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Effect of Hydroprocessing Severity on Characteristics of Jet Fuel From TOSCO II and Paraho Distillates

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NASA
National Aeronautics and Space Administration

Scientific and Technical Information Branch

1981

Summary

Jet A boiling range fuels (121° to 300° C; 250° to 572° F) and broad-property research fuels (121° to 327° C; 250° to 620° F) were produced by hydroprocessing shale oil distillates, and their properties were measured to characterize the fuels. The distillates were the fraction of whole shale oil boiling below 343° C (650° F) from TOSCO II and Paraho (indirect mode) syncrudes. The TOSCO II was hydroprocessed at medium severity, and the Paraho was hydroprocessed at high, medium, and low severities. Fuels meeting Jet A requirements except for the freezing point were produced from the medium-severity TOSCO II and the high-severity Paraho. Target properties of a broad-property research fuel were met by both the medium-severity TOSCO II and the high-severity Paraho except for the freezing point and a high hydrogen content. Because of a high nitrogen content further processing of medium- and low-severity Paraho is required in order to meet Jet A requirements or the target properties for the broad-property research fuel.

Comparison of the TOSCO II results with other reported results shows good agreement. The Paraho results show a linear increase in hydrogen content and an exponential decrease in nitrogen content with hydroprocessing temperature. Significantly more cracking occurred at the high-severity hydroprocessing conditions than at medium- and low-severity conditions.

Yields of final product were compared with yields from representative heavy and light petroleum crudes. Alaskan North Slope and Khafji heavy crudes give yields about equal to those obtained in the present work. The lighter petroleum crudes give yields 30 percent higher.

Introduction

A laboratory-scale hydroprocessing facility at the NASA Lewis Research Center has the capability to produce jet fuels from nonpetroleum sources for fuel characterization studies, analytical methods development, and combustion fundamentals studies. In the present study characteristics of jet fuels produced from two shale oil feedstocks are described. Syncrudes for the feedstocks were obtained from the TOSCO II process and the indirectly heated mode of the Paraho process. These processes are above-ground retorting operations that are candidates for commercial use. Hydroprocessing, which is the catalytic addition of hydrogen, increases the hydrogen content of the feedstock in addition to reducing the content of organic nitrogen, oxygen, and sulfur. Hydroprocessing was conducted at several severities. The severity can be increased by increasing the pressure or temperature or by reducing the reactor throughput. For the present work only temperature was varied to change the severity. The Jet A target properties for the present work are the specifications as defined by ASTM 1655-78. TOSCO II feedstock was included in the present work as a basis for comparing the hydroprocessing facility performance with that of references 1 and 2.

Research for producing liquid fuels from oil shale has been in progress for more than 30 years. In the early 1950's aviation turbine fuel that met military requirements was produced from shale oil (ref. 3). Methods for refining crude shale oil into fuels have been reported (refs. 3 to 5). All methods used catalytic hydrotreating to remove organic nitrogen, oxygen, and sulfur. The effect of temperature on hydrogenation has been reported by Cottingham, et al. (ref. 6), and the effect of hydrocracking pressure has been reported by Frost and Cottingham (ref. 7). Although the references cited showed that synthetic fuels could be produced from crude shale oil, the supply of inexpensive liquid fuels from petroleum was sufficient to prevent the commercialization of synthetic fuels from shale oil.

Because of the oil embargo of 1972-73 and the continuing dependence on foreign petroleum crude, production of fuels from shale oil has become more attractive. The U.S. Navy has sponsored two contracts for the production and refining of crude shale oil into military fuels. In one contract, 10 000 barrels of shale crude were produced and the coker distillate was refined (ref. 8). In the second contract, 100 000 barrels of whole Paraho shale oil were refined (ref. 9). Paraho shale oil was used in the work presented in reference 10, which emphasized gasoline and normal refinery streams. Exploratory studies on upgrading or improving the quality of various shale syncrudes are reported in reference 11. Until recently very little work has been reported on the production and characterization of Jet A from shale oil.

The U.S. Air Force produced and characterized Jet A in their program on aviation turbine fuels in

1975 (refs. 12 and 13). Their procedure was to hydroprocess, at several severities, the fraction of shale oil in the boiling range of jet fuel. This was followed by distillation of the product into many narrow boiling fractions (usually more than 10) and then blending of these fractions to meet Jet A requirements. This was done for several different shale and coal syncrudes. A 1976 NASA program included the preparation and characterization of jet fuel produced from TOSCO II shale oil (refs. 1 and 2). Low-yield samples that met, or nearly met, the Jet A requirements were obtained from the hydroprocessed fraction boiling below 343° C (650° F). Yields of jet fuel were maximized by cracking the heavier ends of the crude shale oil.

Jet fuels are produced commercially from petroleum crudes that only require a small amount of blending and finishing of straight-run refinery streams. Complex blending procedures, as in reference 13, or production from cracked products, as in reference 2, is not frequently used in commercial production of jet fuels. Jet fuel from shale oil will probably be produced from the fraction boiling below 343° C (650° F) of whole shale oil, coker distillate, hydrotreated whole shale oil, or hydrostabilized whole shale oil without complex blending procedures or the addition of cracked products. The goal of most of the previous work was simply to produce specification jet fuel. In the present work full-boiling-range jet fuel was produced from the hydroprocessed product of shale oil distillate boiling below 343° C (650° F). Properties that fail to meet specification values for full-boiling-range fuel are identified herein. Target properties are present Jet A requirements and a wider-boiling-range fuel identified as a broad-property research fuel at a workshop held at the Lewis Research Center (ref. 14).

Apparatus

The apparatus used to produce the jet fuels from shale syncrude included (1) a crude shale oil distillation unit to recover the distillate fraction boiling below 343° C (650° F), (2) a facility to catalytically react the distillate feedstock at high temperature and pressure with hydrogen, and (3) a distillation unit for distilling the hydroprocessed product into the jet fuels. The primary reactions in the high-pressure reactor removed the organic nitrogen, oxygen, and sulfur and saturated the olefin hydrocarbons. Aromatic saturation also occurred, and under some reactor conditions, larger molecules were cracked into molecules of lower molecular weight. The processing is shown schematically in figure 1. Shale oil distillate was metered from a 7.6×10^{-3}-cubic-meter (2-gallon) feedstock tank through a diaphragm feed pump with pneumatic flow control. The feedstock tank rested on an electronic balance that indicated changes in shale oil mass for flow-rate measurement. Hydrogen, which was compressed from a trailer to the desired pressure with an air-driven compressor, and oil entered the top of the downflow, trickle-bed reactor where the hydroprocessing reactions took place. Three pneumatically operated valves shown in figure 1 controlled the desired hydrogen flow rate and reactor pressure. A calibrated orifice was used to measure the hydrogen flow. Hydrogen was separated from the liquid product in a water-cooled high-pressure separator; and product gases, which included water, ammonia, and hydrogen sulfide, were removed from the liquid product in a low-pressure separator. The low-pressure separator had a maximum capacity of about 3.8×10^{-3} cubic meter (1 gallon), and for this reason it was operated batchwise and drained several times during any given run.

Distillation was done in two different distillation units. A 72-liter (19-gallon) unit, shown in figure 2, for crude distillation, and a 4-liter (1 gallon) unit, shown in figure 3, for the final distillation. Both units had an operating pressure range from atmospheric to 2.67×10^{2} N/m^2 (2 torr). Each unit included a vacuum pump and automatic controls for reduced pressure operation and automatic heat input controls. Reflux rates were controlled by a timer that operated the takeoff solenoid.

Both the reactor and the high-pressure separator were designed for operation at conditions to 2×10^{7} N/m^2 (3000 psi) and 538° C (1000° F). The reactor was a 2-inch-diameter reactor with a thermocouple well down the center. The catalyst was American Cyanamid HDS-3A, a Ni-Mo/Al_2O_3 catalyst, and was in the form of nominally 0.25 millimeter (0.01 in.) in diameter extrusions. The reactor-catalyst configuration is shown in figure 4. For temperature and reaction control the reactor consisted of four reactive catalyst zones between nonreactive zones of alumina extrusions 0.3 centimeter in diameter by 0.3 centimeter long. The reactive zone consisted of catalyst diluted with the inert alumina, as indicated in the table in figure 4. The first zone had about 13 percent of the catalyst, and the last zone had about 40 percent of the catalyst. With the high concentration of nitrogen and sulfur in the feedstock a very dilute catalyst zone permitted easier temperature control of the exothermic reaction. As the nitrogen and sulfur concentration was removed from the feedstock a higher concentration of catalyst helped maintain the desired reaction temperature. Total catalyst mass was 680 grams, which is equivalent to a nominal volume of 1×10^{-3} cubic meter. The alumina zone acted as a preheater at the

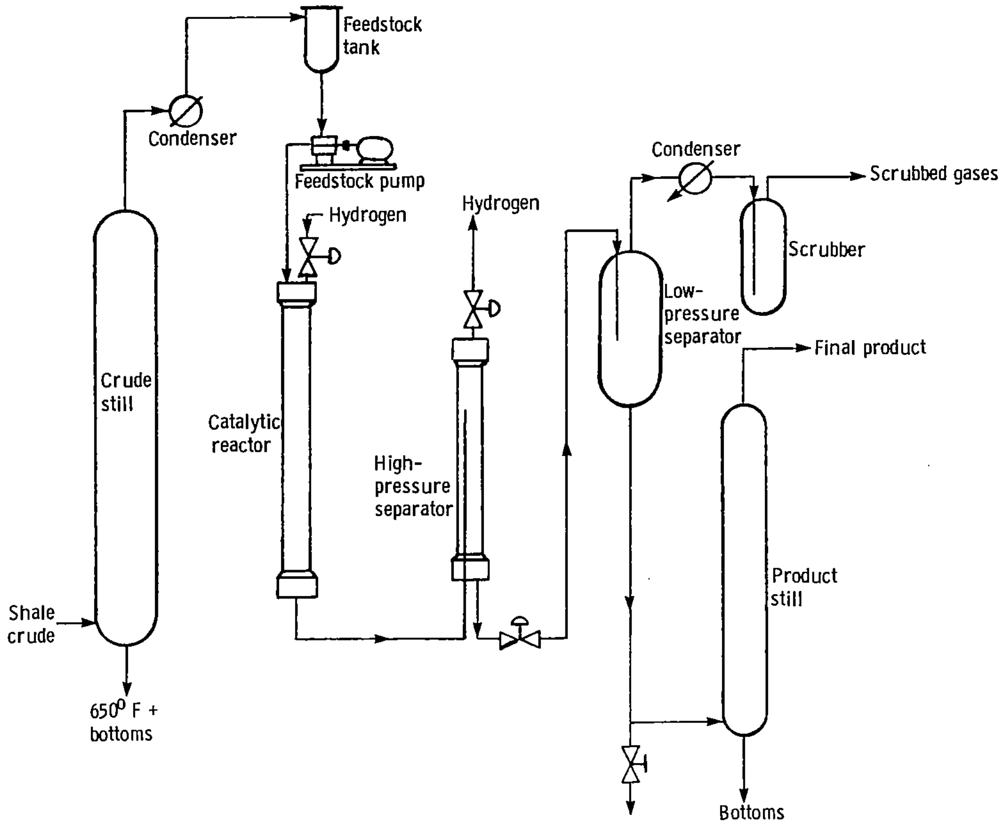


Figure 1. - Process flow diagram.

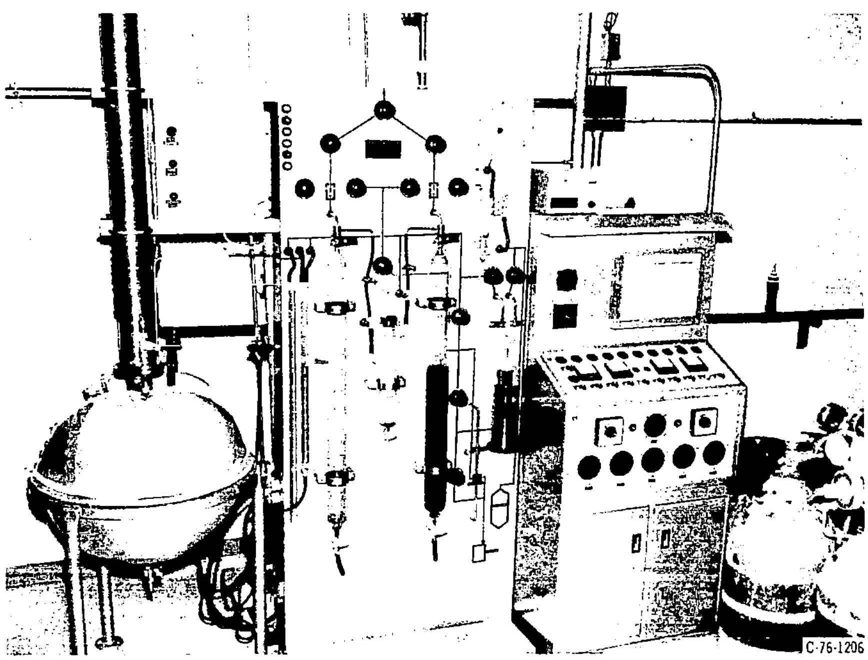


Figure 2. - 72-Liter distillation unit.

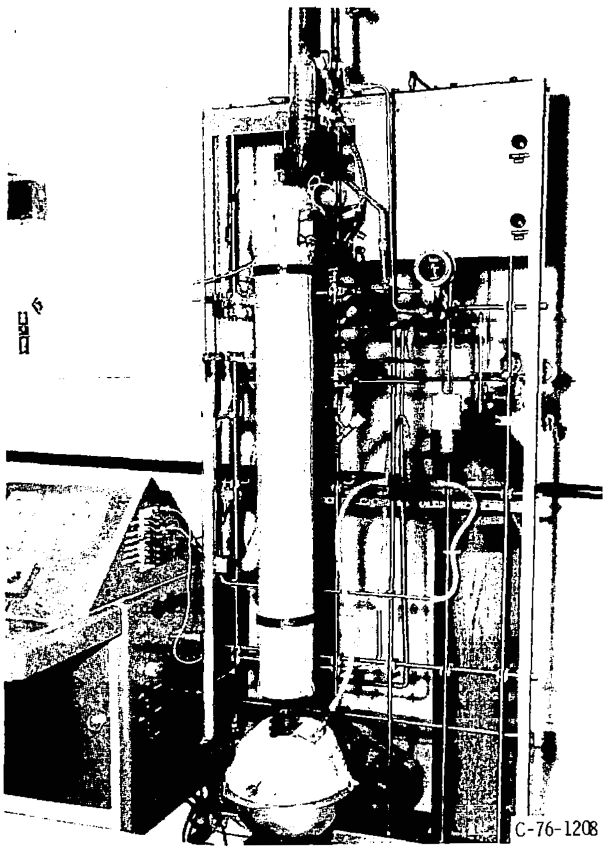
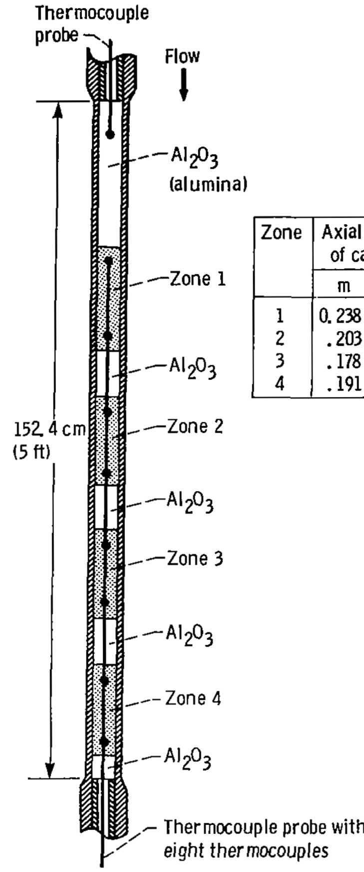


Figure 3. - 4-Liter distillation unit.



Zone	Axial length of catalyst		Catalyst dilution, (Al_2O_3:Ni-Mo/Al_2O_3)
	m	in.	
1	0.238	9.4	3:1
2	.203	8	2:1
3	.178	7	1:4
4	.191	7.5	1:10

Figure 4. - Two-inch reactor - catalyst configuration.

reactor inlet. Between catalyst zones and at the exit the alumina served to cool the gas-vapor mixture. Five electrical resistance heaters, which clamped around the reactor, provided any necessary heat to the reactor. There was one heater per zone and a heater for the preheat section. Each heater was 0.305 meter (12 in.) long and was rated at 1.4 kilowatts. Each heater could be regulated individually through a transformer control of voltage. There was a thermocouple in the preheater inlet and one in the inlet and exit of each catalyst zone. Reactor wall thermocouples were located at the center of the preheat section and at the center of each catalyst zone.

The facility control room was adjacent to the test cell. A window between the two rooms permitted visual observation of the test cell from the control room. All necessary readouts and controls for operating the hydroprocessing facility were located within the control room. Data were recorded on strip charts or tabulated manually.

Procedure

The required quantity of distillate boiling below 343° C (650° F) was distilled from the syncrudes and blended before any hydroprocessing to ensure that the feedstock for hydroprocessing was consistent. The two shale oil crudes used were from the TOSCO II process and the indirect mode of the Paraho process (ref. 12).

Distillation of the TOSCO II was done in one batch of approximately 5.7×10^{-2} cubic meter (15 gallons), which gave 2.3×10^{-2} cubic meter (6 gallons) of the desired distillate feedstock fraction. The distillation was done at 5.33×10^3 N/m^2 (40 torr) or less. The entire distillate fraction was blended together. Two distillation runs of approximately 6.8×10^{-2} cubic meter (18 gallons) each were required for the Paraho crude to give sufficient distillate product for the feedstock required. One batch was run at a distillation pressure of 5.33×10^3 N/m^2 (40 torr) or less. For the other batch approximately the first 3.78×10^{-3} cubic meter (1 gallon) was distilled at atmospheric pressure and the remainder at 5.33×10^3 N/m^2 (40 torr) or less. All distillate feedstock products from the two runs were blended together before being used.

The active form of the catalyst in the reactor was a sulfide. This catalyst was activated a few days before hydroprocessing runs were to begin. This was done with a mixture of 10 percent H_2S and 90 percent H_2 at a pressure of 27×10^5 N/m^2 (390 psi) and a temperature of 227° C (440° F) for 4 hours and then at the same pressure and 315° C (600° F) for 1 hour. To insure that the catalyst was sufficiently sulfided, a small quantity of shale oil was hydroprocessed and analyzed before proceeding with the hydroprocessing. Since there was an extended time between the TOSCO II runs and the Paraho runs, the reactor was repacked before proceeding with the Paraho runs.

About 7.56×10^{-3} cubic meter (2 gallons) of product from each hydroprocessing condition was required to give sufficient quantities of final jet fuel product for characterization. For comparison of the present work with that of reference 1 the TOSCO II distillate was hydroprocessed in two 3.78×10^{-3} cubic meter (1 gallon) runs at temperature, pressure, and flow conditions defined as a medium-severity condition. This provided hydroprocessed product from two different runs so that the reproducibility of the product could be judged. Paraho distillate was hydroprocessed at three different severity conditions. The Paraho runs were 7.56×10^{-3} cubic meter (2 gallons) each. Severity conditions for all hydroprocessing runs are given in table I. These conditions are the weighted average from data taken throughout a run.

For each data run the reactor was heated to about 50 degrees C (90 degrees F) below the desired processing temperature, at which time the shale oil feedstock pump was turned on. Processing conditions were set and allowed to stabilize. After 1 hour the lower pressure separator was drained of product. This product was discarded after measuring the weight and volume. Hydroprocessing continued until the predetermined amount of feedstock in the feedstock tank was used. The reactor temperature and hydrogen flow were maintained for 1 hour after the shale oil flow had stopped. The reactor was cooled to 204° C (400° F) with hydrogen flow and then maintained at operating pressure until a final catalyst temperature of about 100° C (212° F) was reached in order to prevent catalyst coking. During the 7.56×10^{-3} cubic meter (2 gallon) runs the low-pressure separator was drained twice. The hydroprocessed products from all Paraho runs were blended before dividing the result into two equal parts for final distillation.

After each run the volume and weight of product were measured to determine the efficiency of the reactor. These measurements confirmed assumption of 100-percent reactor recovery for calculation purposes. Also, other reported work has shown that 100-percent reactor recovery is a good assumption on both a volume and weight basis (refs. 3 to 5, 10, and 11).

Since the primary purpose of the present work was the characterization of the final distilled product, no attempt was made to measure the hydrogen consumed during hydroprocessing. Hydrogen consumed for each run was computed by using measured properties of feedstock and product and the assumption that the light gases consisted of 20 volume percent each for methane, ethane, and propane and 40 volume percent for butane. This light gas composition assumption is used in refinery modeling programs (ref. 15). Similar gas compositions are reported in reference 4. The computed hydrogen consumption for each run is given in table II. These values agree with other reported results (refs. 5 and 7).

Each Paraho product was distilled into two final products—Jet A boiling range fuel (121° to 300° C;

TABLE I. - HYDROPROCESSING CONDITIONS

Feedstock	Processing severity	Liquid hourly space velocity[a]	Temperature		Pressure	
			°C	°F	N/m^2	psi
TOSCO II	Medium	0.95	376	710	133×10^5	1925
	Medium	.95	376	710	143	2075
Paraho	High	.90	416	780	141	2050
	Medium	.90	382	720	140	2025
	Low	.90	354	670	133	1925

[a]Ratio of volume flow of fuel per hour to dry volume of catalyst.

TABLE II. - HYDROGEN CONSUMPTION

Feedstock	Processing severity	Hydrogen consumption	
		cm^3/cm^3	std. ft^3/barrel
Paraho	Low	234	1314
	Medium	280	1574
	High	330	1856
TOSCO II	Medium	231	1300

250° to 572° F), and a broad-property research fuel (121° to 327° C; 250° to 620° F).

Syncrudes and Synfuels Characterization

The final fuel target properties and the analytical techniques employed to characterize the syncrudes and synfuels are defined in table III. The property measurements performed on the shale oil crudes, shale oil distillates, hydroprocessed products, and final distilled fuels are presented in table IV. Weight percent carbon, which is not included in table III, was determined by using microcombustion. For a number of samples the methods employed to determine the total weight percent nitrogen and total weight percent sulfur were not those described in table III. Those samples having weight percent nitrogen levels below 500 ppm were analyzed by the combustion-microcoulometric method (ASTM D-3431). In several cases samples were analyzed by both nitrogen methods to assure agreement of the results. The total weight percent sulfur of the distilled hydroprocessed products was determined by employing a modification of the general bomb method (ASTM D-129). This method involves the use of an ion chromatograph to quantify the sulfate ion concentration of a sodium bicarbonate solution after bomb oxidation of the fuel (ref. 16).

All kinematic viscosities (ASTM D-445) were determined at 23° and 38° C (73° and 100° F). Those viscosities reported at −12° and −23° C (10° and −10° F) were obtained from viscosity-temperature curves (ASTM D-341) generated from reference and laboratory data for similar fuels. Note that the freezing points of some of the hydroprocessed products and final distilled fuels precluded reporting all the viscosities at −23° C (−10° F).

The final boiling points of the broad-property research fuels were above the limit recommended for the determination of percent naphthalenes by ultraviolet spectrophotometry (ASTM D-1840); therefore the reported naphthalene contents of these fuels may be slightly greater than the true values. For the same reason the hydrocarbon group-type (saturates, olefins, and aromatics) results obtained by the fluorescent indicator absorption method (ASTM D-1319) may be less precise than is indicated by the method description.

Infrared analyses performed on the bottoms of the final distillations of the hydroprocessed products yielded spectra that exhibited no significant differences. The prominent absorption bands observed were typical of hydroprocessed distillates (i.e., aromatic and aliphatic C-H stretch and C-H bend).

Results and Discussion

Limited property measurements of TOSCO II and Paraho syncrudes are given in table V. These values agree with those reported by others (refs. 1 and 17 for TOSCO II; ref. 9 for Paraho). True-boiling-point distillation curves for the two crudes are shown in figure 5. The data points for the Paraho curve (fig. 5(b)) are in very good agreement with Navy data obtained by private communication with L. Lukens, Navy Materials Command, and E. T. Robinson, Standard Oil of Ohio. The distillation curve for TOSCO II (fig. 5(a)) does not agree with that reported in references 1 and 13. Except at the end point of 343° C (650° F) some points on the curve differ by as much as 50 degrees C (90 degrees F) from the reference 13 curve and 80 degrees C (144 degrees F) from the reference 1 curve. The curve, however, does agree with some work done a few years earlier at the NASA Lewis Research Center on the same TOSCO II crude. The difference could be caused by different retort runs with slightly different retort conditions. TOSCO II syncrude gave about a 2 volume percent higher yield of distillate when boiling below 343° C (650° F) than did the Paraho syncrude.

Yields of hydroprocessed product in the jet fuel boiling range were calculated from the syncrude and hydroprocessed product distillation data with the assumption that the hydroprocessing reactor gave 100-percent recovery. This assumption is in agreement with other reported work (refs. 2 to 5, 10, and 11). Accumulative volume and weight data for the hydroprocessed product distillations were taken at 288°, 300°, and 327° C (550°, 572°, and 620° F), which temperatures correspond to specifications for pre-1978 Jet A end point, present Jet A end point, and a broad-property fuel end point. The yields available from whole crude are given in table VI. These yields are compared with some representative straight-run petroleum yields from reference 17 and

TABLE III. - TARGET JET FUEL PROPERTIES

(a) Jet A requirements

Property	Jet A	ASTM test method
Hydrogen content, wt %	----------------	NMR
Aromatics content, vol %	20 max	D-1319
Sulfur content (mercaptan), wt %	0.003 max	D-3227
Sulfur contant (total), wt %	0.3 max	[b]D-1266
Naphthalenes content, vol %	3 max	D-1840
Distillation temperature, °C (°F):		
Initial boiling point	----------------	D-86
10 Percent	204 (400) max	↓
50 Percent	Report[a]	↓
90 Percent	Report	↓
Final boiling point	[a]300 (572) max	↓
Flashpoint, °C (°F)	[a]38 (100) min	D-56
Gravity (API, 15° C)	51 to 37	D-1298
Gravity (specific, 15/15° C)	0.7753 to 0.8398	D-1298
Freezing point, °C (°F)	-40 (-40)	D-2386
Smoke point	20 min	D-1322
Viscosity at -20° C (-4° F), cS	[a]8 max	D-445
Net heat of combustion, kJ/kg (Btu/lb)	42 800 (18 400) min	D-2382
Thermal stability - JFTOT breakpoint temperature (tube deposit rating, 13; pressure difference, 25 mm Hg), °C (°F)	260 (500)	-------

(b) Broad-property research fuel

Property	Referee fuel (ref. 14)	ASTM test method
Hydrogen content, wt %	12.8±0.2	NMR
Aromatics contant, vol %	Report	D 1319
Sulfur content (mercaptan), wt %	0.003 max	[b]D-3227
Sulfur content (total), wt %	0.3 max	[b]D-1266
Nitrogen content (total), wt %	Report	Kjeldahl[b]
Naphthalenes content, vol %	Report	D-1840
Distillation temperature, °C (°F):		
Initial boiling point	Report	D-86
10 Percent	204 (400) max	↓
50 Percent	Report	↓
90 Percent	260 (500) min	↓
Final boiling point	Report	↓
Flashpoint, °C (°F)	[c]38 (100) min	D-56
Gravity (API, 15° C)	Report	D-1298
Gravity (specific, 15/15° C)	Report	D-1298
Freezing point, °C (°F)	[c]-23 (-10) max	D-2386
Viscosity at -23° C (-10° F), cS	12 max	D-445
Net heat of combustion, kJ/kg (Btu/lb)	Report	D-2382
Thermal stability - JFTOT breakpoint temperature (tube deposit rating, 13; pressure difference, 25 mm Hg), °C (°F)	238 (460) min	D-3241

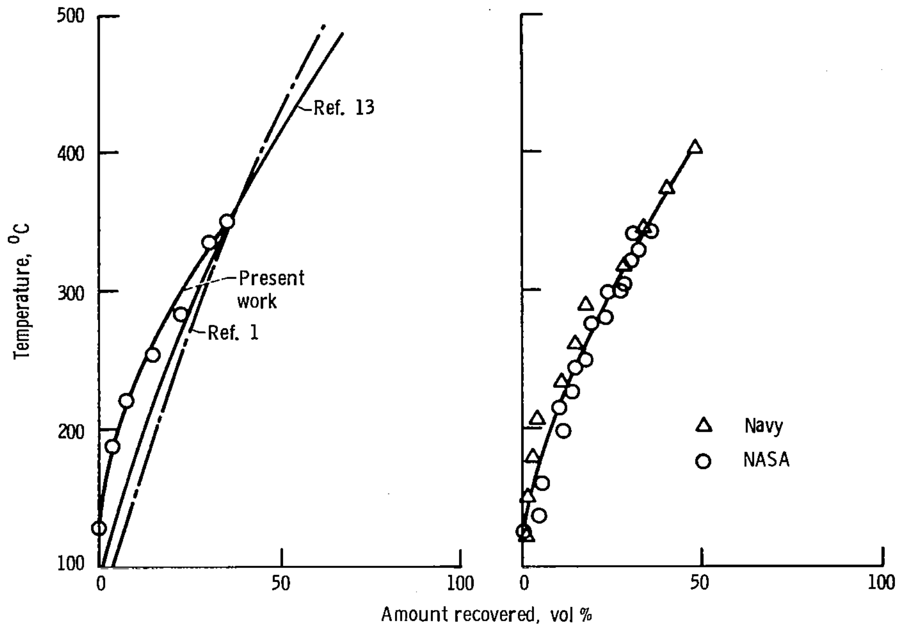
[a]Specification changed in 1978.
[b]See section Syncrudes and Synfuels characterization.
[c]Modified from that in ref. 14.

TABLE IV. - PROPERTY MEASUREMENTS

Property	Crude	Distillate feedstock	Hydro-processed product	Final product
Hydrogen content, wt %	×	×	×	×
Carbon content, wt %				×
Aromatics contant, vol %		×	×	×
Sulfur content (mercaptan), wt %		×	×	×
Sulfur content (total), wt %	×	×	×	×
Nitrogen content (total), wt %	×	×	×	×
Naphthalenes content, vol %		×	×	×
Distillation temperature, °C (°F):		×	×	×
Initial boiling point				
10 Percent				
50 Percent				
90 Percent				
Final boiling point				
Flashpoint, °C (°F)		×	×	×
Gravity (API, 15° C)	×	×	×	×
Gravity (specific, 15/15° C)	×	×	×	×
Freezing point, °C (°F)		×	×	×
Smoke point				×
Viscosity, cS			×	×
Net heat of combustion, kJ/kg (Btu/lb)			×	×
Thermal stability - JFTOT breakpoint temperature, °C (°F)			×	×
Tube deposit rating, 13; pressure difference, 25 mm Hg			×	×

TABLE V. - SHALE OIL CRUDE ANALYSIS

Property	TOSCO II	Paraho (indirectly heated mode)
Gravity (API, 15° C)	19.4	20.9
Gravity (specific, 15/15° C)	0.9377	0.9285
Fraction boiling below 343.3° C (650° F), vol %	34.7	32.6
Fraction boiling below 343.3° C (650° F), wt %	31.6	30.7
Hydrogen content, wt %	10.95	11.27
Total sulfur content, wt %	0.77	0.63
Nitrogen content, wt %	2.25	2.14



(a) TOSCO II crude distillation. (b) Paraho crude distillation.

Figure 5. - TOSCO II and Paraho distillation curves.

TABLE VI. - YIELDS AVAILABLE FROM WHOLE CRUDE FOR SEVERAL JET FUEL BOILING RANGES

Feedstock	Temperature range					
	121° to 288° C (250° to 550° F)		121° to 300° C (250° to 572° F)		121° to 327° C (250° to 620° F)	
	Yield based on whole crude					
	wt %	vol %	wt %	vol %	wt %	vol %
Petroleum (ref. 17):						
Murban crude	----	38.0	----	40.3	----	44.5
Khafji crude	----	23.3	----	25.8	----	29.8
Quatar crude	----	35.2	----	36.7	----	42.0
Selmo crude	----	34.7	----	37.5	----	43.5
Alaskan North Slope crude	----	24.7	----	26.9	----	32.5
Shale oil:						
TOSCO II - medium severity	23.5	26.5	25.4	28.8	29.2	32.7
Paraho:						
High severity	23.2	25.4	25.6	28.1	28.5	31.3
Medium severity	18.3	22.3	20.5	24.7	24.5	29.2
Low severity	18.3	21.6	20.6	24.4	24.4	29.0
TOSCO II (ref. 1)	26.2	----	----	----	[a]29.7	----

[a]Estimated from 121° to 343° C boiling range results.

with TOSCO II results from reference 1. The yields of the high-severity Paraho and the TOSCO II agreed for all three cuts. Medium- and low-severity Paraho runs gave lower yields, because the lower conversions of the reactions produced less lower-boiling-point material in the desired fuel ranges. The distillation curves (ASTM D-86) in figure 6 comparing Paraho feedstock and hydroprocessed product show a decrease in boiling point with increasing severity. A comparison of the TOSCO II yields with results from reference 1 (fig. 5) shows good agreement for the 327° C (620° F) end point cut but only fair agreement with the 288° C (550° F) end point cut. This is because of the difference in the syncrude distillations, which gave a lower volatility distillate feedstock for the present work. The distillation curves for feedstock and product for the present work and those from reference 1 are shown in figure 7. Comparison of the yields with those from petroleum crudes show that the yields are comparable with those of heavy crudes, such as Khafji and Alaskan North Slope crudes. However, other lighter crudes used for producing jet fuel show yields about 30 percent higher for all three boiling ranges.

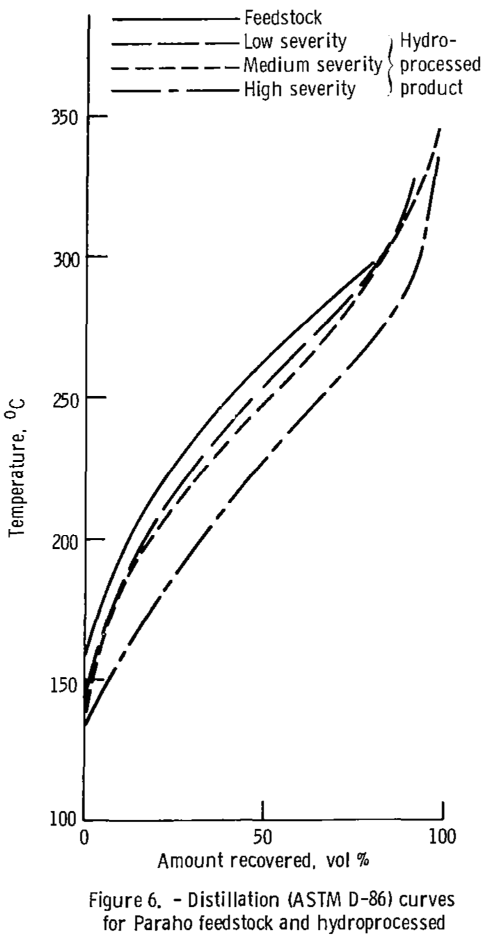
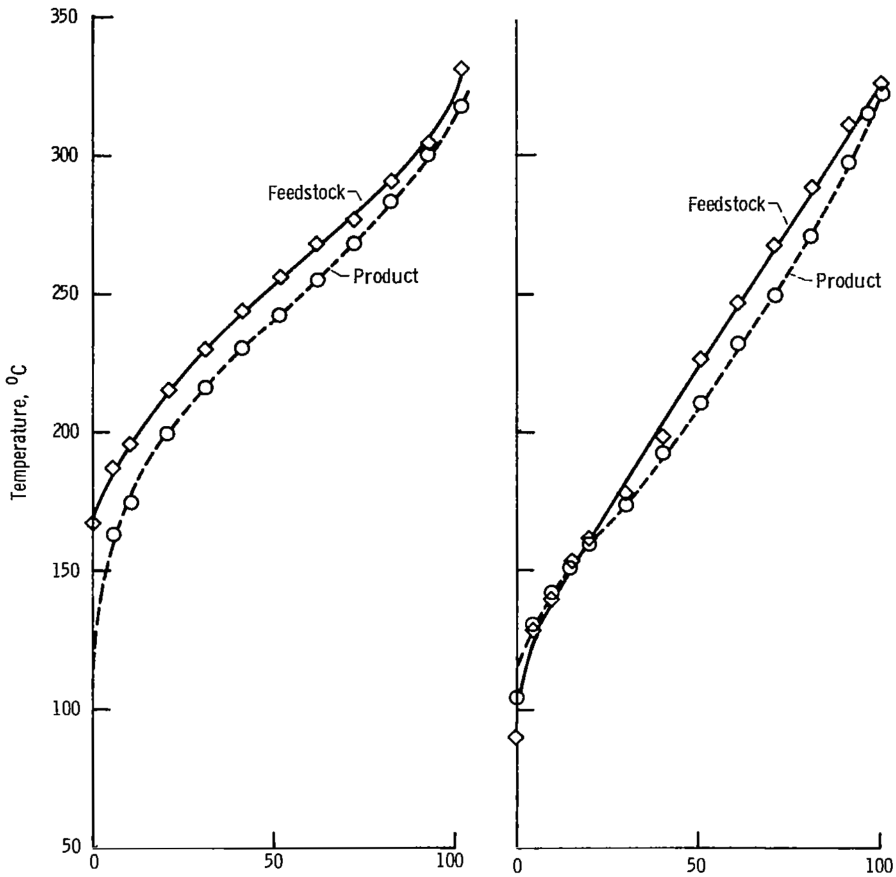


Figure 6. - Distillation (ASTM D-86) curves for Paraho feedstock and hydroprocessed products.

The results of property measurements made on distillate feedstock and hydroprocessed product are given in table VII for TOSCO II and in table VIII for Paraho. Reference 1 results are included in table VII for comparison. The two TOSCO II runs were made under similar hydroprocessing conditions except for slightly different pressures (table I). Results for product properties from these two runs show agreement with reported values in reference 1 except for the freezing point. The difference from reference 1 is caused by the differences in the reactors, slight differences in operating conditions, and differences in the volatility of the feedstock.

The analyses of hydroprocessed Paraho products show that higher severity hydrotreating of Paraho feedstock is necessary to reduce the nitrogen level to that obtained for TOSCO II. The nitrogen level in the medium-severity Paraho product was about an order of magnitude more than the level in the TOSCO II product. Properties for medium-severity Paraho product compare favorably with those for the TOSCO II product except for nitrogen level, freezing point, and thermal stability. None of the Paraho products passed the thermal stability requirement for a broad-property research fuel, which is a JFTOT tube deposit rating (TDR) of 13 at 238° C, but the TOSCO II products did pass this JFTOT test. The hydrogen content of Paraho products increased linearly with processing temperature over the temperature range of the present work (fig. 8). The nitrogen level decreased exponentially with processing temperature (fig. 9). Saturation and cracking of aromatics increased with processing severity, which can be seen from the aromatics level and naphthalene level in table VIII for the three different severities.

Results of property measurements made on the final distilled fuels are given in tables IX and X. Complete results for the ASTM D-86 distillations are presented in table XI. Jet A boiling range TOSCO II and high-severity Paraho product fuels met Jet A specifications except for the freezing point. These product fuels did not pass the 260° C JFTOT thermal stability test, but they would have passed a 245° C JFTOT test (footnote "i" in ASTM D-1655) because the wide-boiling-range product fuels would pass the 245° C JFTOT test (table X). Although low- and medium-severity Paraho product fuels in the Jet A boiling range met most of the specifications, thermal stability and freezing point were not met. High nitrogen content was undoubtedly the cause of the poor thermal stability. In addition the low-severity product fuel did not meet viscosity and net heat of combustion requirements.



(a) Present work.

(b) Reference 1.

Figure 7. - Distillation (ASTM D-86) curves for TOSCO II feedstock and hydroprocessed product.

In figure 10 a composite curve or curve band for the Jet A distillation data in table XI is compared with a petroleum-based Jet A curve for data from one of the Jet A inspections in reference 18. Between the 10-percent and 90-percent points, the TOSCO II and Paraho product fuels gave a slope of about 1.2 percent per degree C, as compared with the Jet A slope of about 0.4 to 0.8 percent per degree C. Although the ASTM D-86 curves for the present work are not identical to that of present commercial Jet A, volatility measurements for all four final product fuels met the ASTM D-1655 requirements. All that would be required for the TOSCO II and high-severity Paraho to meet all ASTM D-1655 requirements (table III) would be a small reduction in the cut point during the final distillation. Reducing the end point from 327° to 300° C (620° to 572° F) decreased the freezing point nearly 10 degrees C (18 degrees F). A further decrease in end point of about 35 degrees C is estimated to be sufficient to meet the freezing point specification at a reduction in yield of approximately 20 percent (fig. 10). Medium-and low-severity Paraho product fuels require further processing in order to meet Jet A requirements.

The broad-property TOSCO II product fuel is compared with results reported in reference 1 (table X and fig. 11). The hydrogen content of all broad-property product fuels is much higher than the target minimum for a broad-property research fuel (table III(b)). This higher hydrogen content improves the overall expected quality of the broad-property research fuel. Reducing the cut point during final distillation would reduce the freezing point. With the relaxing of freezing point to −23° C (−10° F), which would occur at an end point of about 310° C, the target properties for the broad-property research fuel could easily be met by TOSCO II and high-severity Paraho product fuels. The medium- and low-severity Paraho product fuels require further

TABLE VII. - ANALYSIS OF TOSCO II FEEDSTOCK AND HYDROPROCESSED PRODUCT

Property	Feedstock	After processing (pressure, 133×10^5 N/m^2)	After processing (pressure, 143×10^5 N/m^2) (a)	Hydroprocessed product (ref. 1)
Hydrogen content, wt %	12.36	14.05	13.97	13.82
Aromatics content, vol %	37.9	16.6	14.1	13.7
Sulfur content (mercaptan), wt %	0.0029	<0.0003	<0.0003	0.0003
Sulfur content (total), wt %	0.62	0.041	0.024	0.0009
Nitrogen content, wt %	1.20	0.0013	0.0082	0.0161
Naphthalenes content, vol %	--------	0.59	0.54	0.4
Flashpoint, ^{o}C (^{o}F)	--------	43 (109)	51 (123)	-------------
Gravity (API, 15^{o} C)	34.5	43.0	42.7	45.8
Gravity (specific, 15/15^{o} C)	0.8576	0.8109	0.8123	0.7977
Freezing point, ^{o}C (^{o}F)	-35 (-31)	-13 (9)	-12 (10)	-17 (1)
Smoke point	--------	--------	-------------	26
Viscosity at room temperature, cS	--------	2.6	2.6	-------------
Net heat of combustion, kJ/kg (Btu/lb)	--------	--------	43 860 (18 860)	44 120 (18 970)
Thermal stability:				
JFTOT tube deposit rating at 238^{o} C (460^{o} F)	--------	2	4	7
Pressure difference, ΔP, mm Hg	--------	0	0	0

[a]Catalyst required replacement after this run.

TABLE VIII. - ANALYSIS OF PARAHO FEEDSTOCK AND

HYDROPROCESSING PRODUCT

Property	Feedstock	Processing severity		
		High	Medium	Low
Hydrogen content, wt %	12.05	14.33	13.99	13.66
Aromatics content, vol %	------	8.1	15.5	17.7
Sulfur content (mercaptan), wt %	0.0016	<0.0003	<0.0003	0.0008
Sulfur content (total), wt %	0.81	0.02	0.02	0.02
Nitrogen content, wt %	1.53	0.0005	0.0602	0.71
Naphthalenes content, vol %	------	0.31	0.72	2.37
Flashpoint, ^{o}C (^{o}F)	------	35 (95)	38 (100)	42 (107)
Gravity (API, 15^{o} C)	29.8	44.8	41.6	40.3
Gravity (specific, 15/15^{o} C)	0.8767	0.8026	0.8160	0.8232
Freezing point, ^{o}C (^{o}F)	-17 (1)	1 (34)	20 (68)	20 (68)
Smoke point	------	-------	-------	-------
Viscosity at room temperature, cS	------	2.7	3.4	3.8
Net heat of combustion, kJ/kg (Btu/lb)	------	-------	-------	-------
Thermal stability:				
JFTOT tube deposit rating at 238^{o} C (460^{o} F)	------	15	>50	>50
Pressure difference, mm Hg	------	0	-------	0

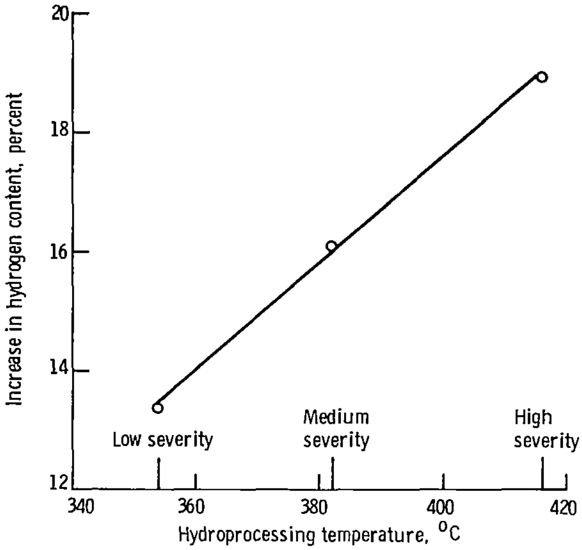


Figure 8. - Effects of hydroprocessing severity on Paraho product hydrogen content.

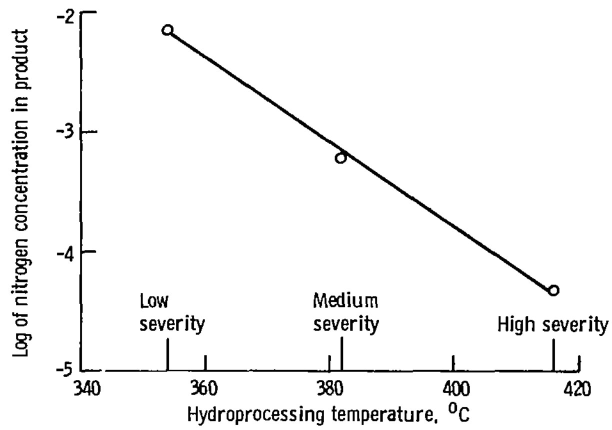


Figure 9. - Effects of hydroprocessing severity on Paraho product nitrogen content.

TABLE IX. - ANALYSIS OF DISTILLED HYDROPROCESSED PRODUCT

[Boiling range, 121° to 300° C (250° to 572° F).]

Property	TOSCO II (medium severity)	Paraho		
		High severity	Medium severity	Low severity
Carbon content, wt %	86.64	85.33	86.29	85.70
Hydrogen content, wt %	13.95	14.29	14.02	13.64
Aromatics content, vol %	16.7	9.5	16.2	19.7
Sulfur content (mercaptan), wt %	0.0004	<0.0003	0.0004	0.0005
Sulfur content (total), wt %	0.022	0.0014	<0.001	0.017
Nitrogen content, wt %	0.0039	0.0009	0.0687	0.63
Naphthalenes content, vol %	0.65	0.19	0.38	1.70
Flashpoint, °C (°F)	51 (124)	48 (118)	48 (118)	52 (125)
Gravity (API, 15° C)	43.0	44.7	43.1	41.2
Gravity (specific, $15/15^{\circ}$ C)	0.8109	0.8029	0.8095	0.8193
Freezing point, °C (°F)	-31 (-24)	-26 (-15)	-30 (-22)	-28 (-18)
Smoke point	29	32	26	26
Viscosity at -23.3° C (-10° F), cS	7.8	8.4	8.4	11.2
Net heat of combustion, kJ/kg (Btu/lb)	42 890 (18 440)	43 050 (18 510)	42 990 (18 450)	42 510 (18 280)
Thermal stability:				
JFTOT tube deposit rating at 260° C (500° F)	15	14	34	>50
Pressure difference, mm Hg	0	10	2	0

TABLE X. - ANALYSIS OF DISTILLED HYDROPROCESSED PRODUCT

[Boiling range, 121° to 327° C (250° to 620° F).]

Property	TOSCO II		Paraho		
	Medium severity	Reference 1	High severity	Medium severity	Low severity
Carbon content, wt %	86.21	------------	85.21	85.72	86.35
Hydrogen content, wt %	13.95	13.86	14.29	14.01	13.68
Aromatics content, vol %	16.7	17.4	8.2	16.8	18.6
Sulfur content (mercaptan), wt %	0.0008	<0.0003	<0.0003	<0.0003	0.0005
Sulfur content (total), wt %	0.002	0.0003	0.002	<0.001	0.01
Nitrogen content, wt %	0.0132	0.0168	0.0010	0.0602	0.66
Naphthalenes content, vol %	0.75	0.4	0.22	0.46	1.79
Flashpoint, °C (°F)	49 (121)	39 (102)	46 (114)	48 (118)	49 (120)
Gravity (API, 15° C)	42.6	43.6	44.5	42.4	40.3
Gravity (specific, 15/15° C)	0.8126	0.8081	0.8042	0.8137	0.8232
Freezing point, °C (°F)	-19 (-2)	-15 (5)	-17 (1)	-19 (-2)	-17 (1)
Smoke point	33	26	34	27	27
Viscosity at -12.2° C (10° F), cS	6.8	------------	6.7	7.3	6.6
Net heat of combustion, kJ/kg (Btu/lb)	43 860 (18 860)	43 860 (18 860)	42 930 (18 460)	42 740 (18 380)	42 430 (18 240)
Thermal stability:					
JFTOT tube deposit rating at 238° C (460° F)	<13	[a]<13	10	21	>50
Pressure difference, mm Hg	0	0	0	0	0

[a]Reference 19.

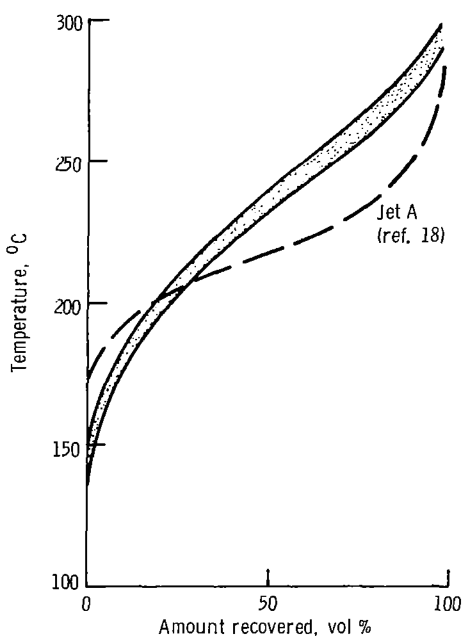


Figure 10. - Composite distillation (ASTM D-86) curves for Jet A cut from both TOSCO II and Paraho hydroprocessed products and curve for petroleum-based Jet A (ref. 18).

processing to reduce nitrogen level and to improve thermal stability.

Concluding Remarks

Aviation turbine fuel yields comparable to those produced from distillation of petroleum crudes can be obtained by hydroprocessing the products of TOSCO II or Paraho (indirect mode) shale oils. If all fuel property requirements are to be met, the product synfuel may require some finishing processes. For the TOSCO II and high-severity Paraho products, specification fuel can be obtained by slightly reducing the end point during the final distillation. The medium-severity Paraho product would require a finishing process before final freezing point adjustment. Significantly more processing, such as further hydrotreating or extraction of nitrogen-containing molecules, would be required for the low-severity Paraho product before a satisfactory final product could be obtained.

Except for freezing point and thermal stability the medium-severity Paraho product in the Jet A boiling range met Jet A requirements. However, the nitrogen content was still too high (687 ppm) for satisfactory

TABLE XI. - ASTM D-86 DISTILLATION RESULTS FOR PRODUCT FUELS

Amount distilled, percent	Jet A cut (121° to 300° C; 250° to 572° F)								Broad-property cut (121° to 327° C; 250° to 620° F)							
	TOSCO II (medium severity)		Paraho						TOSCO II (medium severity)		Paraho					
			High severity		Medium severity		Low severity				High severity		Medium severity		Low severity	
	Recovered temperature															
	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
Initial boiling point	149	300	141	285	135	275	143	290	152	305	146	295	146	295	143	290
5	171	340	169	336	168	335	174	345	172	342	171	340	174	345	178	353
10	183	362	179	355	183	361	185	365	187	366	181	358	189	372	189	372
20	196	384	196	384	198	387	202	396	203	397	200	392	207	405	209	409
30	208	407	213	415	211	412	216	421	218	425	214	418	223	434	226	438
40	220	428	221	430	222	432	229	444	231	448	228	442	233	451	237	461
50	232	450	233	452	232	450	239	463	243	470	241	465	248	478	253	487
60	242	468	245	473	243	469	250	482	254	490	253	488	257	495	264	508
70	252	485	253	488	252	486	260	500	268	515	268	514	270	518	277	530
80	262	504	267	512	263	505	270	518	281	538	283	541	282	540	288	551
90	274	526	283	542	274	526	283	541	297	566	300	573	297	566	302	576
Final boiling point	289	553	298	568	289	553	294	562	313	595	314	597	310	590	313	596
Residue, percent	---		1.4		1.2		1.4		---		1.1		---		1.5	
Loss, percent	---		.1		.8		.6		---		1.4		---		.5	

thermal stability. Increased processing severity will remove the remainder of the nitrogen but at the expense of an increase in energy consumption. Depending on the given refinery configuration as well as other factors, a finishing process such as acid wash and clay treatment of the medium-severity product may be more attractive.

The TOSCO II feedstock was noticeably easier to upgrade than the Paraho feedstock for the production of jet fuels. However, acceptable jet fuels can be made from either crude.

Summary of Results

The fractions of whole shale oil boiling below 343° C (650° F) obtained from TOSCO II crude and Paraho crude (indirect mode) were hydroprocessed and characterized. The TOSCO II feedstock was hydroprocessed at a medium-severity condition, and the Paraho feedstock was hydroprocessed at low-, medium-, and high-severity conditions. Fuel in the Jet A boiling range and a broad-property research fuel were distilled from each hydroprocessed

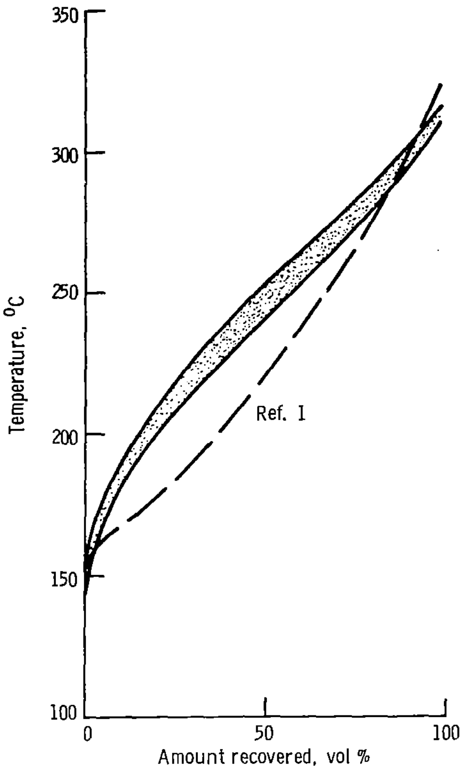


Figure 11. - Composite distillation (ASTM D-86) curve for broad-property cut from both TOSCO II and Paraho hydroprocessed products and curve from reference 1.

product, and these final products were characterized. The results obtained included the following:

1. Fuels produced from TOSCO II and Paraho shale oils met Jet A current specifications with the exception of freezing point. The Paraho feedstock required high-severity treatment.

2. Fuels produced from both TOSCO II crude and Paraho crude met the target properties of a broad-property research fuel except for freezing point and hydrogen content. The hydrogen content was about 1 percent higher than the target.

3. It took more severe hydroprocessing to upgrade the shale oil fraction from Paraho crude than the shale oil fraction from TOSCO II crude.

4. The hydrogen content of the hydroprocessed product increased linearly with processing temperature over a temperature range of 354° to 416° C (670° to 780° F).

5. The Jet A produced exhibited a steeper slope in the ASTM D-86 distillation curve between the 10-percent and 90-percent points than did the commercial Jet A.

6. Significantly more cracking occurred at the high-severity hydroprocessing conditions than at the medium- and low-severity conditions.

7. High-severity hydroprocessing decreased the aromatics content; this decrease is the result of aromatic saturation and possibly cracking.

8. Increasing the hydrogen content of the shale oil distillate was easier than reducing the nitrogen content. This resulted in a high hydrogen content for the broad-property research fuel.

9. Yields of jet fuel in the target boiling range approached the yields obtained from straight-run Khafji and North Slope crudes, which are heavy crudes. Light petroleum crudes normally used for jet fuel production give yields that are about 30 percent higher.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, January 8, 1981

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16. Abstract

Jet A boiling range fuels (121° to 300° C; 250° to 572° F) and broad-property research fuels (121° to 327° C; 250° to 620° F) were produced by hydroprocessing shale oil distillates, and their properties were measured to characterize the fuels. The distillates were the fraction of whole shale oil boiling below 343° C (650° F) from TOSCO II and Paraho (indirect mode) syncrudes. The TOSCO II was hydroprocessed at medium severity, and the Paraho was hydroprocessed at high, medium, and low severities. Fuels meeting Jet A requirements except for the freezing point were produced from the medium-severity TOSCO II and the high-severity Paraho. Target properties of a broad-property research fuel were met by the medium-severity TOSCO II and the high-severity Paraho except for the freezing point and a high hydrogen content. Medium- and low-severity Paraho jet fuels did not meet thermal stability and freezing point requirements. Since a high nitrogen content was the reason for poor thermal stability, further processing is required for the medium- and low-severity Paraho fuels. Comparisons are made with other reported work and with yields from petroleum crudes.

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