

The Commercial Scale Refining of Paraho Crude Shale Oil
Into Military Specification Fuels

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Introduction

In September, 1977 The Standard Oil Company (Ohio) was contracted by the U.S. Navy to refine up to 100,000 barrels of crude Paraho shale oil into military transportation fuels. The objective of the program was to demonstrate that shale oil could be converted into stable, specification military fuels utilizing conventional refining technology and in sufficient volumes to support an extensive engine testing program. Yields of JP-5 and DFM were to be maximized while minimizing the yield of residual fuel.

The crude shale was produced by Paraho Development Corp. over the three year period from 1976 to 1978. Paraho's Anvil Point, Colorado works utilizes a vertical direct heat retort to recover the oil from crushed shale^[1].

For contractual reasons the program was divided into three phases. During Phase I, the proposed shale oil processing scheme was tested and developed in appropriate pilot plants. Phase II constituted engineering preparation and the actual refinery run. Post run analysis and report writing were completed in Phase III.

Paraho Shale Oil

The unique nature of crude shale oil requires special consideration in handling and processing. Table I summarizes some typical inspections of raw shale oil and a West Texas crude. In comparison to conventional petroleum, shale oil has several deleterious characteristics:

- [1] High nitrogen and oxygen content.
- [2] Low hydrogen/carbon ratio.
- [3] Low yield of 650° minus material (<30 vol.%).
- [4] Moderate arsenic and iron content.
- [5] Suspended ash and water.

The high nitrogen content is probably the largest area of concern, as it is an order of magnitude higher than that found in petroleum. The technology for processing high nitrogen crudes is not nearly as advanced as comparable technologies for desulfurization or cracking (increasing yield of lower boiling hydrocarbons).

Nitrogen compounds are known poisons for many petroleum processing catalysts such as fluid bed catalytic cracking, naphtha reforming and hydrocracking catalysts. In addition, nitrogen compounds have been found to create stability problems in gasoline, jet and diesel fuels. Fuel bound nitrogen will also increase the NO_x emissions from practically any type of combustor. Finally, nitrogen compounds quite often have a peculiar and offensive odor which is uncommonly difficult to remove^[2].

Shale Oil Refining Process

A schematic of the process developed for this program is shown in Figure 1. The crude shale oil is initially allowed to settle batchwise at above ambient temperature. This has been found to be effective in breaking the water/oil emulsion, thereby precipitating suspended water and ash to the bottom of the tank. The shale oil is also pumped through a 20 micron filter enroute to the hydrotreater to remove any entrained debris left in the tank.

After settling, the shale oil is mixed with hydrogen, preheated and passed through a guard bed. The purpose of the guard bed is to remove the organic Fe and As as well as any ash and solids which survived the settling and filtering procedure.

Following the shale oil pretreatment steps (settling and guard bed demetallization) the whole shale oil is catalytically hydrotreated at elevated temperature and hydrogen partial pressure. Hydrotreating, the most important processing step, is the catalytic reaction of hydrogen with sulfur, oxygen and nitrogen compounds to form H₂S, H₂O and NH₃, respectively, plus heteroatom-free hydrocarbons. In addition, aromatic saturation and cracking occur to some extent -- thereby increasing the hydrogen/carbon ratio and increasing the yield of military fuel feedstock (650°F minus material).

The hydrotreated shale oil is fractionated by distillation methods into gasoline, jet, diesel, and 650°F bottoms (residua). The jet and diesel fuel boiling ranges were determined experimentally to meet flash and freeze or pour requirements while maximizing yields. The residua or bottoms material could not be utilized in the diesel or lighter cuts due to pour point requirements. Some of the residua was recycled back to the hydrotreater to increase jet and diesel fuel yields.

A final finishing step, acid and clay treating, was included to meet military specification gum and stability requirements.

Refinery Modifications

Prior to the shale oil operation, facilities modifications at the Toledo refinery were required to be able to receive, store and process the shale oil and its products without contamination from normal refinery stocks.

Raw shale oil was shipped from the Paraho facilities to Toledo by railroad tank car. An underutilized railcar rack was revamped to provide a new unloading as well as a product loading system. A new steam heated tank was built in which to store the shale oil as it was received over a 3 month period.

A hydrocracker which normally processes distillate fuels into gasoline products was modified to process the shale oil. New catalyst (Shell 324) was charged to the first stage reactor. A guard bed packed with alumina extrudate was placed in the feed preheat train. A 20 micron filter was installed on the inlet line from the shale oil storage tank. A new stripper tower was installed on the distillation tower to strip the DFM product. Numerous instrumentation and piping modifications were made to allow for a single stage hydrotreater operation.

For acid treating of the DFM and JP products a "new" acid treater was designed and built, the major vessels of which were refinery surplus equipment. These vessels included a settler, clay contactor and sludge storage tank.

To provide product storage for JP-5 and DFM, two tanks were removed from refinery service and cleaned prior to processing.

All lines used for shale oil material which interconnected with lines containing normal refinery stocks were either blanked or had the isolating valves chained and locked.

Refinery Logistics and Process Flow

When all the shale oil had been received, the storage tank was heated to 185°F, and an attempt was made to drawoff any free water. No free water was found. The shale oil received at Toledo measured only ~0.06 vol.% sediment and water, (BS&W) whereas earlier pilot plant samples contained ~0.8 vol.% B.S. and W. The shale oil was pumped continuously from the tank through the 20 micron feed filter into the hydrotreater surge drum. From here it was pumped through the feed preheat section and guard bed together with hydrogen gas and into the reactor. Reactor effluent was cooled, water washed and recycle hydrogen and light ends removed, prior to entering a multidraw distillation column. Here four products were recovered from the effluent: an overhead gasoline stock, a jet fuel cut (JP-5 or JP-8), a marine diesel fraction (DFM) and a bottoms residual fuel fraction. The gasoline stock was sampled, but not recovered in bulk, instead it was used as feed to another hydrocracker. The JP-8 was acid treated on rundown to a railcar, while JP-5 and DFM were run down to storage for later acid treating. Any off spec JP-5, JP-8 or DFM were returned to the shale oil storage tank. Part of the bottoms residua were recycled through the hydrotreater to increase conversion, while the remainder was used as cat cracker feed with a small

amount rundown directly to railcars for recovery as heavy fuel oil.

Refinery Run

The hydrotreating run began on November 4, 1978 and ended on December 4, 1978. In that time 73,100 barrels of the 88,225 barrels of shale oil received were hydrotreated. However some of the products from this volume were returned to the shale oil storage tank as off specification product. An excessively high pressure drop across the Guard Bed caused the run to be terminated before all the shale oil was processed. The hydrocracker was first shutdown on day 25 of the run because of a high guard bed pressure drop. The top 25% of the Guard Bed packing was removed because a black viscous sludge was present on the top of the bed. When returned to operation, the Guard Bed soon redeveloped a high pressure drop and the run was terminated due to contractual time limitations.

Original plans called for the JP products to be acid treated on rundown to tankage or railcar. This plan was modified after acid treater start-up problems resulted in poor denitrification. The JP-5 was rundown to tankage without acid treating, as was the DFM, and both were treated after the hydrotreating run was complete. Fortunately, the acid treating problems were resolved in time to treat the JP-8 on rundown to a railcar.

The residual hydrotreated shale oil was mixed with regular refinery cat cracker feed at a rate of 3%, with no detectable shifts in yields or other adverse consequences. Similarly, the gasoline range cut had no detectable effect on hydrocracker operations at 1.5% of feed.

The shale oil which remained after the processing run was burned as boiler fuel. No problems developed over the 1 month combustion period.

Following conclusion of the run, an examination of the Guard Bed contents revealed two separate problems, the sludge at the top of the bed and FeS_x fines throughout the bed. The sludge was theorized to have been formed by a reaction between shale oil, iron, and sulfuric acid. The acid had been unwittingly introduced into the shale oil feed tank by recycling off-spec JP-5 from the acid treater during startup. A large quantity of fines containing a high concentration of FeS_x was found throughout the bed. Apparently FeS_x had been depositing throughout the run and filled the interstitial spaces among the extrudate, thus causing a high pressure drop.

Material Balances

Essentially all of the conversion of 650°F plus bottom material to transportation fuel occurs in the hydrotreating step. Table II summarizes the overall material balance and yield structure from our hydrotreating section. Table II also compares the actual yields and nitrogen levels obtained at Toledo with original pilot plant results. These data indicate that the denitrification activity of the catalyst was consistent with prior results, however the apparent yield structure was different. The differences in yields are attributed to two factors: [1] poorer distillation efficiency in the refinery operation and [2] lower DFM pour point and flash point targets during the refinery run. The actual conversion of 650°F plus bottoms material attained in the refinery run is very similar to the pilot plant results. The distillation curve of whole hydrotreated products (minus recycle) shown in Figure 2, illustrates this observation.

Net hydrogen consumption metered in the refinery run was significantly less than pilot plant results [-1500 versus -1050 SCFB]. Chemical analyses of the various hydrotreated products indicate that the level of aromatic saturation, cracking and heteroatom removal for both refinery and pilot plant were nearly the same. The difference in measured hydrogen consumption is most probably a result of scale-up and pilot plant error. Needless to say, hydrogen consumption is a very important parameter in determining overall shale oil economics.

The total amount of each finished fuel produced is shown in Table III. In acid treating the yield losses were found to be proportional to nitrogen content and molecular weight of the fuel. For a 3300 ppm nitrogen JP-5 stock, yield loss was 4 wt.% and on a 3300 ppm nitrogen DFM the loss was 5.4 wt.%. Other losses incurred in the system were start-up and line-out slop, heel left in feed tanks and treating vessels and losses during the clay column changes.

Product Analyses

Gasoline Stock

Analyses of the refinery and pilot plant gasoline stocks are shown in Table IV. Both materials are very similar in aromatic content, nitrogen level and octane. Neither is usable as a direct gasoline blending stock or as reformer feed. Additional hydrotreating is required to reduce the nitrogen content to levels acceptable to catalytic reforming, which is required to boost the octane of this material.

Jet Fuels

Product JP-5, before and after acid treating is compared to pilot plant prepared material in Table V. Again both stocks have similar nitrogen, hydrogen and aromatic content. Note that the thermal stability of the untreated fuel is poor. However, once the nitrogen compounds are selectively removed by acid treating, the fuels' stability as determined by gum and JFTOT (ASTM D-3241) measurements is very good. In addition, storage stability characteristics of the fuels were tested by aging the material for 1 month at 140°F and then repeating the JFTOT and gum tests. The aging test results, shown in Table VI for a composite sample of all treated JP-5 produced at the refinery, indicate that this fuel has very good storage stability properties.

Diesel Fuel Marine

Physical inspections of pilot plant and refinery DFM are compared in Table VII. As previously mentioned, the distillation (hence nearly everything else) are different due to refinery fractionation practices and altered target specs. Again, acid treating is required to meet fuel stability specifications, i.e. ASTM 2274 - (accelerated oxidation gum test). These fuels have good combustion properties, as shown by the cetane number (>50) and hydrogen contents (>13 wt.% hydrogen).

Residual Fuel

The residual fuel produced by both the pilot and refinery meets all government specifications for low sulfur, high pour #6 fuel oil. The residual fuels are in fact very "clean" as shown in Table VIII by the high hydrogen and low sulfur, metals, carbon and asphaltene content. This stock is better utilized as cat cracker feed than residual fuel, since higher value gasoline and kerosine fuel can be easily produced via catalytic processing.

Product Fuels Distribution

All 6165 bbls of the treated JP-5 produced at the Toledo refinery was shipped to Rickenbacher Air Force Base in Lockbourne, Ohio. The treated DFM was shipped to four destinations: 3021 bbls went to General Motors Detroit Diesel, Allison Plant #5 in Indianapolis, Ind., 8334 bbls were shipped to Philadelphia Naval Base in Philadelphia, Pa., 235 bbls were sent to Wright Patterson Air Force Base, Fairborn, Ohio and 4785 bbls went to the Defense Fuel Support Point in Cincinnati, Ohio. Of the 4670 bbls of residual fuel reserved for shipment, 4345 bbls were sent to the U.S. Navy at Mechanicsburg, Pa., and the remaining 325 bbls were shipped to the E.P.A. at the Naval Ship Yard in Long Beach, California. These fuels are undergoing extensive engine testing and evaluation by the parties involved. In addition to the fuels produced, numerous samples of feed, intermediate and product streams were taken for health effect studies by the D.O.D. and D.O.E.

Conclusions

- 1) Fuels meeting military specifications and possessing good storage stability characteristics can be produced from crude shale oil, utilizing conventional refinery equipment.
- 2) The processing scheme utilized in this study requires:
 - (a) Settling and a guard bed to protect the hydrotreating catalyst.
 - (b) Hydrotreating to remove heteratoms, increase the hydrogen/carbon ratio and improve the 650°F minus liquid yield of shale oil.
 - (c) Acid and clay treating to meet thermal and storage stability requirements of the jet and diesel fuel.

Acknowledgement

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References

- 1) Jones, J. B., Heistand, R.N., "Recent Paraho Operations", 12th Oil Shale Symposium Proceedings, Colo. School of Mines, April 18-20, 1979 pg. 184-194.
- 2) Robinson, E. T., "Refining of Paraho Shale Oil Into Military Specification Fuels", IBID, pg. 195-212.

Table I Properties of Paraho Shale Oil and West Texas Sour Crude

	Paraho Shale Oil	West Texas Sour
Gravity, °API	20.4	34.1
Specific Gravity @60°	0.9315	0.8545
Pour Point, °F	+85	Fluid @ -30
Viscosity, SSU		
@ 60°F	Too heavy	57.1
@ 100°F	213	43.1
@ 210°F	44.9	--
Viscosity-Gravity Constant	0.8899	0.722
RVP, lbs.	--	5.1
Total Acid No., mgKOH/g	1.988	0.265
Asphaltenes, wt. %	0.889	1.028
Ramsbottom Carbon, wt. %	2.977	2.65
BS&W, Vol. %	0.05 (0.06 unsettled)	0.30
Salt, lb./M Bbls.	4.9 (8.2 unsettled)	3.3
Elemental Analysis		
C, wt. %	83.68	--
H, wt. %	11.17	--
O, wt. %	1.36	--
N, wt. %	2.02	0.10
S, wt. %	0.70	1.40
Metals		
As, ppm	7.5	--
Na, ppm	<0.3	--
K, ppm	0.17	--
V, ppm	0.17	4.4
Ni, ppm	2.4	2.6
Fe, ppm	53	2.0
TBP 650°F Point, vol. %	28.24	58.64

Table II Shale Oil Hydrotreating Yields.

	Toledo Refinery			Pilot Plant	
	Bbls.	Vol. %	Wt. % N	Vol. %	Wt. % N
Gasoline stock (including Butanes)	8743	11.96	0.067	11.00	0.050
JP-5	9546	13.73	0.220	25.30	0.250
JP-8	490				
DFM	18939	25.90	0.340	34.50	0.430
Residual Fuel	37220	50.91	0.380	35.20	0.220
	<u>74938</u>	<u>102.50</u>		<u>106.00</u>	
H ₂ Cons. SCFB		1050		1500	

Table III Net Fuels Produced After Acid/Clay Treating

	Bbls.
Gasoline Stock	7,718
JP-5	6,615
JP-8	462
DFM	16,375
Residual Fuel	37,220

Table IV Gasoline Stocks Analyses.

	Pilot Plant	Toledo
API Gravity	57.8	54.7
RVP, psi	1.3	5.6
Distillation	D-86	D-86
IBP, °F	190	200
10	226	249
50	258	283
90	288	317
EP	332	370
% Rec.	99.0	98.0
% Res.	1.0	1.0
Paraffins	58.87	49.95
Monocyclo. Par.	29.61	31.62
Dicyclo Par.	1.11	2.40
Alkylbenzenes	9.97	15.20
Indans + Tetralins	0.11	0.51
Naphthalenes	0.33	0.32
Carbon No. Par.	8.01	9.36
Carbon No. Alkybenzenes	7.81	7.85
Nitrogen, Wt. %	0.040	0.078
Research Octane, clear	47	Not run

Table V

JP-5 Analyses

A - Untreated JP-5

	<u>Pilot Plant</u>	<u>Toledo</u>	<u>Mil Spec</u>
API Gravity	41.8	42.7	API < GR < 48
Flash, °F	157	158	140 Min.
Freeze, °F	-52	-57	-51 Max.
Existent gum (D-381) Mg/100 cc	12.2	Not run	7.0 Max.
Distillation	<u>D-86</u>	<u>D-86</u>	<u>D-86</u>
IBP, °F	356	370	R
10	380	384	401 Max.
50	415	400	R
90	456	436	R
EP	477	480	554 Max.
Nitrogen, Wt. %	0.32	0.29	--
Paraffins, Vol. %	43.9	42.5	--
Naphtenes, Vol. %	33.1	36.0	--
Aromatics, Vol. %	23.0	21.5	25% Max.
JFTOT Visual	4 (Fail)	--	< 3

B - Treated JP-5

	<u>Pilot Plant</u>	<u>Toledo</u>	<u>Mil Spec</u>
API Gravity	43.0	43.6	36 < API Gr < 48
Nitrogen, PPM	8	0.5	--
TAN, mg KOH/gm	Nil	0.005	0.015 Max.
WSIM	86	95	85 Min.
Existent gum Mg/100 cc	0.6	1.4	
JFTOT @ 500°F			
Visual	2	1	< 3
Max Spun Rate	10	0	< 17
Max ΔP mm Hg	1.0	0.5	.25
Paraffins Vol. %	46.0	43.7	
Naphtenes Vol. %	33.1	34.5	
Aromatics Vol. %	20.9	21.8	25% max.

Table VI

Refinery JP-5 Stability Properties

	<u>Unaged Fuel</u>	<u>Aged @ 140°F for 1 month</u>
JFTOT Break Point, °F	625	> 500
Color	+ 30	+ 30
D-381 Existent Gum Mg/100 cc	1.4	1.6
JFTOT @ 500°F, visual	< 2	< 2
JFTOT @ 500°F, Max Spun Tube	1.0	3.0
JFTOT @ 500°F, Max Spot Tube	2.0	2.0
JFTOT @ 500°F, Σ TDR	1.5	6.5
JFTOT @ 500°F, Δ P MM Hg	0.0	0.0

Table VII

Diesel Fuel Marine AnalysesA - Untreated DFM

	<u>Pilot Plant</u>	<u>Toledo</u>	<u>Mil Spec</u>
API Gravity	33.4	36.8	R
Pour, °F	15	0	20 Max
Flash, °F	290	162	140 Min
Distillation	<u>D-86</u>	<u>D-86</u>	<u>D-86</u>
IBP	507	396	--
10	529	456	--
50	553	512	R
90	595	562	675 Max
EP	628	582	725 Max
% Res	1.0	1.0	3 Max
Nitrogen, Wt. %	0.40	0.33	
Cetane Index	50.1	52.5	45 Min

B - Treated DFM

	<u>Pilot Plant</u>	<u>Toledo</u>	<u>Mil Spec</u>
API Gravity	34.8	38.1	R
Carbon, Wt. %	86.75	86.27	--
Hydrogen, Wt. %	13.02	13.28	--
Nitrogen, ppm	90	3.9	
Paraffins Vol. %	42.2	45.5	--
Naphthenes, Vol. %	25.8	25.5	--
Aromatics, Vol. %	32.0	29.0	--
TAN, Mg KOH/gm	0.029	0.010	0.30 Max
Cetane Number	55.3	50.1	45 Min
ASTM 2274 Mg/100 cc (acc. oxid. test)	0.37	0.51	2.5 Max

Table VIII

Residual Fuel Analyses

	<u>Pilot Plant</u>	<u>Toledo</u>
API Gravity	30.3	29.6
Pour Pt., °F	105	80
Rams Bottom Carbon, Wt. %	Not run	0.096
Asphaltenes, Wt. %	0.244	0.059
Vis. @ 210°F, CST	6.45	2.00
Distillation	<u>D-2887</u>	<u>D-2887</u>
IBP	689	331
10	739	582
50	830	732
90	958	900
EP	1000	1032
Carbon Wt. %	87.32	86.71
Hydrogen, Wt. %	12.59	12.75
Nitrogen, Wt. %	0.33	0.44
Oxygen, ppm	102	182
Sulfur, ppm	< 20	< 20

Table VIII, Continued

	<u>Pilot Plant</u>	<u>Toledo</u>
Saturates, Vol. %	57.1	Not run
Aromatics, Vol. %	42.9	Not run
Iron, ppm	0.93	0.10
Arsenic, ppm	0.13	0.4
Vanadium, ppm	0.36	0.02
Sodium, ppm	0.79	0.6
Potassium, ppm	< 0.10	0.6

FIGURE 1

Shale Oil Processing Block Flow Diagram

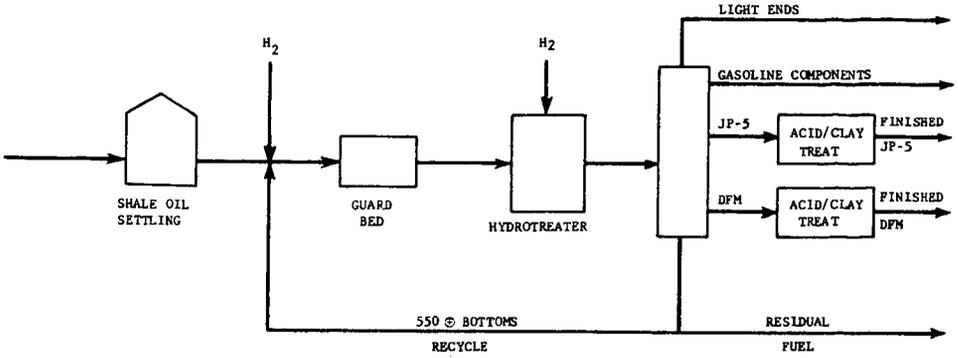


FIGURE 2

T.B.P. Distillation Comparison of Pilot Plant and Refinery Whole Hydrotreated Product

