UNOCAL CORPORATION'S COMMERCIAL EXPERIENCE IN UPGRADING SHALE OIL TO PRODUCE A HIGH QUALITY SYNCRUDE

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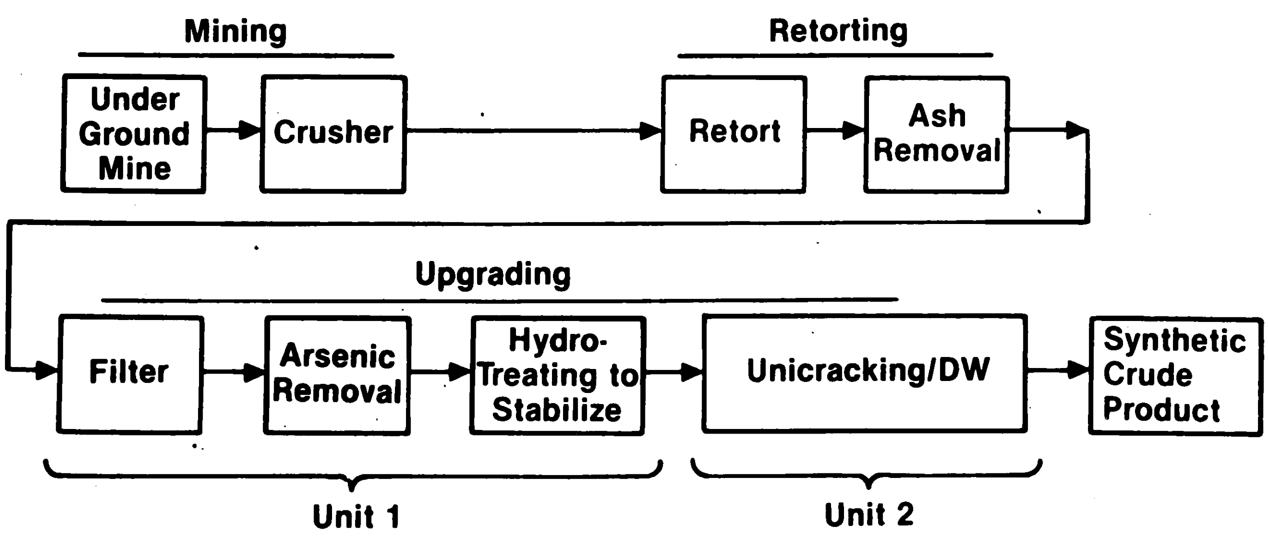
ABSTRACT

Unocal Corporation operates a commercial oil shale facility in the U.S. A. The facility is designed to produce 66 m^3/h of premium syncrude. Syncrude produced from this facility is processed in Unocal's conventional petroleum refineries. Syncrude is a higher quality refinery feedstock than the best Middle East crudes. Jet and diesel fuels distilled from syncrude are superior. Performance of Unocal's commercial Upgrading Plant that converts raw shale oil to syncrude has been excellent. Properties of raw shale oil, syncrude, jet fuel and diesel fuel are presented.

GENERAL FACILITIES

Unocal has been operating a commercial oil shale facility since 1983. The complex is located near Parachute, Colorado, U.S.A. and is designed to produce 66 m^3/h of synthetic crude oil. Mining, retorting and upgrading are conducted at this integrated facility. An overall block flow diagram is shown in Figure 1.

Figure 1
Unocal's Commercial Oil Shale Facilities



The mine is an underground, room-and-pillar operation. Oil shale rock is transported by diesel-powered trucks from the mine face to underground crushers. After being crushed to a maximum particle size of 50 mm, it is moved to the surface by belt conveyors and screened to remove fines of less than 3 mm.

Unocal's retort is located just outside the mine entrance. Design capacity is 11,600 metric tonnes of oil shale per day. Shale is pumped upward through the retort. As the shale moves upward, it is heated to retorting temperature by downward flowing recycle gas which has been heated in a furnace. Liquid and gas are withdrawn from the lower section of the retort. This retorting process was developed by Unocal. Unocal's first-generation retort was demonstrated in a large-scale, on-site retort in the late 1950's. The current, second-generation retort was developed to improve retorting economics by decreasing capital investment, increasing liquid yield and increasing the value of product gas.

In Table 1 properties of raw shale oil produced from Unocal's retort in 1987 are compared to properties of the following oil: syncrude produced from Unocal's Upgrading Plant in 1987, Arabian Light Crude and Murban Curde. Arabian Light is a premium multi-purpose crude and Murban is a high-quality source of middle distillates and catalytic reforming feedstocks.

Table 1. Properties of Raw Shale Oil, Syncrude Product, Arabian Light Crude, and Murban Crude

	Raw Shale Oil[a]	Syncrude Product[b]	Arabian Light Crude	Murban Crude
Gravity, °API	27.0	39.4	34.2	39.4
Boiling Range, °C	38/577 (98% rec.)	43/527 (99% rec.)	21/577 (87% rec.)	21/588 (95% rec.)
Nitrogen, wppm	12,400	10	500	380
Sulfur, wppm	7,300	7	17,000	8100
Oxygen, wppm	6,400	100	nil	nil
Bromine Number	34.1	0.6	nil	nil
Arsenic, wppm	23.0	<0.01	nil	nil
Carbon/Hydrogen Ratio	6.8	6.0	6.2	6.3
Pour Point, °C	24	-21	-34	-12
Viscosity, @ 38°C, mm²/s	10.8	3.7	5.6	3.3
Carbon Residue Conradson, wt % Full Range	2.5		3.1	1.5

a Feed to the Upgrading Plant in July 1987.
b Product from the Upgrading Plant in July 1987.

High nitrogen content and the presence of arsenic make raw shale oil unsuitable for processing in a conventional petroleum refinery. However, shale oil has a higher hydrogen content than oils produced from coal or tar sands. This fact makes shale oil a much more economically attractive raw material to upgrade to synthetic crude.

UPGRADING PLANT

Raw shale oil is not stored at the retort site. It is sent directly to the Upgrading Plant about eight miles away. As shown in Figure 1, the Upgrading Plant consists of the following steps: filtering, arsenic removal, stabilization and denitrogenation and pour point reduction by Unocal's Unicracking/DW process.

This paper presents recent commercial operating data from the Upgrading Plant. Properties of raw shale oil feed were those shown in Table 1. Feedrate was 66 m^3/h.

The Upgrading Plant consists of two units. The first unit contains the filtering, arsenic removal and stabilizing (hydrotreating) steps. The second unit is the Unicracking/DW process which provides the denitrogenation and hydrocracking steps.

The first unit contains five reactors: two for filtering, two for arsenic removal, and one for hydrotreating. There is no separation of gas and liquid between reactors. Therefore, there is no repumping or recompression.

The second unit has three reactors in series: two for denitrogenation and one for hydrocracking. As in the first unit, there is no separation of gas and liquid between reactors.

Filter

The purpose of the two filter reactors is to protect all other reactors from excessive pressure drop buildup. These filter reactors contain highly porous, inert alumina spheres. These spheres have the ability to trap and retain large quantities of particulate matter. These two reactors (or filter chambers) have done an excellent job of removing particulate matter from the raw shale oil feed. This is confirmed by the fact taht pressure drop in all other reactors has not increased since the plant was first commissioned.

Arsenic Removal

Arsenic poisons most refinery catalysts. Since few refineries are equipped to handle high-arsenic crudes, one of the major functions of Upgrading Plant is arsenic removal.

Effluent from the filter reactors flows directly into the first dearseniting reactor. The two reactors that comprise the arsenic removal step normally operate in series. However, the design permits either reactor to be removed from service for a catalyst change-out while the other reactor remains in service. Either reactor may be in the lead position. Both reactors contain the same catalyst. It is a catalyst/adsorbent Unocal developed especially for removing arsenic from shale oil.

Table 2 compares properties of liquid effluent from each reactor with inspections of raw shale oil from Table 1.

Table 2. Performance of Dearseniting Reactors

		Arsenic Removal Reactors	
	Raw Shale Oil	First Reactor Effluent	Second Reactor effluent
Gravity, 'API	27.0	25.8	25.5
Boiling Range, °C	38/577	49/577	93/585
Nitrogen, wt %	1.24	1.31	1.34
Sulfur, wt %	0.73	0.67	0.53
Bromine Number	34.1	29.0	24.6
Arsenic, wppm	23.0	0.7	<0.01

control of the dearseniting reactors has been simple and smooth. The overall temperature in both reactors is set to reduce the arsenic content of the effluent from the last reactor to less than 0.5 wppm. This is controlled by taking line samples of the second reactor effluent once per day. reactor temperatures are adjusted accordingly.

Performance of the dearseniting step to date had been better than predicted in the design.

Hydrotreating

The final step in the first unit is hydrotreating. The purpose of hydrotreating is to stabilize the very reactive raw shale oil. Hydrotreating does this by saturating all diolefins and about one-half the mono-olefins. This prevents fouling and plugging of the high-temperature, high-pressure equipment in the second unit.

Table 3 shows properties of raw shale oil, liquid effluent from the dearseniting reactors and liquid effluent from the hydrotreating reactor.

Table 3. Performance of Hydrotreating Reactor

	Raw Shale Oil	Effluent from Arsenic Removal Step	Effluent from Hydrotreater
Gravity, °API	27.0	25.5	25.9
Boiling Range, °C	38/577	93/585	85/585
Nitrogen, wt %	1.24	1.34	1.29
Sulfur, wt %	0.73	0.53	0.37
Bromine Number	34.1	24.6	18.5
Arsenic, wppm	23	<0.01	<0.01

This hydrotreating step has been effective in stabilizing shale oil. To date there has been no indication of heat exchanger fouling in the high pressure Unicracking/DW unit.

Unicracking/DW Unit

There are two major upgrading steps in the Unicracking/DW unit: denitrogenation and hydrocracking. Both these steps require higher pressure than the dearseniting and hydrotreating steps of the first unit. There are three reactors in the unit: two for denitrogenation and one for hydrocracking. There is no separation of gas or liquids between reactors.

Denitrogenation

Raw shale oil has a much higher nitrogen content than petroleum crude oils. Nitrogen is harmful to catalysts used in processing petroleum. Most refineries cannot handle feedstocks with high nitrogen contents. Therefore, upgrading raw shale oil to premium syncrude requires removing most of the nitrogen. This is also necessary to prevent rapid deactivation of catalyst used in the hydrocracking step.

Unocal's denitrogenation step consists of two reactors in series. Both reactors contain the asme catalyst. It is a proprietary catalyst that Unocal has used for several years for deep denitrogenation of heavy stocks.

As shown in Table 4, at full feed rate nitrogen content of raw shale oil was reduced from 12,400 to 155 wppm. This is 99% denitrogenation.

Table 4. Performance of Denitrogenation Reactors

	Raw Shale Oil	Effluent from First Unit	Effluent from last HDN Reactor
Gravity, °API	27.0	25.9	34.6
Boiling Range, °C	38/577	85/585	79/546
Nitrogen, wppm	12,400	12,900	155
Sulfur, wppm	7,300	3,700	259
Bromine Number	34.1	18.5	1.4
Pour Point, °C	24	--	27

Hydrocracking

The final step in Unocal's upgrading scheme is hydrocracking. The high pour point, 24°C, of raw shale oil creates pumping, storage and transporting problems. To reduce pour point to an acceptable level the straight-chain paraffins in raw shale oil must be cracked into smaller molecules. Unocal developed a special, selective hydrocracking catalyst to do this. Although this catalyst was developed especially for shale oil, the Unicracking/DW process has now been commercialized for other applications.

The hydrocracking step consists of one multi-bed reactor. Overall temperature in the catalyst is set to give the desired pour point of the product. During the period under review the product pour point was -21°C.

SYNCRUDE PRODUCT

The comparisons shown in Table 1 illustrate that syncrude from shale oil is a more valuable comodity than high quality Middle East crudes. Syncrude from the Upgrading Plant is being processed in Unocal's existing refineries. It is blended with the normal crude slate charged to the refineries. No special facilities are required.

Comparison of Jet Fuel Production

A sample of syncrude product from the Upgrading Plant was distilled in the laboratory to produce jet fuel. Thirty-seven volume percent of jet fuel was obtained from this distillation. The yield of jet fuel from syncrude varies with the severity of the dewaxing operation. If the -6°F pour point of snycrude were reduced by more severe dewaxing the yield of jet fuel would increase.

Table 5 compares properties of this jet fuel with U.S. Department of Defense JP-4 specification MIL-T-5624L. All specifications are exceeded.

The low sulfur content, high smoke point, and low aromatics content make jet fuel from syncrude a premium product.

Table 5. Comparison of Jet Fuel Cut with JP-4 Specifications

	Syncrude	JP-4 Specification
True Boiling Point Cut Points, °C	10-249	--
Yield, vol. %	37.0	--
wt %	24.6	--
Gravity, °API	51.7	57 maximum
Distillation, ASTM D-86		
IBP/EP, °C	53/249	-/270 maximum
Sulfur, wppm	2.0	4000 maximum
Freeze Pt., °C	<-60	-58 maximum
Smoke Point, ASTM D-1322, mm	35.2	20 minimum
Aromatics, FIA, vol %	6.0	25 miximum

Comparison of Diesel Fuel Production

A sample of syncrude product from the Upgrading Plant was distilled in the laboratory to produce diesel fuel. Yield of diesel fuel was 60.6 volume per cent of syncrude.

Properties of this diesel fuel are shown in Table 6 along with comparisons to diesel cuts from Arabian Light and Murban crudes. The diesel fuel cut from syncrude has lower sulfur content, lower pour point, higher cloud point, and, based on aniline points, a lower aromatic content than diesel cuts from either Middle Eastern crude. It has a high cetane index similar to the cuts from Middle Eastern crudes. These data show that diesel from shale oil syncrude is a high quality fuel.

Table 6. Comparison of Diesel Fuel Cuts from Syncrude, Arabian Light Crude and Murban Crude

	Snycrude	Arabian Light	Murban
True Boiling Point cut Points, °C	132-371	160-343	160-343
Yield, vol. %	60.6	33.3	38.5
wt %	60.3	32.2	38.0
Gravity, °API	40.6	40.6	41.5
Sulfur, wppm	1.4	6100	2610
Pour Point, °C	-42	-29	-32
Cloud Point, °C	-20	-23	-27
Viscosity @ 38°C, mm^2/s	2.5	2.0	2.0
Aniline Point, °C	74	66	67
Cetane Index	56	56	58

Comparison of Naphtha Cut Preceding Diesel Fuel Cut

Properties of the naphtha cut distilled ahead of the previously described diesel fuel cut are shown in Table 7 along with comparisons to naphtha cuts from Arabian Light and Murban crudes. The naphthene plus aromatic content is 39.3 volume percent compared to 16.8 and 23.7 for naphthas from Arabian Light and Murban crudes. This indicates that syncrude naphthas is an excellent reforming feedstock.

Table 7. Comparison of Naphtha Cuts from Syncrude Arabian Light Crude, and Murban Crude

	Syncrude	Arabian Light	Murban
True Boiling Point Cut Points, °C	10-132	20-150	20-150
Yield, Vol %	9.9	19.2	22.2
Wt %	8.7	16.0	19.2
Gravity, °API	64.8	69.2	66.5
Distillation, ASTM D-86 IBP/EP,°C	44/153	53/148	52/152
Sulfur, wppm	1.6	270	170
Nitrogen, wppm	<1.0	-	-
Hydrocarbon Types, vol %			
Paraffins	60.7	83.2	76.3
Naphthenes	33.2	10.0	13.5
Aromatics	6.1	6.8	10.2

Comparison of Vacuum Gas Oil Cut Following Diesel Fuel Cut

The properties of the vacuum gas oil remaining after removal of the diesel fuel cut are shown in Table 8 along with comparisons to vacuum gas oil cuts from Arabian Light and Murban crudes. The high hydrogen content of syncrude vacuum gas oil makes it an attractive feed-stock to convert to gasoline or middle distillate fuels. Its low sulfur content and low nitrogen content make it an excellent source of lube oil and waxes.

Table 8. Comparison of Vacuum Gas Oil Cuts from Syncrude,Arabian Light Crude, and Murban Crude

		Syncrude	Arabian Light	Murban
True Boiling Point Cut Points, °C		371 +	343 +	343 +
Yield, Vol %		28.6	43.5	35.5
Wt %		30.4	48.7	39.4
Gravity, °API		29.6	17.0	22.8
Sulfur, wppm		2.3	27500	16500
Nitrogen, wppm		35	1600	
Pour Point, °C		30	10	29
Viscosity, mm^2/s	@ 38°C	46.1	350.0	112.0
	@ 99°C	6.5	18.8	9.6

CONCLUSIONS

Unocal's commercial Shale Oil Upgrading Plant has been in operation over three years. There have been no major operating or design problems. Performance of all steps in the upgrading process has been excellent.

Syncrude is a premium quality refinery feedstock. With conventional petroleum refinery processes, essentially 100% of this syncrude is converted to transportation fuels. The quality of the fuels equals or exceeds those made from high quality petroleum crudes.