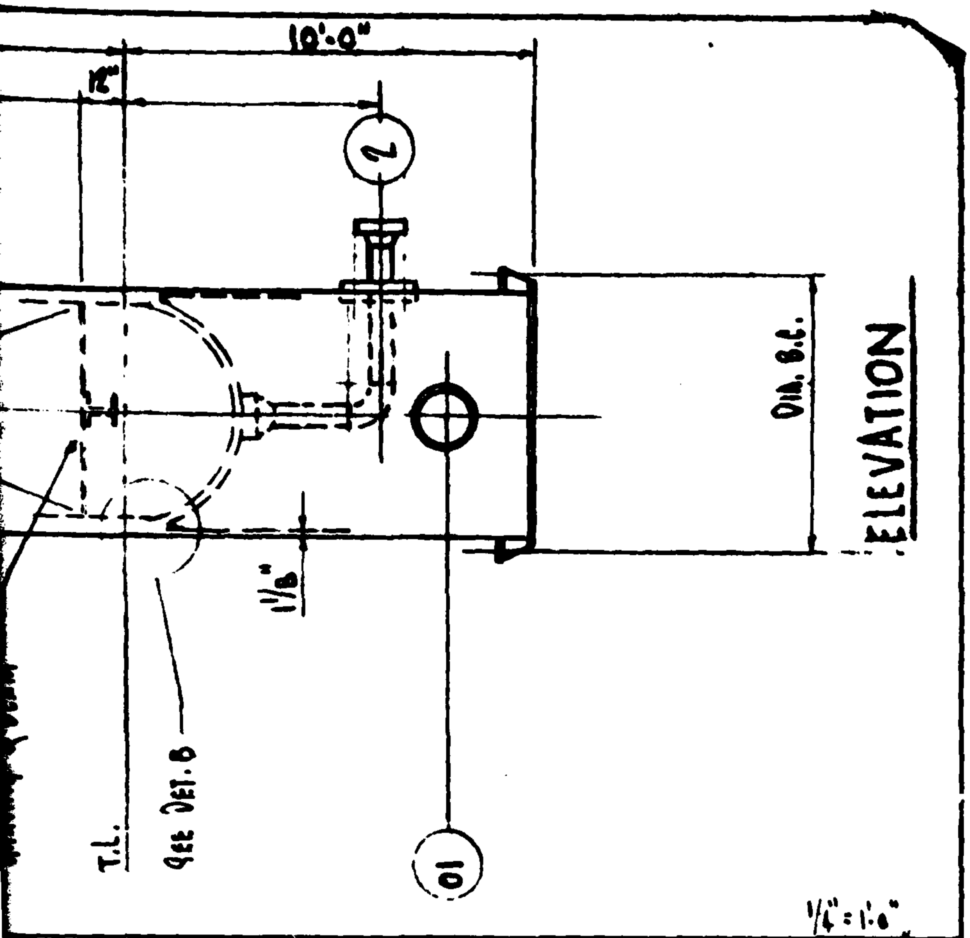


ERED NOTES LISTED ON
FOR ELSEWHERE ON THE

E.
IS DIAGRAMATIC ONLY.

TIONS FROM THE INSIDE
ZZLE (MANHOLE) SIZES

DIA. ____________
DIA. ____________
GASKET CONTACT FACE
ISED FACE OF FLANGE.
VESSELS ARE EQUALLY

LL NOTES FOR QUOTA-

NTEGRALLY

K. PROVIDE INTERNAL RING SPARGER FOR CONN. 11.
L. HYDROGEN PARTIAL PRESSURE IS 2000 PSIA.
M. REGENERATION CONDITIONS: 28 PSIG @ 932F
REDUCTION CONDITIONS: 28 PSIG (H_2) @ 770F

FIGURE 7

HYDROTREATER REACTOR NO. 1
CLIENT USAF
LOCATION
IFP JET FUEL
100,000 MTA
ITEM NO. L-101
STONE & WEBSTER ENGINEERING CORPORATION

	DK		VK	AREA	J.O. NO.	DRAWING NO.	ISSUE
TION	BY	CHK.	APP.		13248	L101-BA1	1

This mixture is heated to the second stage reaction temperature in process furnace F-101. The second-stage hydrotreater reactor, L-102, shown in Figure 8 consists of five beds of IFP catalyst HR-354. Recycle hydrogen quench is provided between each bed to limit the temperature rise. The reactants enter the reactor at 605F and exit the reactor at 716F (start of run conditions). There is considerable heat of the reactor effluent which is recovered in a series of exchangers before the cooled vapor-liquid mixture is separated in drum M-101. First, the hot reactor effluent is used to reboil the stabilizer in T-103; next, the stream raises 200 psig steam in exchanger T-110; and the stream is finally cooled against feed to the first-stage reactor in T-101.

Part of the liquid from M-101 is used as recycle liquid to the second-stage reactor. The rest is mixed with liquid from the second flash drum M-102, and fed to stabilizer A-101. M-101 overhead vapor is cooled further in air cooler T-104, and sent to drum M-102, where the condensate is separated, mixed with the liquid from the M-101, and the combined mixture fed to the stabilizer. The vapor from M-102 is sent to the recycle hydrogen compressor, R-102, except for a bleed stream, which purges the accumulated methane and inerts from the system. The recycle hydrogen compressor is a single stage reciprocating compressor.

Stabilizer feed is first heated in the feed/bottoms exchanger T-106, before being sent to the stabilizer, A-101, where light ends are removed from the product. The stabilizer overhead is cooled by two exchangers in series, T-109, and T-107. Sixty psig steam is generated in T-109 while air-cooled exchanger T-107 completes the cooling. The vapor and liquid are separated in the reflux drum, M-104, and the reflux pumped back to the stabilizer by P-102. Reboiler heat is provided by hot reactor effluent. Jet fuel product from the stabilizer is cooled in air cooler T-105 before being sent to storage.

Fuel for the fired heater is provided by purge gas from the unit. The plant uses no process cooling water, except in the case that the final product needs to be cooled to a lower temperature than the air cooling system can provide. Steam and excess purge gas are exported from the unit. A summary of utilities required and produced is listed in Table 10.

2. Process Optimization

The process has evolved somewhat from the Institute Francais du Petrole (IFP) laboratory test work and process configuration. The original test work employed 99.9 percent hydrogen with the reactors operating at about 800 and 2000 psig. This design for commercial operation required additional interstage equipment and was less energy efficient. Equipment which was deleted by the high pressure operation comprised an interstage compressor, two drums, two pumps, and an air cooler.

The incremental cost associated with increasing the first stage pressure is significantly less than the cost of the deleted equipment. The elevated first-stage pressure also introduces an additional degree of conservatism into the design. Hydrogen partial pressure has more than doubled in the first stage while the catalyst quantity has remained the same.

Ninety-five percent hydrogen is the standard by-product from olefin plants. Since the proposed unit is likely to be built by olefin plant owners, the use of 95 percent hydrogen was proposed. Consequently the operating pressure was increased to 2600 psi to maintain hydrogen partial pressure.

Operation at the proposed 2600 psig level has been demonstrated commercially in hydrocrackers which, incidentally also operate at higher temperatures than have been proposed. For economical reasons, it would be advantageous to reduce the pressure below the suggested 2600 psig level, A5037 1B

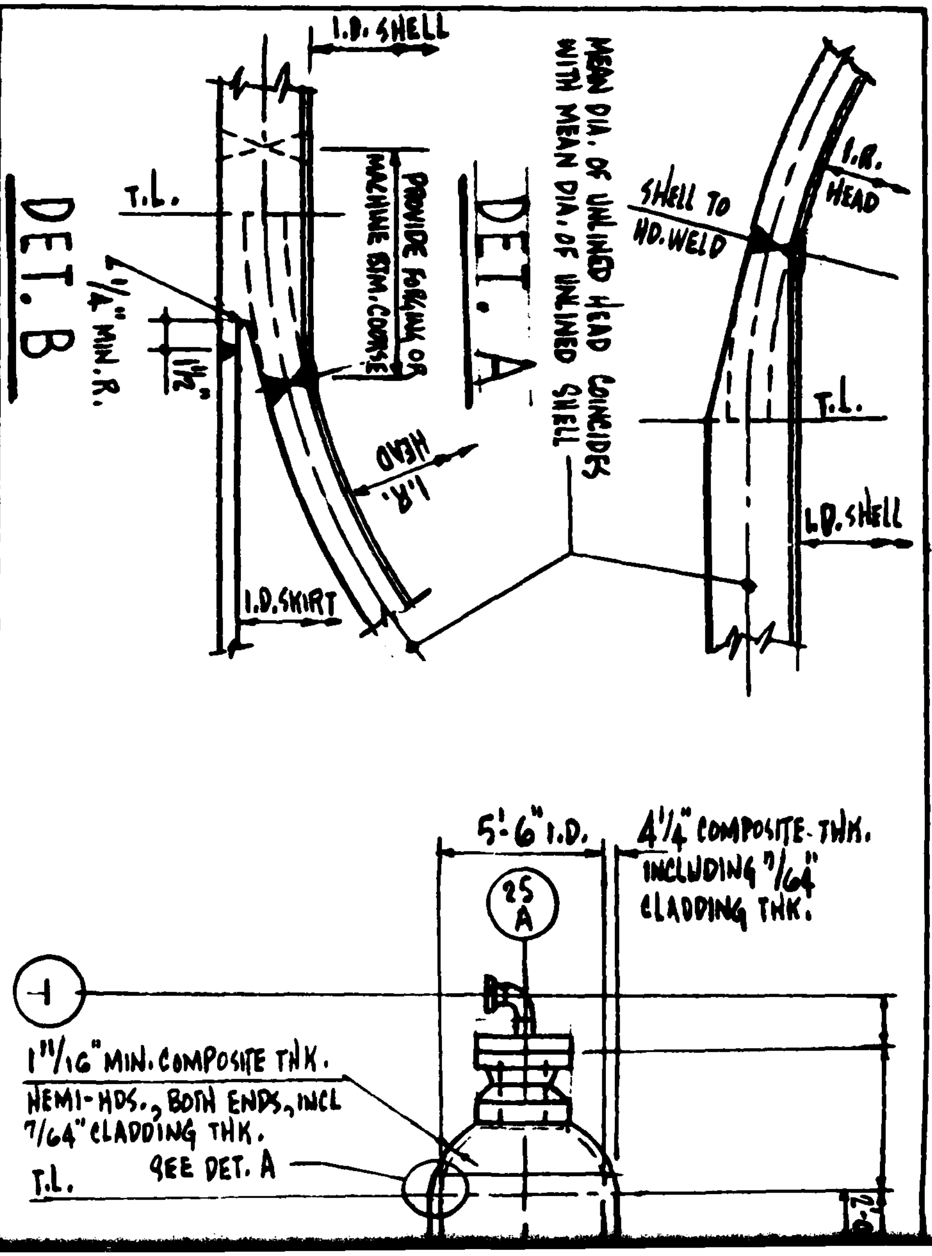
DESIGN DATA (ALSO SEE NOTE N)			
OPERATING PRESSURE	2550 PSIG	DESIGN PRESSURE	2678 PSIG
OPERATING TEMPERATURE	716 F	DESIGN TEMPERATURE	716 F
EMERGENCY VACUUM (7.5 PSIG AT F)		YES [✓ NO]	
LONG. JOINT EFFICIENCY	100%		
CODE	ASME SECT. VIII, DN.2		
CODE STAMP		[✓ YES] NO	
RADIOGRAPHY	[✓ 100% FULL]	FULL LONG. PARTIAL GIRTH SPOT	
POSTWELD HEAT TREATMENT REQ'D.		[✓ YES] NO	
CORROSION ALLOWANCE IN.		7/64" (CLADDING THK.)	
ALLOW STRESS AT DESIGN METAL TEMP.		22,768	
HYDRO TEST HORIZ. LIMITED BY			
PAINTING			
INSULATION (BY OTHERS) HOT COLD		INSULATION THICKNESS (NOTE 41) IN.	
SKIRT FIREPROOFED (BY OTHERS)		FIREPROOF THICKNESS (NOTE 43) IN.	
EMPTY WEIGHT (EXCLUDES TRAYS)		211,000 LB.	
OPERATING WEIGHT (INCLUDES TRAYS)		LB.	
WEIGHT OF TRAYS		LB.	
MAX. LOAD ON FOUNDATION (FULL OF WATER)		LB.	
ERECTION MOMENT AT BASE		FT. LB.	
MAX. MOMENT AT BASE INCL. MOMENT DUE TO PIPE THRUST		FT. LB.	
MAX. SHEAR AT BASE		LB.	
TYPE OF TRAYS & LIQUID FLOW			

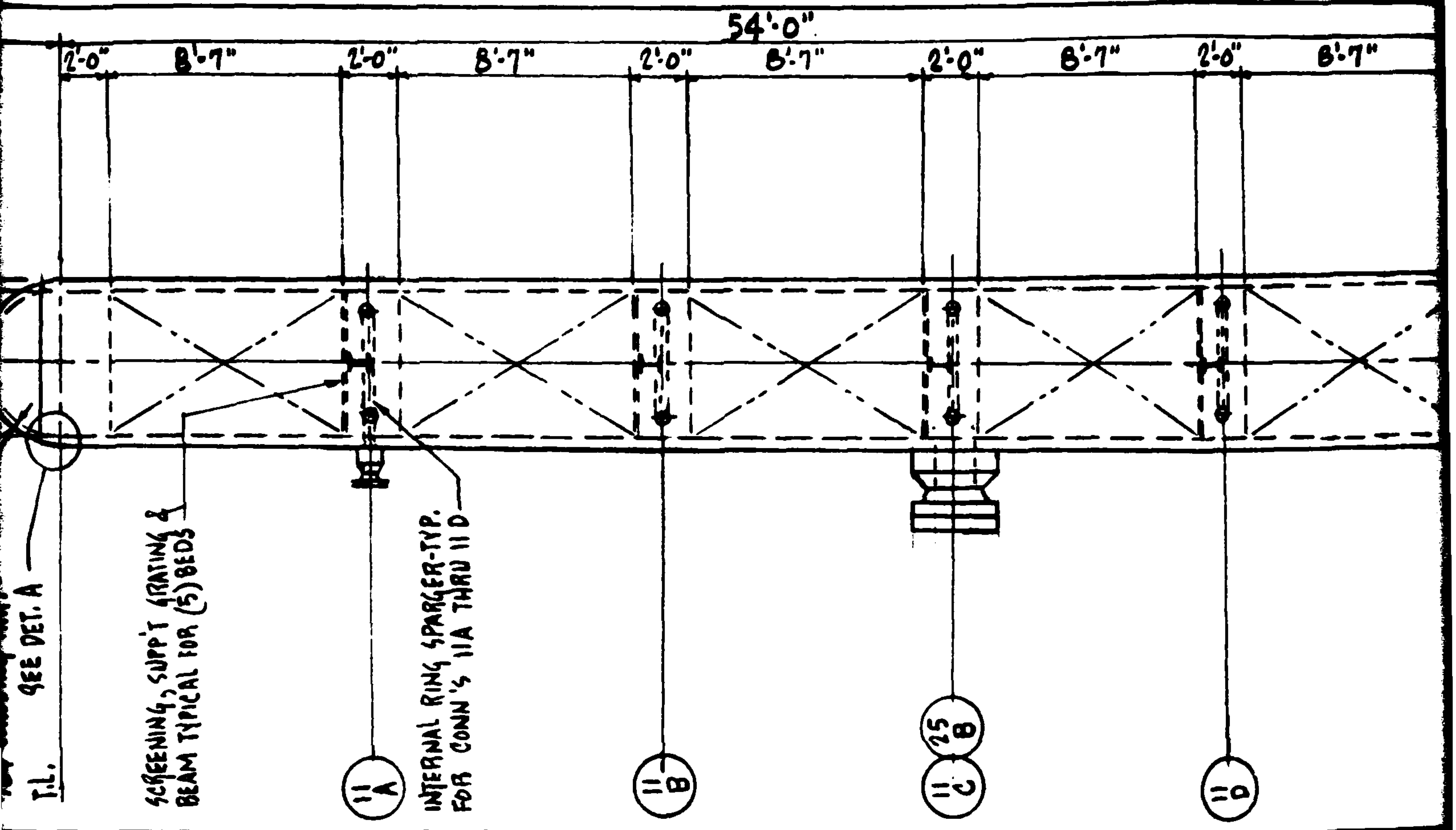
MATERIALS

VESSEL MAT'L CLASS (ESA-A02) SA264 TYPE 304L; BASE MATERIAL SA387-GR 22 CL2 (2¼ CR-1 MO)· NOTE M NOZZLES: 2¼ CR-1MO LINED WITH 304L; INTERNALS: 304L, 321 OR 347

NOZZLES & MANHOLES

SERVICE	MARK	SIZE	RATING	FACING	ORIENT	TAIL DIM. OR ELEV.	NOTES AND REMARKS (NOTE A)
INLET	1		1500#	RTJ			
VAPOR OUT	2		1500#	RTJ			
QUENCH #1	11 A		1500#	RTJ			
QUENCH #2	11 B		1500#	RTJ			
QUENCH #3	11 C		1500#	RTJ			
QUENCH #4	11 D		1500#	RTJ			





QUENCH #3	11 C		1500#	RTJ
QUENCH #4	11 D		1500#	RTJ
MANHOLE	25A	18"	1500#	RTJ
MANHOLE	25B	1[illegible]"	1500#	RTJ
ACCESS OPNG	01	18"		

GENERAL NOTES

A. ALL GENERAL NOTES LISTED APPLY TO THIS VESSEL. NUMBERED NOTES L ESA A-03 SHOWN IN SQUARES (☐) APPLY ONLY IF CALLED FOR ELSEWHER SKETCHES OR DRAWINGS.

B. TAIL DIMENSIONS ARE MEASURED FROM THIS TANGENT LINE.

C. THE POSITION OF ALL NOZZLES, MANHOLES, CLIPS, ETC. IS DIAGRAMAT THE TRUE LOCATION IS SHOWN IN THE PLANS AND TABLES.

D. UNLESS OTHERWISE NOTED, NOZZLE (OR MANHOLE) PROJECTIONS FROM T OF VESSEL SHALL BE AS FOLLOWS FOR THE NOMINAL NOZZLE (MANHO GIVEN
3 IN. DIA. AND LESS ________ 12 IN. TO 16 IN. DIA. ____
4 IN. TO 10 IN. DIA. ________ 18 IN. TO 24 IN. DIA. ____

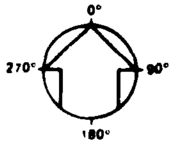
E. ALL FLANGE PROJECTIONS AND DIMENSIONS ARE TO THE GASKET CONT EXCEPT FOR RING JOINT FLANGES WHICH ARE TO CENTER RAISED FACE O

F. UNLESS OTHERWISE NOTED ANCHOR BOLTS FOR VERTICAL VESSELS ARE SPACED AND STRADDLE 0°-180°, 90°-270° CENTERLINES.

G. DRAWING AND REFERENCES ARE NOT COMPLETE UNTIL ALL NOTES F TIONS ARE REMOVED.

H. FATIGUE ANALYSIS NOT REQUIRED

J. ALL NOZZLES & MANWAYS TO BE OF THE INTEGRALLY REINFORCED TYPE (FIG. AD-610.1g).



1	8-17-79	FOR PROPOSAL
ISS.	DATE	DESCRIPTION

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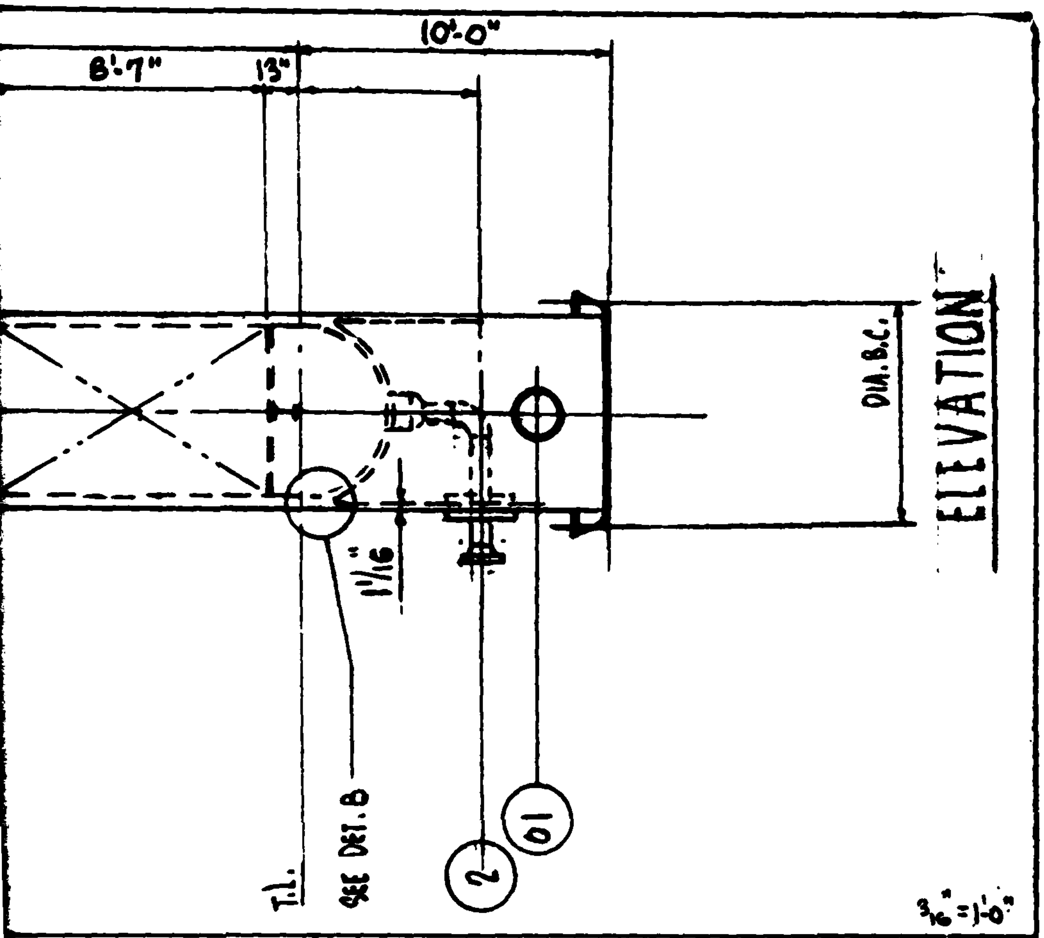
FOLD GUIDE



ES

EL. NUMBERED NOTES LISTED ON
CALLED FOR ELSEWHERE ON THE

ENT LINE.
PS, ETC. IS DIAGRAMATIC ONLY.
TABLES.
) PROJECTIONS FROM THE INSIDE
INAL NOZZLE (MANHOLE) SIZES

TO 16 IN. DIA. ______
TO 24 IN. DIA. ______
TO THE GASKET CONTACT FACE
ENTER RAISED FACE OF FLANGE.
ERTICAL VESSELS ARE EQUALLY
NES.
UNTIL ALL NOTES FOR QUOTA-

THE INTEGRALLY
14).

K. HYDROGEN PARTIAL PRESSURE IS 2000 PSIA.
L. HYDROGEN SULFIDE PARTIAL PRESSURE IS 0.25 PSIA.
M. ALTERNATE SHELL CONSTRUCTION MAY BE WELD OVERLAY.
N. REGENERATION CONDITIONS: 28PSIG @ 932F.
REDUCTION CONDITIONS: 28PSIG (He) @ 770 F.

FIGURE 8

				HYDROTREATER REACTOR NO.2
				CLIENT USAF
				LOCATION
				IFP JET FUEL 100,000 MTA — ITEM NO. L-102
	DJK			STONE & WEBSTER ENGINEERING CORPORATION
DESCRIPTION	BY	CHK.	APP.	AREA: — / J.O. NO.: 13248 / DRAWING NO.: L102-BA1 / ISSUE: 1

1

3

TABLE 10

UTILITY SUMMARY

STEAM	
Production	
M. P. Steam (200 psig), lb/hr	30,200
L. P. Steam (60 psig), lb/hr	1,340
Consumption	
None	
FUEL GAS	
Production	
MM Btu/hr*	26.408
Consumption	
MM Btu/hr*	15.764
POWER	
Consumption, kwh/h	1351
COOLING WATER	
Circulating Cooling Water, gpm 80-100F	56

* Lower Heating Value

CATALYST SUMMARY

TYPE	STAGE	QUANTITY CU FT	DENSITY LB/FT^3	ESTIMATED COSTS $/LB	ESTIMATED COSTS INITIAL CHARGE
LD-265	1	562	43.7	$10.60	$260,330
HR-354	2	1021	55.5	7.00	396,659
					$656,989

however, to establish the minimum operating pressure with the use of 95 percent hydrogen, some additional pilot test work may be required.

3. Process Design Comments

The process sequence selected is typical of many hydrogenation processes. It employs two high pressure reactors in series followed by a simple recovery system. Ninety-five percent hydrogen, readily available as a by-product from ethylene facilities, is used.

It should be noted that fairly extensive heat integration and recovery facilities are designed into the unit. The philosophy employed emphasizes generation of steam from the system. If steam is not required, excess heat could easily be used for feed/effluent exchanger with co-current reduction or even elimination of the fired heater during normal operation. In any event, a fired heater would be required to start up the plant and also for catalyst regeneration.

The use of ultra-pure hydrogen (99.9+%) is feasible and would, in fact, reduce the operating pressure of the reactors to about 2000 psig. However, this approach would preclude using by-product hydrogen derived from ethylene production and thus was not selected.

Another recovery feature which might be studied is the use of a liquid expander on the stabilizer feed. This would, however, introduce another mechanical device and was not used for this design study.

Hydrogen recovery from vent gas streams should also be considered. Integration with an ethylene plant would be the least expensive manner of recovering hydrogen. Alternatively a cryogenic system could be used.

4. Process Economics

Process economics are presented in Table 11. These economics were based on a capital cost of $9,700,000 and a feedstock cost of $3.00 per million Btu.

Hydrogen was priced at $1.08 per 1000 SCF, a value appropriate for by-product hydrogen from an olefin facility. The capital cost estimate for the unit was developed from a sized equipment list by professional estimators within the Stone & Webster organization. Additional backup information is listed in Tables 12 to 14. Production cost of jet fuel at these values amounted to 53¢ gal. In the same mid-1979 period, aviation fuel contract prices, FOB major airports as shown in Table 15, were in the 55-69¢/gal range.

TABLE 11

TYPICAL PRODUCTION COST OF FULLY HYDROGENATED JET FUEL
(100,000 MTA Plant)

FEEDSTOCK COSTS	
Fuel Oil ($3.00/MM Btu)	$ 11,166,000
Hydrogen ($1.075/MSCF)	3,024,000
TOTAL FEED COSTS	$ 14,190,000
OPERATING COSTS	$ 3,300,000
UTILITIES (Credit)	($533,000)
	$ 16,957,000
Annual Production, gallon (31,947,300)	
Production Cost, ¢/gallon	53.1

Light pyrolysis fuel oil is not a widely traded commodity and has few uses. Most of the material is burned directly or used as a cutter stock and consumed with other residual fuels from refinery sources. Being such - it was difficult to determine its market value. The assigned $3.00 per MM Btu fuel value (equal to the 1979 average refiners' acquisition cost of crude petroleum) appeared to be a realistic figure for feedstock cost.

TABLE 12

CAPITAL AND OPERATING COSTS

CAPITAL REQUIREMENT

Plant Investment (IBL)	$ 9,700,000
Working Capital	2,000,000
Initial Catalyst Charge	657,000
Paid-up Royalties*	250,000
Total Capital	$12,607,000

OPERATING COSTS

Direct Labor (@ $12/hr)	$ 105,000
Maintenance Labor (3% IBL costs)	291,000
Maintenance Materials (2% IBL costs)	194,000
Interest on Working Capital (@ 10%)	200,000
Annual Catalyst Charges	219,000
Local Taxes and Insurance (@ 3% IBL)	291,000
Interest and Depreciation (10 years)	$ 2,000,000
Total Operating Costs	$ 3,300,000

* Order of Magnitude

TABLE 13

PROCESS ECONOMICS - PRODUCT COST FROM VARIOUS FEEDSTOCK AND HYDROGEN VALUES

COST BASIS	*	REFORMER HYDROGEN								
Fuel Gas ($/MM Btu)	2.50	2.50	2.50	2.50	3.00	3.00	3.50	3.50	3.50	3.50
Steam, H.P. ($/1000 lb)	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Steam, L.P. ($/1000 lb)	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
Power ($/kwh)	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Feedstock ($/MM Btu)	3.00	3.00	4.00	5.00	3.00	4.00	5.00	3.00	4.00	5.00
Hydrogen ($/MSCF)	1.075	1.31	1.31	1.31	1.54	1.54	1.54	1.77	1.77	1.77
ANNUAL COSTS - M $/YR										
Feedstock	11,164.8	11,164.8	14,886.4	18,608.0	11,164.8	14,886.4	18,608.0	11,164.8	14.886.4	18.608.0
Hydrogen	3,024.4	3,685.5	3,685.5	3,685.5	4.332.6	4,332.6	4,332.6	4,979.7	4,979.7	4,979.7
Total Utilities (Credit)	-532.2	-532.2	-532.2	-532.2	-532.2	-532.2	-532.2	-532.2	-532.2	-532.2
Total Operating & Capital	3,300	3,300	3,300	3,300	3,300	3,300	3,300	3,300	3,300	3,300
Product Cost ¢/gal	53.1	55.2	66.8	78.5	57.0	68.7	80.3	58.9	70.6	82.2

* By-product Hydrogen from Ethylene Plant

TABLE 14
OVERALL MATERIAL BALANCE

COMPONENT	LIGHT FUEL OIL FEED	MAKE-UP HYDROGEN	TOTAL VENT GAS	JET FUEL PRODUCT
Hydrogen	-	1,682	193	-
Methane	-	705	705	-
Fuel Oil	26,089	-	20	27,558
LB/HR	26,089	2,387	918	27,558
BPSD	1,818	-	-	2,045
SCFH	-	261,150	53,010	-

Using the set of economics given in Table 11 and the jet fuel prices in Table 15, one can conclude that: (1) in the given case only 20 percent of the total cost was attributable to operation; the balance was fuel related, (2) The difference between production cost and the mid-1979 jet fuel market prices, in the range of 2-16¢ gal, should provide sufficient margin for upgrading.

It is obvious that fuel prices will continue to rise and most likely the amount of hydrogen required for the processing may not be available from the olefin plant, hence, economics were also prepared, as presented in Table 13, to reflect these generally less favorable conditions. The quantities of hydrogen required for a commercially viable plant could strain and possibly be greater than the by-product hydrogen supply. Accordingly, reformer hydrogen economics have been worked out based on methane reforming. Guidelines provided by Howe-Baker Coporation of Tyler, Texas were used in the calculations.

In Figure 9, the effect of increasing liquid fuel value (feed) and the rising cost of natural gas (reformed hydrogen) is summarized on the cost of jet fuel produced. It is interesting to note that even with feedstock as high

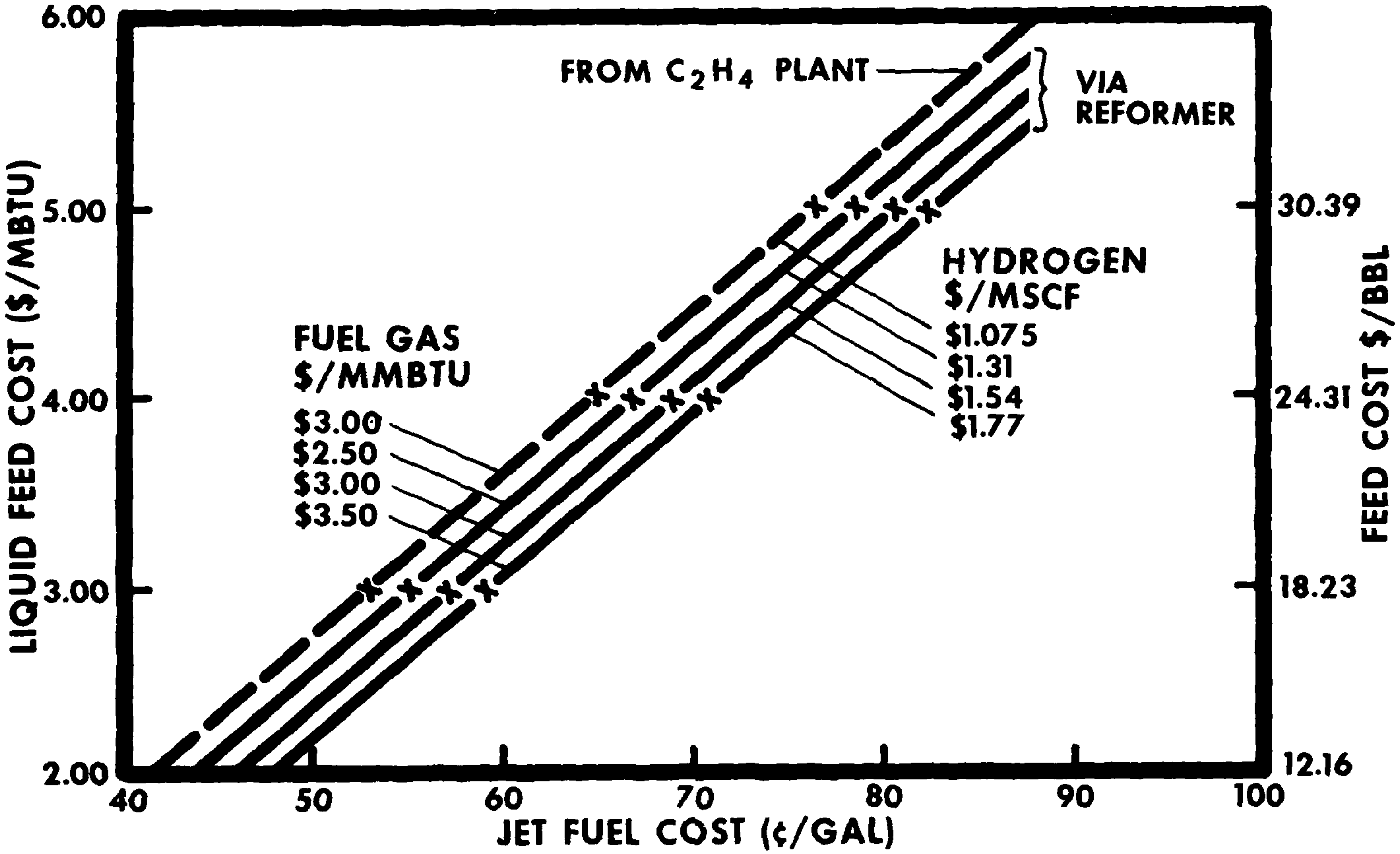
TABLE 15

FUEL COSTS

	CRUDE PETROLEUM				AVIATION FUELS				No.2 DIESEL
	$/Bbl (Refiners Acquisition Cost)			$/MM Btu*	¢/gal	¢/gal (Retail)	$/Bbl (Retail)	$/MM Btu**	¢/gal (Retail)
	Domestic	Imported	Composite	Composite	Wide Cut	Kerosine	Kerosine	Kerosine	
1974	(1) 7.18	12.52	9.07	1.56	(3) 21.79				
1975	(1) 8.39	13.93	10.38	1.79	(3) 27.47	29.83	12.53	2.24	51.05
1976	(1) 8.34	13.48	10.89	1.88	(3) 31.54	31.17	13.09	2.34	52.08
1977	(1) 9.55	14.53	11.96	2.06	(3) 35.00	35.75	15.02	2.69	56.52
1978	(2) 10.61	14.57	12.46	2.14	(At Major Airports)				
1979	(2) 13.80	20.45	16.94	2.93					
'79 1Q	(2) 11.27	15.92	13.41	2.31		(4) 40.67	17.08	3.06	
2Q	(2) 12.56	19.23	15.64	2.70		(4) 50.25	21.10	3.78	
July						(4) 55	23.10	4.14	
Sept						(5) 68.9	28.94	5.18	
					(Spot Prices July, Aug. '79)				
					Rotterdam	(6)116	49	8.77	113
					Gulf Coast	(6) 82	34	6.09	73

( ) Sources
(1) DOE/EIA - 0036/3 Annual Report to Congress, May 1978
(2) Shearson, Hayden-Stone Inc. (Union Carbide), Chemical Notes, Sept. 12, 1979
(3) D. B. Shonka, Transportation Energy Conservation Data Book, 3 ed. DOE/Oak Ridge National Lab. Report 5493, 1979
(4) Defense Fuel Supply Center, Private Communication (see Table 16)
(5) Fuel Cost and Consumption, Sept. 1979; CAB, Washington, DC 20428
(6) Platt's Oilgram Price Report Daily, August 1979, McGraw Hill, Inc.

* Crude 138,100 Btu/gal (Gross)
** Kerosine 133,000 Btu/gal (Gross)



PRODUCTION COST OF JET FUEL VS FEED COST

BASIS: 100,000 MTA PLANT

FIGURE 9

79-14,831A

as $5.00 per million Btu and natural gas at $3.50 per million Btu, the cost of jet fuel produced remained at par with the 82¢/gal mid-1979 Gulf Coast spot price of jet fuel.

Encouraged by these findings, we believe that the upgrading of LPFO for jet fuel could become as much of a standard feature of a gas oil steam cracking plant as the hydrotreating of the by-product pyrolysis gasoline is presently in the use of motor fuel.

SECTION VII

MARKET AVAILABILITY OF LIGHT PYROLYSIS FUEL OIL

1. Fuel Statistics

In order to assess the possible impact of jet fuel production from pyrolysis fuel oil on the total consumption, reference is to be made to Table 16 and Figure 10.

Table 16 provides historical and projected statistics on the number of US jet aircraft, estimated hours flown and fuel consumed. Whereas Figure 10 depicts the total US petroleum demand in 1977 by products and users sectors. One can summarize from these tables that the jet fuel represents nearly 6 percent of the total petroleum demand, and its quantity is on the order of a million barrels per day. The military's share of the kerosine type jet fuel consumption is about 20 million barrels per annum (approximately 2.6 million metric tons). This narrow user sector, although not exclusively, is the prime target of our interest for further consideration.

2. Raw Fuel Oil from Gas Oil Cracking for Jet Fuel

Related ethylene production statistics are summarized in Tables 17-21. Diverse sources concur in predicting an average yearly 5-6 percent growth in future US ethylene demand but it is more significant to note in Table 17 that an increasing shift from light gaseous feedstocks to liquid hydrocarbons, especially gas oil, is taking place in the production of ethylene. According to this table, nearly 9 billion lb ethylene production capacity, or about 21 percent of the total US capacity will be gas oil based in 1980.

A cross check, derived from the individually listed plant capacities of Table 19, results in a somewhat smaller 7 billion lb, share for the gas oil. (The discrepancy is not alarming, since exact categorization of flexible ethylene plants by feedstock is a rather elusive task.)

TABLE 16

AVIATION STATISTICS

Source: US Dept of Transportation FAA Aviation Forecasts, Sept 1978

	Number of Jet Aircrafts			Estimated Hours Flown(Jets) (in millions)			Estimated Jet Fuel Consumed (1000 million gallons/year)					Jet Fuel Total MBD (7)
	General Aviation (3)	US Air Carriers (4)	Active US Military	General Aviation	US Air Carriers	Active US Military	General Aviation (5)	US Air Carriers (5)	Military(6)		Total	
									JP-4	JP-5		
1977(1)	1900	NA	9168	1.0	NA	2.9	0.54	8.38				
1978(2)	2100	2188	9247	1.1	5.9	3.0	0.61	8.67				
1979	2300	2240	9167	1.2	6.0	3.1	0.65	8.96	3.12	0.84	13.57	885
1985	3900	2622	9545	2.1	7.0	3.2	1.03	10.98				
1990	5400	2960	NA	3.0	7.9	NA	1.41	12.99				

(1) Estimate (2) Forecast (3) All civil aviation except certificated carriers and commuter lines.

(4) All passenger and cargo aircraft owned or leased by US carriers used in domestic or international service.

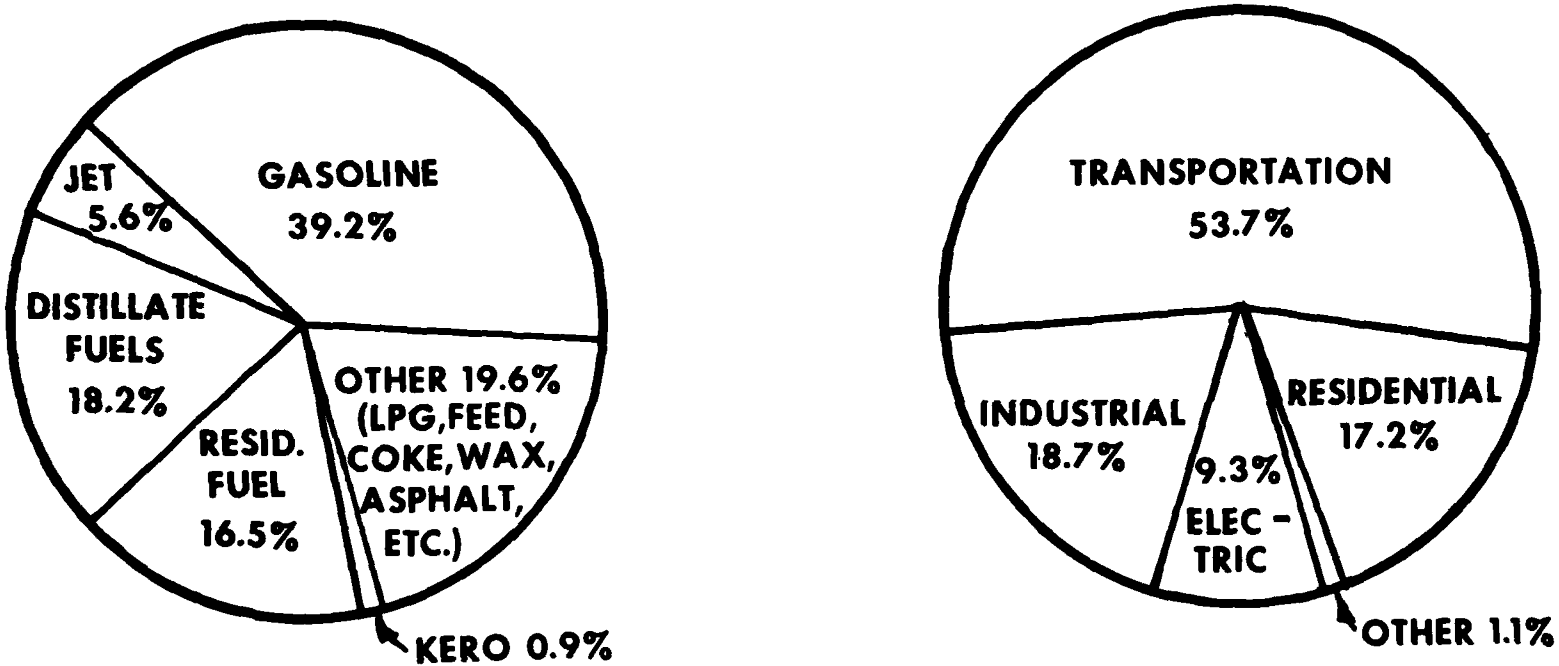
(5) Civil aircraft flights which originate and terminate in the 50 states, test flights excluded.

(6) Private communication, Defense Fuel Supply Center, Market Research, Cameron Station, VA 223314. Domestic defense use only, foreign use on the order of 40% of domestic.

(7) 1000 barrels per day.

PRODUCTS (1000 BARRELS/DAY)	
GASOLINE	7,214
JET FUEL	1,037
DIST. F.O.	3,345
RESID. F.O.	3,048
KEROSENE	165
OTHER	3,613
TOTAL	18,422

USERS (1000 BARRELS/DAY)	
RESIDENTIAL	3,180
INDUSTRIAL	3,443
TRANSPORTATION	9,912
ELECTRIC UTILITY	1,708
OTHER	199
TOTAL	18,442



*DOE/EIA-0036/3 ANNUAL REPORT TO CONGRESS, MAY 1978

U.S. PETROLEUM DEMAND, 1977*

FIGURE 10

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TABLE 17

US ETHYLENE PRODUCTION FORECAST BY FEEDSTOCKS
(Chemical & Engineering News, May 28, 1979)

	In Billions of Pounds							
	1977		1980		1985		1990	
	lb	%	lb	%	lb	%	lb	%
DEMAND	25.4		31.4		41.0		54.0	
Capacity breakdown								
LPG	21.4	65.8	22.5	54.7	22.9	46.5	21.7	34.1
Naphtha	6.1	18.8	9.8	23.9	13.2	26.8	16.0	25.1
Atm. Gas Oil	3.9	12.0	6.4	15.6	8.9	18.0	15.0	23.5
Vac. Gas Oil	1.1	3.4	2.4	5.8	4.3	8.7	11.0	17.3
TOTAL Capacity	32.5	100.0	41.1	100.0	49.3	100.0	63.7	100.0

TABLE 18

US ETHYLENE CAPACITY AND DEMAND
(Source: Union Carbide, via Shearson Chemical Notes Sept 12, 1979)

	Capacity	Demand
	In Billions of Pounds	
1977	30.1	25.3
1978	32.1	28.7
1979	34.8	30.6
1980	38.7	33.4
1981	40.6	34.4
1982	41.4	36.3
1983	42.8	37.3

TABLE 19
US 1979 ETHYLENE CAPACITY BY PRODUCERS*

in Millions of Pounds

			FEEDSTOCK	
		TOTAL	NAPHTHA	GAS OIL
Allied/BASF/Borg-Warner	Geimar, LA	700		
AMOCO Chem	Chocolate Bayou, TX	2,000	1,500	
ARCO	Channelview, TX	2,700	650	1,950
Chemplex	Clinton, LA	600		
Cities Service	Lake Charles, LA	975		
CONOCO	Lake Charles, LA	700		
Dow	Freeport TX; Plaquemine, LA	3,700		
DuPont	Orange, TX	800		
Eastman	Longview, TX	1,200		
El Paso	Odessa, TX	500		
Exxon Chem	Baton Rouge, LA; Baytown TX	3,170	600	2,500
Goodrich	Calvert City, KY	350		
Gulf Chem	Cedar Bayou, Port Arthur, TX	2,925	780	400
Mobil	Beaumont, TX	900	450	
Monsanto	Chocolate Bayou, TX	750	350	
Northern Petrochem	East Morris, Illinois	900		
Olin	Brandenburg, KY	110		
Phillips	Sweeny, TX	2,150		
Puerto Rico Olefins**	Penuelas, P.R.	1,000	600	400
Shell Chemical	Deer Park, TX, Norco, LA	4,175		2,500
Sun/Olin	Claymont, DL	250		
Texaco	Port Arthur, TX; Port Neches	1,550	1,000	
Union Carbide	Texas City, Seadrift TX Taft, LA, Ponce, PR	4,710	1,610	
USI Chemicals	Tuscola, Illinois	400		
US Steel Chemicals	Houston, TX	500		
		37,715	7,540	5,800
	US, Under Construction			
Corpus Christi Petrochem. (1980)	Corpus Christi, TX	1,200	800	400
Dow (1980)	Plaquemine, LA	1,000	1,000	
Monsanto/Conoco (1980)	Chocolate Bayou, TX	870	870	
Shell (1981)	Norco, LA	1,500	750(?)	750(?)

TABLE 20
EUROPEAN NAPHTHA/GAS OIL PLANTS

ESSO	Port Jerome, France	440
Shell	Berre, France	800
Dutch States Mines	Holland	1,000
Shell	Moerdijk, Holland	1,200
Gulf	Rotterdam, Holland	760
OMV	Schwechat, Austria	550
Montedison/Anic	Italy	1,200
Enpetrol	Puertollano/Spain	440
VEBA	Gelsenkirchen, Germany	1,200

* Source: Chemical Week, October 3, 1979 and Union Carbide

** Inactive

TABLE 21

WORLD WIDE ETHYLENE CONSUMPTION

(Stanford Research Institute, Process Economics Program, March 1978)

	1976 Consumption			1981 Demand Forecast		
	1000 M Tons	Billion Lb	Percent	1000 M Tons	Billion Lb	Percent
North America	10,767	23.7	42.2	14,900	32.8	42.2
South America	98	0.2	0.4	154	0.3	0.4
Western Europe	10,296	22.6	40.3	14,175	31.2	40.2
Far East	4,367	9.6	17.1	6,065	13.3	17.2
TOTAL	25,528	56.2	100.0	35,294	77.6	100.0

In assessing the quantity of potentially available LPFO for jet fuel manufacture, the following assumptions are to be made.

a. The overall yield of total pyrolysis fuel oil, derived from the steam cracking of various gas oil feedstocks, will be about the same magnitude as the ethylene produced.

b. The split for light and heavy fractions in the pyrolysis fuel oil will be around 1:1.

c. Half of the light pyrolysis fuel oil produced will be used for other than jet fuel manufacture purposes.

Under these assumptions, the quantity of LPFO available for jet fuel production in 1980 is estimated to be on the order of 0.8 million metric tons. This quantity could nearly cover 30 percent of the JP-5 type fuel consumed by the military. The quantity of LPFO available for jet fuel manufacture in 1985 using the same assumptions as above, will increase by 50 percent. Other considerations than feedstock supply, such as co-product demand, could accelerate the use of gas oil in steam cracking.

Table 21 reveals that the North American ethylene demand is about 40 percent of the western world consumption and it is nearly equal to that of Europe.

In Europe, naphtha served as traditional feedstock for ethylene production because of the lack of LPG and the large demand for fuel oil fractions. This picture, however, has been recently changing. LPG is reaching Europe now, and due to rising gasoline consumption, fuel oil, especially heavy fraction, is available for ethylene feedstock in increasing quantities. In Table 20 a list of European naphtha plants with gas oil cracking capability is given. It is very difficult to establish what portion of the mixed feed capacity is used for actual gas oil cracking. Hence, the quantity of LPFO available from these sources for jet fuel manufacturer is rather uncertain. Still, a conservative estimate of 0.3 - 0.5 million tons for 1980 appears to be a realistic quantity.

In summary, the quantity of LPFO from gas oil cracking currently available for jet fuel production on a world wide basis is on the order of 1.0 to 1.3 million metric tons. This potential supply could cover 40-50 percent of the entire JP-5 fuel needs of the military.

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