

GULF SHALE OIL UPGRADING
PROCESS TECHNOLOGY

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ABSTRACT

A description of the Gulf Shale Oil Hydrotreating Process, which is designed for upgrading full range shale oil to premium quality synthetic crude, is presented. The process consists of two sections: (1) a low severity pretreating section which stabilizes the raw oil, removes iron, arsenic, trace metals and particulates, and sulfur; and (2) a two-stage, high severity hydrotreating section which completes the upgrading. The second section hydrotreats the bulk oil to a specified nitrogen content, allowing for a quality FCC feedstock in the 650F+ (343C+) residue. The main reactor effluent is flashed with subsequent hydrotreating of the flash vapor oil to achieve a low nitrogen level in the naphtha and middle distillate. The benefit of this flash configuration is hydrogen addition selectivity which maximizes syncrude quality while minimizing overall hydrogen consumption; this selectivity relationship is detailed. Finally, the product quality of the syncrudes produced with the Gulf Shale Oil Hydrotreating Process using shale oils derived from three different retort technologies and for Western and Eastern shales are discussed.

INTRODUCTION

It is well recognized that the refining of synthetics presents more difficult problems than do most petroleum based crudes. The properties of raw shale oil, as produced by current retorting technology, preclude its use without some form of upgrading or conversion to a syncrude. Because of its composition, it is inherently unstable and subject to condensation and polymerization reactions in storage.

Raw shale oil's exceptionally high nitrogen content, which is at least an order of magnitude greater than that of the worst crude, is an effective catalyst poison. Introduction of raw shale oil into a refinery's primary crude tower would result in corrosion and plugging with the dissemination of arsenic compounds into all process streams -- compounding environmental problems. Each stream would require an upgrading unit. Ammonia recovery systems would be required; and in some cases, additional sulfur recovery capacity might be needed.

The numerous problems associated with raw shale oil are solvable, but they need to be isolated at a dedicated syncrude production facility, either at the retort site or a refinery.

The Gulf Shale Oil Hydrotreating Process evolved to its present configuration over a number of years of research and development. GR&DC's initial concept was to mildly stabilize the raw oil, while attempting to remove arsenic, using off-the-shelf hydrotreating technology and following this by severe hydrotreating of the full range shale oil.

It became apparent that the pretreating problem and the hydrotreating problem had to be attacked separately, since a stable, dearsenated shale oil was required to give acceptable cycle length and operability for hydrotreating. Successful pretreating had to achieve several major objectives which included arsenic removal, iron removal, and oil stabilization. Experience showed that shale oil's instability would also be a major concern because frequent shutdowns were often required to alleviate pressure drop in the first reactor. This was caused by particulates formed during preheating the oil

and other "undesirables" present in the oil itself. GR&DC's conclusion was that the pretreating catalysts would have to be low cost and the operation would have to allow resolution of pressure drop buildup without affecting the hydrotreatment step.

Hydrotreating the shale oil to produce an acceptable refinery feedstock was an early goal. Work done to hydrotreat full range shale oil showed that much hydrogen would be consumed and the naphtha fraction would require further denitrogenation. The finished syncrude in this operation contained a marginal quality light end and an over treated heavy end. It was concluded that a successful hydrotreating process would better select where the hydrogen was added to the shale oil and would do this with minimum additional equipment.

The following describes the Gulf Shale Oil Hydrotreating Process which successfully upgrades raw shale oil to a high quality syncrude.

PROCESS OVERVIEW

The Gulf Shale Oil Hydrotreating Process (shown in Figure 1) is a two stage process to produce a high quality synthetic crude from a deashed raw shale oil. The process consists of a pretreatment stage and a hydrotreating stage which are discussed below.

Pretreating

The pretreating section is designed to remove iron, arsenic, trace metals, and residual solids as well as to stabilize the oil before it enters the hydrotreating section. This section is designed to operate at relatively low hydrogen partial pressure, at moderately high liquid hourly space velocity and temperature. Operation at these conditions, particularly the low pressure, allows for adequate stabilization and contaminant removal without the need for excessive hydrogen consumption.

The pretreating is done in a two reactor series where the first reactor is designed to

remove the majority of the arsenic, iron, and trace solids with a minimum of hydrogen consumption. Because of its position in the reactor sequence, the first reactor will have, relative to the overall upgrading process, a short cycle life with the potential for pressure drop problems to occur. To avoid frequent shutdowns due to contaminant breakthrough or pressure drop buildup, this first reactor is designed to swing to a duplicate reactor so that it can be recharged with catalyst without interrupting the overall operations. The catalyst used in this first reactor is an inexpensive catalyst.

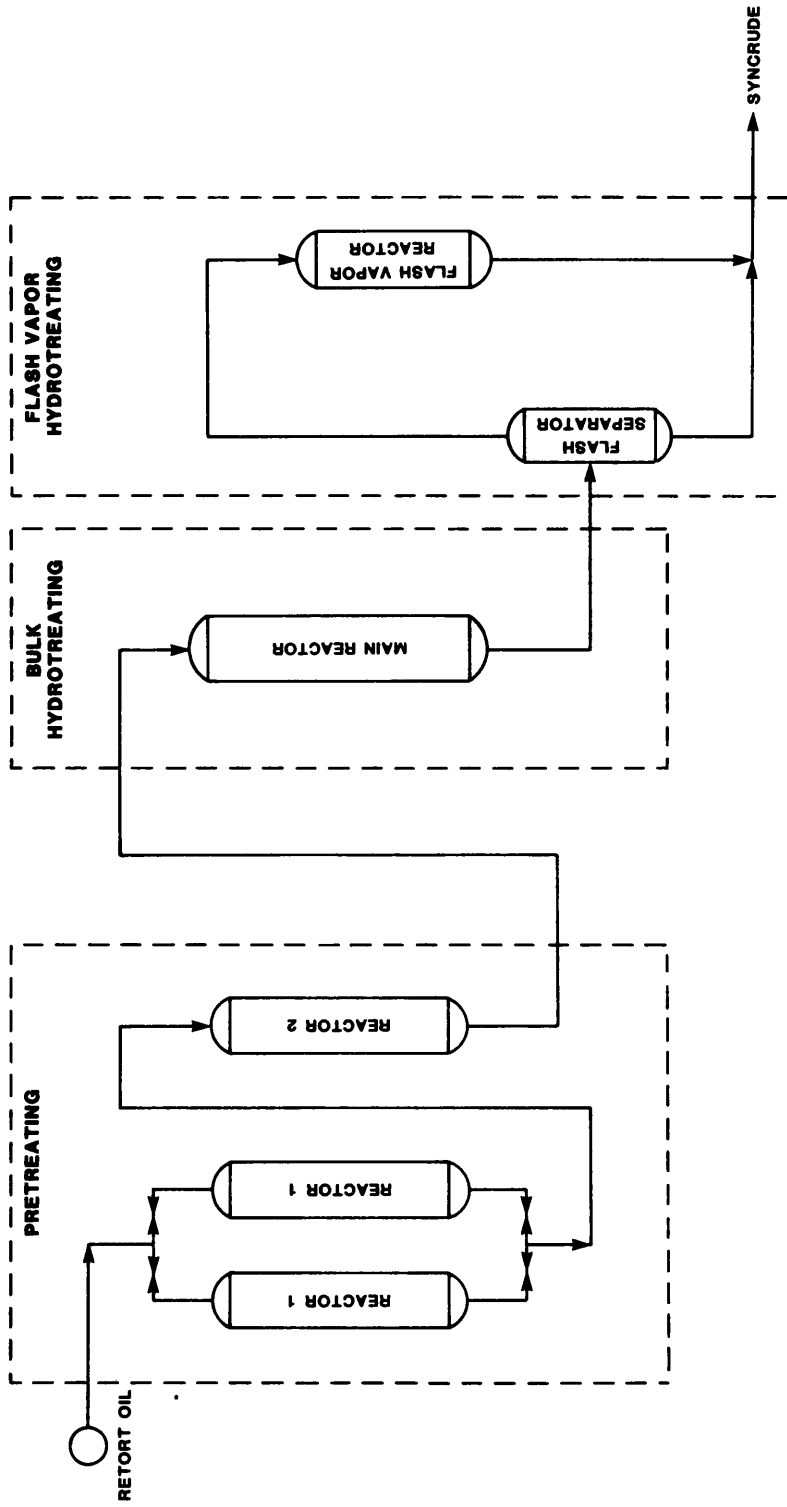
The second reactor in the pretreating series contains catalyst which is intended to stabilize the shale oil as well as remove a substantial portion of the sulfur before the oil enters the main hydrotreater. The cycle life of this reactor will be considerably longer than the first reactor, primarily because the oil entering this reactor has had a majority of the contaminant metals and solids removed by the first reactor. The catalyst used in this reactor contains a hydrogenation component intended to begin the high degree of saturation that is required by the chemistry of nitrogen removal. Hydrogen consumption amounting to about 25% of the process total is expected in the pretreating section.

Stabilization of the shale oil in the pretreating section is necessary to insure proper operation in the main hydrotreater and to allow storage of the pretreated oil in the event of a shutdown of the main hydrotreater.

Hydrotreating

The hydrotreating section is broken down into a main hydrotreater which removes a moderate amount of nitrogen from the whole, pretreated oil, and a flash vapor hydrotreater for improved denitrogenation of the naphtha and distillate fractions. This design allows for production of a very high quality synthetic crude at a minimum overall hydrogen consumption.

FIGURE 1
GULF SHALE OIL HYDROTREATING PROCESS



The main hydrotreater contains a highly active catalyst intended primarily for removal of nitrogen. The severity of the main hydrotreater can be varied to produce a synthetic crude with the desired properties. Typically, a synthetic crude with a specification of 500 wppm total nitrogen content will be produced. This requires an operating severity in the main hydrotreater to produce an effluent of about 750 wppm nitrogen. The hydrogen consumed in the main hydrotreater is about two-thirds of the process total.

The effluent from the main hydrotreater enters a flash vapor separator and the vapors from the separator enter another hydrotreating reactor. The purpose of this smaller reactor is to remove the nitrogen from the naphtha and distillate fractions to a low enough level to be compatible in most existing refineries. The catalyst used in this section may be the same catalyst used in the main hydrotreater. This reactor accounts for about 15% of the total hydrogen consumed to produce the synthetic crude. The flash vapor reactor effluent is then combined with the flash separator bottoms to produce the high quality synthetic crude.

Note that the synthetic crude contains a very low nitrogen content front end and a moderately high nitrogen content residual fraction. The Gulf Shale Oil Hydrotreating Process allows flexibility to achieve varying synthetic crude quality while maintaining a high quality naphtha and middle distillate fraction. The process selectively adds hydrogen to the front end which requires a low nitrogen content to be compatible with current refining technology. A higher nitrogen content in the residual fraction can be tolerated, particularly if the residual (650°F+, 343C) fraction is charged to an FCC unit. In that case, a nitrogen content of 1000 wppm or greater can be easily managed.

Proper specification of the synthetic crude quality to meet specific needs can result in optimized hydrogen consumption without undue penalty to the end user.

BENEFITS OF FLASH VAPOR CONCEPT

The two stage hydrogenation approach taken in the Gulf process provides significant flexibility in apportioning the total hydrogen input among the various fractions of the whole shale oil. For example, naphthas and middle distillates with nitrogen contents below 10 ppm can be produced without overtreatment of the gas oil fraction, which makes an excellent FCC chargestock with nitrogen contents of 1000 ppm or higher. The two stage strategy allows minimization of total hydrogen consumption for any desired combination of heavy oil and light oil quality.

Because reformer chargestock requirements and jet fuel specifications generally fix the nitrogen level of the flash vapor hydrotreater product at very low levels, it is the nitrogen content of the flash bottoms which sets other reactor sizes, unit yields, and hydrogen consumptions. The severity of operation of the bulk hydrotreater is, therefore, the most significant independent process variable. A series of pilot scale trials have been performed at GR&DC to simulate the operation of the Gulf process at several different bulk hydrotreater severities. The chargestock used in these studies was a full range, deashed Paraho retort product. Figures 2 through 5 demonstrate how reactor sizes, yields, nitrogen contents and hydrogen consumptions vary with bulk hydrotreater severity. In each case the measure of bulk hydrotreater severity is taken to be the nitrogen content of its total liquid product (TLP).

The relative sizes of the bulk and flash vapor hydrotreater reactors as functions of bulk hydrotreater severity are presented in Figure 2. For this analysis, the average temperature is held constant in each of the two hydrogenation reactors. In the flash vapor hydrotreater, the space velocity is adjusted so that its effluent contains 10 ppm nitrogen. Of course, as the severity of its operation increases, the bulk hydrotreater becomes

larger. At the same time, despite its increasing throughput, the size of the flash vapor reactor decreases. This reflects the fact that the quality of the flash vapor feed improves with increasing bulk hydrotreater severity. Figure 3 shows how the relative amounts of the two major components of the syncrude, the hydrotreated flash overheads and the flash bottoms change with bulk hydrotreater severity. At high severities, the lighter product dominates because of the boiling range shift which occurs in the bulk reactor.

In Figure 4 the variation of the nitrogen contents of the flash overheads, flash bottoms, and syncrude with bulk reactor severity is given. As expected, each decreases with increasing severity. As noted earlier, a target on flash bottoms quality will generally set the severity of the bulk hydrotreater operation, which, in turn, fixes the other nitrogen levels.

The relative hydrogen consumption in each of the two reactors is presented in Figure 5. As bulk hydrotreater severity increases, the contribution of the flash vapor hydrotreater to total hydrogen consumption diminishes because of the declining nitrogen content of its feed. Figure 6 is a plot of total hydrogen consumption as a function of syncrude nitrogen content. Note that the incremental hydrogen consumption required to reduce the syncrude nitrogen level from 1900 ppm to 385 ppm is only 325 SCFB ($58 \text{ m}^3/\text{m}^3$).

Micro Activity Tests (MATs) have been used to provide an estimate of the performance of the flash bottoms as an FCC chargestock. The cracking catalyst employed for these trials was a conventional, equilibrium gas oil catalyst. Figure 7 describes the variation of MAT conversion with the nitrogen content of the flash bottoms. As the figure shows, conversion falls off rapidly with nitrogen level. However, depending upon the needs of a particular refiner, any of the materials in this nitrogen range may make a suitable component of FCC feed. More important is the fact that the

incremental hydrogen consumption required to make a substantial improvement in the quality of the flash bottoms as an FCC charge is quite moderate; an incremental 325 SCFB ($58 \text{ m}^3/\text{m}^3$) raises MAT activity from 59.5 to 83.0.

In summary, the two stage hydrogenation approach taken in the Gulf Process provides the flexibility to set independent quality targets on the heavy and light portions of the syncrude, thereby minimizing total hydrogen consumption. Therefore, significant syncrude quality improvements can be made with modest incremental hydrogen inputs. Finally, it has been shown that process operating parameters and yields can be easily related to the quality targets.

SYNCRUDE QUALITY

The Gulf Shale Oil Hydrotreating Process is designed to produce a high quality syncrude that can be universally used in existing refineries. Inspections of the raw feed and the full range syncrudes produced from upgrading Western shale oils from the Paraho and Union B retorts are given in Tables I and II. Similarly, a highly aromatic eastern shale oil and resultant syncrude produced from the Dravo retort process are given in Table III. These full range syncrudes have total nitrogen contents ranging from 385 wppm to 570 wppm yet are very good quality crudes, even when compared to a South Louisiana Crude. The syncrudes have all of the measurable arsenic, iron and ash removed.

The fractions from distillation of these syncrudes are shown in Table IV. The naphtha fraction (OP-375F, OP-191C) contains less than 4 ppm nitrogen in all cases and should be easily processed in an existing refinery's naphtha pretreater and reformer. Predicted C_5+ reformat yields are given in Table V and range from about 75 volume % for the Union B syncrude to over 85 volume % for the Dravo syncrude when an 85 MON clear gasoline is produced.

The light distillate or kerosene fraction (375F-520F, 191C-271C) derived from Western

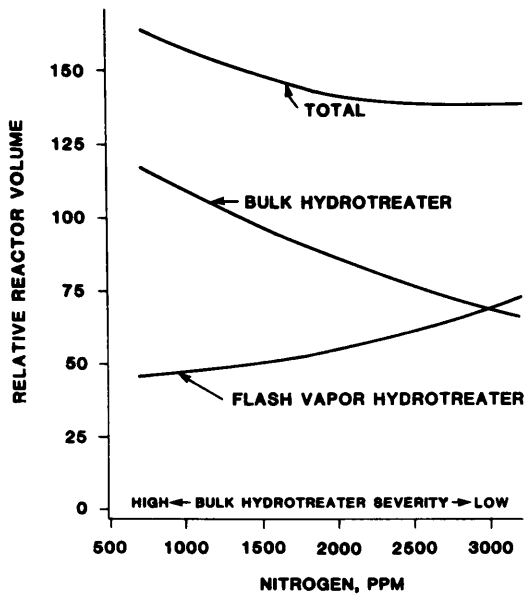


FIGURE 2
RELATIVE REACTOR VOLUMES AS FUNCTIONS OF BULK HYDROTREATER TLP NITROGEN CONTENT.

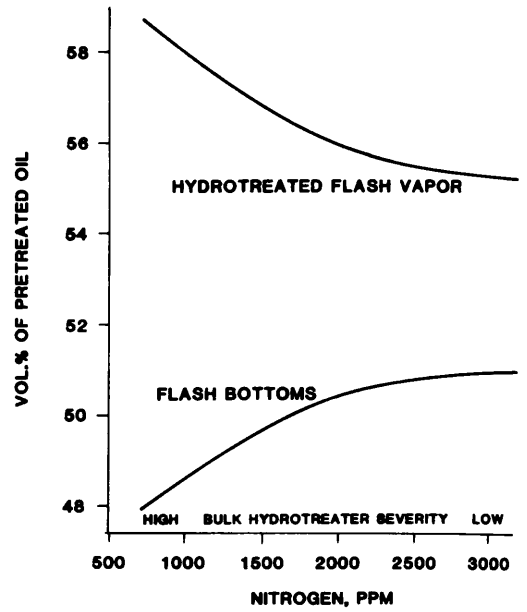


FIGURE 3
RELATIVE VOLUMES OF PRODUCT FRACTIONS AS FUNCTIONS OF BULK HYDROTREATER TLP NITROGEN CONTENT.

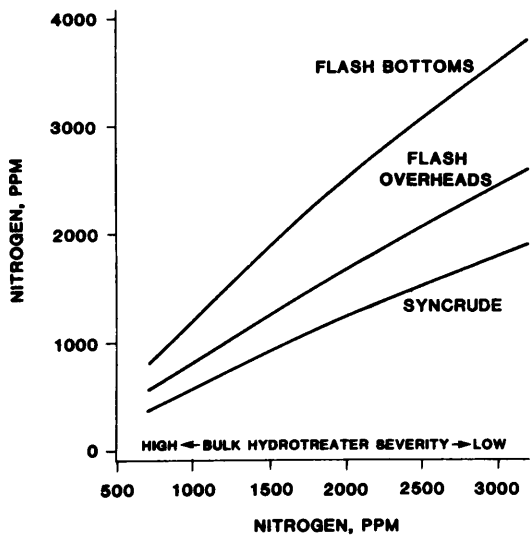


FIGURE 4
NITROGEN CONTENTS OF PRODUCT FRACTIONS AS FUNCTIONS OF BULK HYDROTREATER TLP NITROGEN CONTENT.

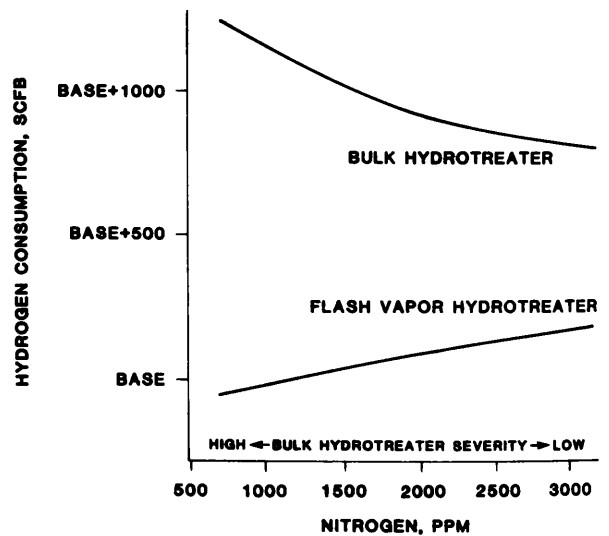


FIGURE 5
HYDROGEN CONSUMPTIONS AS FUNCTIONS OF BULK HYDROTREATER TLP NITROGEN CONTENT.

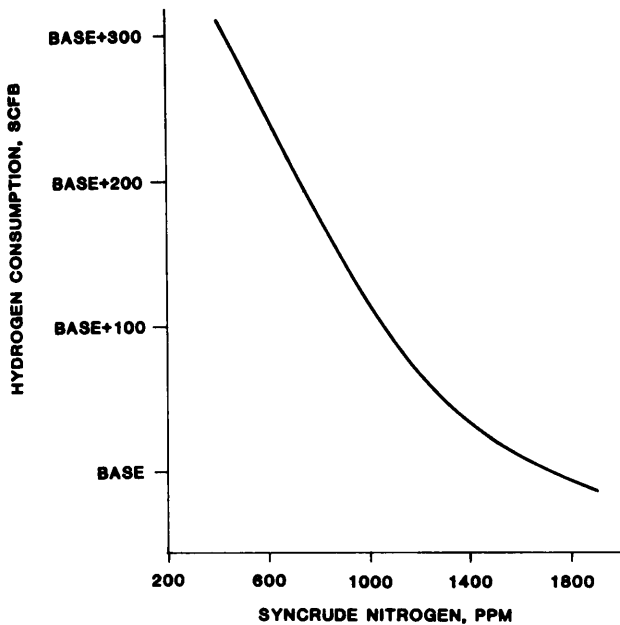


FIGURE 6
TOTAL HYDROGEN CONSUMPTION
AS A FUNCTION OF SYNCRUDE
NITROGEN CONTENT.

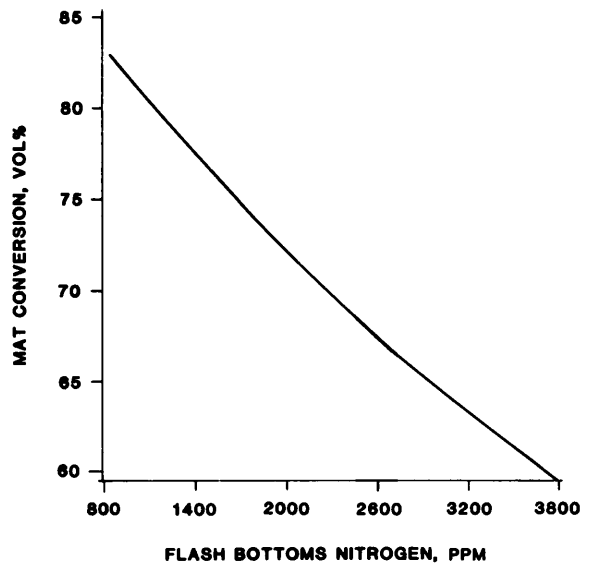


FIGURE 7
MAT CONVERSION OF FLASH BOTTOMS
AS A FUNCTION OF ITS NITROGEN
CONTENT.

shale oils meet Jet-A specifications, while the corresponding fraction from Eastern shale oil falls short due to excessive aromatic content. The high aromatic content of the Eastern shale oils would require either a more severe flash vapor hydrotreatment or a lower light distillate end point.

The heavy distillate fractions (520-650F, 271-343C) as well the full range distillate (375-650F, 191-343C) are given in Table IV. These fractions should yield high quality diesel fuels in a high volume yield. Cetane index for the Western shale oils exceed 50 while that from the Eastern shale oil is about 41.

The 650F+ (343C+) residual from these syncrudes are quality FCC feedstocks. The Union B and Dravo syncrudes were evaluated in a

MAT test and compare quite favorably to the South Louisiana crude. The Paraho ATB was processed in an FCC pilot unit, again with good results. The results of the MAT and FCC tests are given in Table VI.

The preceding discussion assumed that the syncrude from the Gulf Shale Oil Hydrotreating Process would be the exclusive feedstock to an existing refinery. This scenario is not likely to be the case and the syncrude would most likely be co-mingled with petroleum crudes. In this scenario, the syncrude could be tailored to give an overall good crude mix while reducing operating costs and hydrogen consumption by utilizing the flexibility of the Gulf Shale Oil Hydrotreating Process.

TABLE II
WESTERN OIL SHALE
UNION B RETORT OIL

	FEED	PRODUCT
GRAVITY, D287: API	22.0	36.5
CARBON: WT%	85.30	86.37
HYDROGEN: WT%	11.36	13.53
NITROGEN: WT% (WPPM)	2.05	(570)
SULFUR: WT% (WPPM)	0.77	(100)
OXYGEN: WT% (WPPM)	1.20	(393)
ARSENIC: WPPM	35	<1
IRON: WPPM	26	<1
ASH: WPPM	30	<1
HYDROCARBON TYPE		
SATURATES	22.6	-
AROMATICS	38.4	-
POLAR COMPOUNDS	32.9	-
INSOLUBLES	0.7	-
VOLATILES	5.4	-
DISTILLATION, D1160: °F		
5%	428	328
10%	484	384
20%	578	463
30%	655	527
40%	723	575
50%	779	625
60%	831	691
70%	884	756
80%	939	813
90%	1007	857
95%	1022	962

TABLE I
WESTERN OIL SHALE
PARAHO RETORT OIL

	FEED	PRODUCT
GRAVITY, D287: API	19.3	35.5
CARBON: WT%	84.63	86.51
HYDROGEN: WT%	11.26	13.62
NITROGEN: WT% (WPPM)	2.14	(385)
SULFUR: WT% (WPPM)	0.64	(47)
OXYGEN: WT% (WPPM)	1.16	(397)
ARSENIC: WPPM	18	<0.1
IRON: WPPM	22	<1
ASH: WPPM	85	<1
HYDROCARBON TYPE: WT%		
SATURATES	24.8	63.1
AROMATICS	34.9	16.2
POLAR COMPOUNDS	36.3	0.8
INSOLUBLES	0.9	0.0
VOLATILES	3.1	19.9
DISTILLATION, D1160: °F		
5%	432	400
10%	503	430
20%	581	495
30%	649	550
40%	710	605
50%	767	655
60%	820	725
70%	865	780
80%	917	850
90%	983	910
95%	-	950

TABLE III

EASTERN OIL SHALE
DRAVO RETORT OIL

TABLE IV
GULF PROCESSING SYNCRUDE ANALYSIS

PARAHO SYNCRUDE UNION SYNCRUDE DRAVO SYNCRUDE SOUTH LA. CRUDE

	FEED	PRODUCT	OP-375F NAPHTHA	PARAHO SYNCRUDE	UNION SYNCRUDE	DRAVO SYNCRUDE	SOUTH LA. CRUDE
GRAVITY, D287: API	12.0	28.8		52.0	54.6	48.3	54.2
CARBON: WT%	83.19	87.46	NAPHTHA (0-375F) INSPECTIONS:				
HYDROGEN: WT%	9.84	12.45	GRAVITY: API	0.7	2.0	4.0	1.0
NITROGEN: WT% (WPPM)	1.14	(480)	NITROGEN: WPPM				
SULFUR: WT% (WPPM)	3.86	(110)	HC TYPES: VOL%				
OXYGEN: WT% (WPPM)	1.97	(350)	SATURATES	88.6	92.0	81.5	88.3
ARSENIC: WPPM	100	<1.0	OLEFINS	0.0	-0.0	0.5	0.5
IRON: WPPM	110	<1.0	AROMATICS	13.4	18.0	18.0	11.2
ASH: WPPM	920	-	N+2A	61.9	51.1	84.6	64.4
HYDROCARBON TYPE			YIELD ON CRUDE: VOL%	6.6	12.8	10.0	26.7
SATURATES	11.4	47.0	375-520 F LIGHT DISTILLATE				
AROMATICS	54.7	53.0	GRAVITY, API	40.9	41.8	36.2	43.3
POLAR COMPOUNDS	14.6	-	NITROGEN, WT% (WPPM)	(0.7)	(29)	(7.8)	(0.4)
INSOLUBLES	3.2	-	AROMATICS, WT%	16.5	14.6	33.2	19.0
VOLATILES	16.1	-	POUR POINT, F	-56	0.0	-60	-40
DISTILLATION, D1160: °F			VISCOSITY, SUV @ 100F (CST)	31.9	32.3	32.3	(1.7)
5%	439	388	YIELD OF CRUDE VOL %	23.5	20.6	27.5	11.9
10%	477	435	375-650F FULL RANGE DISTILLATE				
20%	537	486	GRAVITY, API	38.8	38.6	31.3	37.8
30%	598	523	NITROGEN, WPPM	1.1	86	42	40
40%	660	561	AROMATICS, WT%	-	18.9	36.1	26.5
50%	714	599	POUR POINT, F	-15	0	-40	-5
60%	773	648	VISCOSITY, SUV @ 100F (CST)	34.8	36.9	36.5	36.8
70%	836	697	CETANE INDEX	51.3	52.5	41.3	52
80%	909	739	YIELD OF CRUDE VOL %	-	40.3	56.0	25.9
90%	981	799	520-650F HEAVY DISTILLATE				
95%	-	904	GRAVITY, API	36.2	35.8	27.7	33.4
			NITROGEN, WPPM	1.5	163	75	70
			AROMATICS, WT%	-	23.2	36.8	33.5
			POUR POINT, F	+15	+20	0	+20
			VISCOSITY, SUV @ 100F (CST)	44.3	42.8	46.4	42.4
			CETANE INDEX	53.7	54.5	41.8	51
			YIELD OF CRUDE VOL %	19.2	19.7	28.5	14.0
			650+F RESID				
			ATB (650+F) INSPECTIONS:				
			GRAVITY: API	29.0	30.0	20.1	23.9
			SULFUR: WT% (WPPM)	<0.04	(126)	(180)	0.66
			NITROGEN: WT% (WPPM)	(700)	(1100)	(800)	(2000)
			ANILINE POINT: F	210	213.8	164	195
			METALS: WPPM	<1	<1	<1	7.5
			AROMATICS	25.0	22.9	57.4	36.1
			YIELD ON CRUDE: VOL%	41.3	46.9	34.1	47.4

TABLE V
GULF PROCESSING SYNCRUDE ANALYSIS

NAPHTHA REFORMING
(85.3 MON SEVERITY)

<u>PRODUCT YIELDS; WT%</u>	<u>UNION SYNCRUDE</u>	<u>DRAVO SYNCRUDE</u>	<u>SOUTH LA. CRUDE</u>
HYDROGEN, (SCFB)	1.5 (750)	1.81 (939)	1.81 (910)
METHANE	2.0	1.09	1.57
PROPANE	6.0	2.69	4.04
I-BUTANE	3.3	0.90	1.96
N-BUTANE	4.3	1.81	2.73
I-PENTANE	4.1	1.34	2.64
N-PENTANE	3.0	0.67	1.82
C ₅ + REFORMATE (VOL%)	79.3 (74.8)	89.9 (85.5)	85.3 (80.6)
HYDROGEN PURITY	72.3	86.3	81.2

TABLE VI
GULF PROCESSING SYNCRUDE ANALYSIS

FCC CONVERSION & PRODUCT YIELDS

	<u>PARAHO SYNCRUDE</u>	<u>UNION SYNCRUDE</u>	<u>DRAVO SYNCRUDE</u>	<u>SOUTH LA. CRUDE</u>
CONVERSION: VOL%	83.5*	76.9 (78.0)	72.8	76.6
SUMMARIZED PRODUCT YIELD				
TOTAL C ₃ : VOL%	13.1*	8.7	11.92	10.11
TOTAL C ₄ : VOL%	21.8*	16.9	14.66	14.16
C ₅ -430F GASOLINE: VOL%	61.8*	62.9	64.67	69.41
LIGHT CAT GAS OIL: VOL	8.4*	12.1	17.27	16.49
DECANTED OIL: VOL%	8.1*	11.0	9.93	6.92
COKE: WT%	6.6*	2.7	5.45	7.04
GASOLINE: RON CLEAR	89.3*	92.0	92.0	91.0

*DATA FROM ACTUAL FCC PILOT PLANT RUN.