

## The Chemistry of Shale Oil and Its Refined Products

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"Oil Shale" is a term used to cover a wide range of materials which are found in many parts of the United States. The Green River oil shales are particularly high grade and are the only U.S. deposits having adequate size and availability for potential commercial value with present technology. The Green River formation contains the equivalent of 1.8 trillion barrels of shale oil. Assuming that only 600 billion barrels or one third of this oil is ultimately recoverable, this would still be 20 times the U.S. proved crude oil reserves.

The Green River oil shale is a marlstone (calcareous mudstone) that was formed in shallow lakes about 45 million years ago (1). The climate at this time probably varied from subtropical to arid. During wet periods these lakes may have been as large as 75 to 100 miles in diameter.

Sediment, mineral salts, minor plant debris and wind-transported pollen were carried into the lakes by small local streams, but the majority of the organic material that is in the oil shale came from colonies of algae that thrived in the lakes.

The organic matter found in the Green River shales formed in the deeper, central part of the lake. Rocks formed under these conditions are characterized by thin, alternating layers of carbonate and organic matter. The layers vary in thickness from 0.01 to 10 millimeters.

The layers are believed to have been formed by the precipitation of calcium carbonate in early summer, when the surface water temperature rises, followed by the seasonal high productivity of algae which occurs in late summer. The heavy carbonate minerals were deposited quickly; the organic matter settled more slowly-- which gave an alternation of light and dark laminations.

The typical composition of Green River oil shale is shown in Table 1. The organic portion of the Green River oil shale is composed of around 0-5% bitumen, extractable organics, and 95-100% kerogen, unextractable organics. The kerogen is an organic matrix of high molecular weight, containing on the average several saturated rings with hydrocarbon chains having an occasional isolated carbon-carbon double bond and also containing, in addition to small amounts of nitrogen and sulfur, approximately 6% oxygen. There is also the possibility that considerable amounts of non-crosslinked, long-chain compounds are trapped in the matrix.

If the nitrogen and sulfur are formally replaced by oxygen, for example by hydrolysis, then a simple formula weight is  $C_{20}H_{32}O_2$ , and the weight ratio of C/H is 7.5. This is about what would be expected for algae derived organics, since algae produce fatty acids in the  $C_{18}$  range as well as other hydrocarbons such as carotenoids at  $C_{40}$ . It has been shown that the extractable hydrocarbons from oil shale have a bimodal distribution at  $C_{17}$  and  $C_{29}$  supporting this contention (2). Strong evidence for the biogenesis of kerogen was shown when it was found that the ratio of odd to even number of carbon atoms in the extracted hydrocarbons was as high as four to one. A ratio of one to one would be expected from a nonbiological source. The higher proportion of the odd number hydrocarbons would be anticipated if their source was the decarboxylation of algal fatty acids, since these acids are predominantly even number acids.

An interesting question is: how did these predominantly algal acids become crosslinked to form kerogen? It can be seen from the kerogen formula that there are on the average four units of unsaturation, while it is known that under some conditions algae form fatty acids that are 95% unsaturated, and with some acids, such as arachidonic, an essential fatty acid, there are four olefinic linkages. It has also been shown that these polyunsaturated algal acids, under mild heating,

become crosslinked. It is clear that the unsaturated acids on diagenesis in the oil shale react to form naphthenes, the cyclic compounds found in kerogen. One reaction of this type is the Diels-Alder reaction which can occur at mild temperatures (3).

One big advantage of shale oil as compared to coal is the more favorable atomic composition of kerogen noted in Table 2. The hydrogen content of kerogen is almost twice that of many coals, and the oxygen content is lower. The sulfur content of kerogen is similar to that of coal. The nitrogen is higher in kerogen. Consequently, less hydrogen is required to remove the unwanted oxygen, nitrogen and sulfur, and less hydrogen is needed to bring the carbon/hydrogen ratio down to values required in liquid fuels such as gasoline, turbine and diesel fuels or heating oils.

Because of the impervious nature of the oil shale and the chemical nature of the kerogen, it is necessary to heat the shale to around 250°C (900°F) to thermally break up the kerogen. Under these conditions, kerogen decomposes to give oil (65-70%), gas (10-15%), coke (15-20%) and water (2-7%).

Also, during the retorting operation, there is significant loss of oxygen. About two-thirds is lost as carbon dioxide and about one-third as water. Because of the loss of carbon dioxide, the C/H ratio has beneficially decreased from 7.8 in kerogen to 7.3 in shale oil.

Some insight into the utility of shale oil can be gained by comparing its composition with coal-derived liquids and petroleum crude oil. See Table 3. Two representative liquid products from coal are shown: COED product, produced by carbonization or coking, which, like retorting of shale, is a thermal step (4), and a liquid from the H-Coal process by coal hydrogenation (5). Arabian Light crude oil is also shown.

Of the two thermally produced liquids, shale oil has a better (lower) carbon-to-hydrogen ratio, and a lower specific gravity which indicates the absence of high boiling aromatic tars. Both have high pour points; shale oil because of paraffins, COED liquid because of heavy polyaromatics. The liquid yields per ton of raw material mined are in the same order of magnitude. The solid residue of shale retorting is largely mineral matter, while the solid residue from coal carbonization, called a char, is a usable fuel containing more energy than the oil fraction. Conversion of the COED liquid product to transportation fuels, however, is a more difficult task because of its high tar, lower hydrogen and higher hetero atom contents.

The hydrogenated product from coal, H-Coal liquid, is more aromatic than shale oil but somewhat comparable in hetero atom content even though a considerable amount of hydrogen has already been added to the product.

Arabian Light crude is a wider boiling material than crude shale oil and is lower in all hetero atoms except sulfur. It has a more favorable carbon/hydrogen ratio because it contains fewer aromatics and no olefins.

In the upgrading of crude shale oil, solids removal is first achieved by optimal centrifuging, settling and filtering. Next, arsenic removal is achieved with a catalyst-absorbent.

In the third step, the hydrotreating step, the sulfur, nitrogen, and oxygen containing compounds are hydrogenated over metallic sulfide catalysts to hydrogen sulfide, ammonia, water and hydrocarbons. Olefins present in the raw shale oil are also hydrogenated.

The hydrotreated shale oil (or syncrude) now, save for pour point, resembles crude oil more closely. The amount of hydrogen consumed is listed in Table 4 either as the volume of hydrogen per barrel of product or the number of hydrogen atoms absorbed per hetero atom, that is, nitrogen plus sulfur plus oxygen atoms. The ratio of 10.8 exceeds the theoretical hydrogen consumption because double bonds are saturated and hetero as well as other compounds are hydrocracked.

The specific gravity and composition of hydrotreated shale oil are compared to a syncrude from coal. Note that we have converted crude shale oil to syncrude with much less hydrogen than would be required for a similar product from coal: 1,350 SCF per barrel compared with 6,000 SCF per barrel or more, and made a higher quality product, as indicated by the composition and carbon/hydrogen ratio.

The high pour points, and also high viscosities of the raw shale oil and of the hydrotreated shale oil, are a cause for concern. It appears that both the raw shale oil with its high nitrogen content, its high pour point and high viscosity and the hydrotreated shale oil with its high pour point may not be suitable for undedicated (to such oils) pipelines. In the absence of dedicated pipelines, conversion to pipelineable products (gasoline, diesel fuel, jet fuel, etc.) at or near the retorting site is one alternative. Another is to subject the raw shale to a coking operation which lowers the pour point and, when followed by hydrotreating, gives a low-sulfur, low-nitrogen oil of about 45°F pour point. The hydrotreated shale oil can be doped with a pour point depressant to give a 35 to 40°F pour point oil acceptable in common carrier pipelines.

If the thermal coking has to be used to make a product suitable for common carrier pipelining, an overall liquid yield loss of 15% to 20% will be incurred.

Shale oil from the retort contains on the order of 10% heavy naphtha, a precursor to gasoline. When hydrotreating the shale oil to reduce the nitrogen content to 1,000 ppm, some additional naphtha is formed. The syncrude will have close to 14% naphtha which is somewhat similar in quality to naphtha from Light Arabian crude. See Table 5. The octane number of the naphtha is low and will have to be improved by catalytic reforming. Reforming primarily dehydrogenates naphthenic rings to form high-octane aromatics, and also cyclizes or isomerizes low-octane straight-chain paraffins and hydrocracks some of the high-boiling paraffins. Reforming was developed to upgrade petroleum naphthas and will also be required for comparable liquid stocks from coal. The relatively high naphthene content of shale oil naphtha permits reforming to high-octane gasoline with only moderate yield loss, compared with Light Arabian naphtha. Naphthas from coal generally contain aromatic rings as well and so would give slightly better yields; but, because of the higher number of hetero compounds, lose some advantage.

The Department of Defense is interested in alternative sources of turbine fuels for military aircraft. JP-4 is the large-volume fuel they require. See Table 6. Shale oil is well suited for yielding turbine fuels because of its relatively low aromaticity. All specifications for JP-4 are met by separating the JP-4 boiling range material from crude shale oil by distillation and hydrotreating that fraction.

Refining of jet fuels from coal syncrude poses more of a problem because of the high aromatic content.

The diesel fuel fraction from the raw shale oil is too high in sulfur and olefins and too low in cetane number and storage stability to meet specifications. Product which meets all specifications can be made, however, by hydrotreating crude shale oil followed by distillation, refer to Table 7. An increasing number of petroleum crudes also require hydrotreating of the diesel fraction to reduce sulfur content.

The portion of shale syncrude boiling above the diesel fuel fraction can be used as a premium low-sulfur fuel oil or cracked to produce more valuable lower-boiling transportation fuels such as gasoline, jet and diesel fuels. This fraction is a better material than the corresponding fraction from crude (such as Arabian Light), because the shale oil has been upgraded by prior processing: retorting, which thermally cracked the highest boiling fractions and reduced its carbon residue, and hydrotreating which reduced the sulfur content. The corresponding crude oil fraction (from Light Arabian crude) still contains 32% (14% of crude) as a nondistillable asphalt. It is difficult to use as boiler fuel because of its 2.75% sulfur content. It is often utilized by blending it in bunker fuel or by converting it to acceptable distillate fuels by coking followed by hydrotreating.

## REFERENCES

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2. Ibid, p. 66.
3. Ibid, p. 51.
4. Synthetic Fuels Data Handbook, Cameron Engineers, Inc., 2nd Edition, 1978, p. 193.
5. Ibid, pp. 238-42. H Shaw et al., (Exxon) Evaluation of Methods to Produce Aviation Turbine Fuels from Synthetic Crude Oils, Phase 1, For Air Force Aero Propulsion Laboratory, March 1975.

TABLE 1  
TYPICAL COMPOSITION OF  
GREEN RIVER OIL SHALE

Kerogen Content	15 Wt%	(25 Gal/Ton Shale Oil)
Kerogen Composition:		<u>Wt%</u>
Carbon		80.5
Hydrogen		10.3
Nitrogen		2.4
Sulfur		1.0
Oxygen		<u>5.8</u>
		100.0
Simple Chemical Formula (Sulfur & Nitrogen Replaced by Oxygen)		$C_{20}H_{32}O_2$
Mineral Content	85 Wt%	
Carbonates		48.0
Feldspars		21.0
Quartz		15.0
Clays		13.0
Analcite & Pyrite		<u>3.0</u>
		100.0

TABLE 2  
KEROGEN VS COAL

	Kerogen	Weight Percent		
		Bit	Subb	Lignite
Moisture and Ash Free				
Carbon	80.5	78.8	73.5	72.5
Hydrogen	10.3	5.7	5.3	4.9
Oxygen	5.8	8.9	19.7	20.8
Nitrogen	2.4	1.4	1.0	1.1
Sulfur	1.0	5.2	0.5	0.7
C/H Ratio	7.8	13.8	13.9	14.8

TABLE 3  
CRUDE SHALE OIL,  
COAL LIQUIDS, CRUDE OIL

	Crude Shale Oil	Coal Liquids		Arabian Light Crude
		COED*	H-Coal	
Gravity, Specific	0.92	1.13	0.92	0.85
°API	22.2	-4	23.0	34.7
Boiling Range, °C	60-540	-	30-525	5-575+
Composition, Wt%				
Nitrogen	1.8	1.1	0.1	0.08
Sulfur	0.9	2.8	0.2	1.7
Oxygen	0.8	8.5	0.6	-
C/H Ratio	7.3	11.2	8.1	6.2
Pour Point, °F	60	100	<5	-15
Viscosity, 100°F, SUS	98	133	-	44
Hydrogen Added				
Scf/Bbl Product	0	0	6000	0
Wt%	0	0	10	-
Yield, Gallons/Ton	25-35	30-48	60-90	-

\*COED: Char Oil Energy Development

TABLE 4  
HYDROGEN REQUIREMENT TO  
HYDROTREAT SHALE OIL

	Hydrotreated Shale Oil	H-Coal
Hydrogen Consumption		
Scf/Bbl Product	1350	6000
Atoms/Atom Hetero	10.8	---
Wt% Product	2.4	10
Gravity,		
°API	34	23
Specific	0.86	0.92
Pour Point, °F	+80	<5
Viscosity, 100°F, SUS	55	---
Composition, Wt%		
Nitrogen	0.08	0.01
Sulfur	0.002	0.2
Oxygen	-	0.6
C/H Ratio	6.5	8.1

TABLE 5

SHALE OIL PRODUCTS VS PETROLEUM PRODUCTSNAPHTHA (GASOLINE PRECURSOR)

Naptha From:	<u>Shale Oil*</u>	<u>Light Arabian Crude</u>	<u>Exxon Donor Solvent</u>
Boiling Range, °C	70-205	25-190	70-205
50% Point, °C	154	123	177
Yield, Vol% Crude	13.6	26.7	10
Gravity, °API	51.6	63.0	30
Specific	0.77	0.73	0.88
Sulfur, ppm	9	320	4700
Nitrogen, ppm	34	---	2100
C/H Ratio	5.9	5.7	7.8
Octane Number			
Research, Clear	32.5	38.3	-
+ 3 ml TEL	61.9	63.6	-
Composition, wt%			
Paraffins	45	75	22
Naphthenes	44	14	42
Aromatics	11	11	36

\*From shale oil which has been hydrotreated to reduce sulfur to 530 ppm.  
1350 scf H<sub>2</sub> consumed per barrel of crude shale oil.

TABLE 6

SHALE OIL PRODUCTS VS PETROLEUM PRODUCTSTURBINE FUEL

<u>Source</u>	<u>JP-4 From Shale Oil</u>	<u>Typical JP-4</u>
Boiling Range, °C	100-240	60-240
50% Point, °C	182	143
Gravity, °API	51.9	54
Specific	0.77	0.76
Sulfur, ppm	5	350
Freeze Point, °C	<-60	-62
Aromatics, Vol%	3.0	12.3
Smoke Point, mm	40	27.5
Thermal Stability, JFTOT at 260°C		
Pressure Drop, mm Hg	0	0.2
Preheater Deposit Code	0	1

TABLE 7

SHALE OIL PRODUCTS VS PETROLEUM PRODUCTSDIESEL FUEL

<u>Source</u>	Diesel Fuel From <u>Shale Oil</u>	<u>Typical</u>
Boiling Range, °C	200-360	188-327
Yield, Vol%	42.3	--
Gravity, °API	37.2	36
Specific	0.84	0.84
Sulfur, ppm	19	2500
Nitrogen, Wt%	0.022	--
Pour Point, °F	-23	-4 to -48
Cetane Number	50	46
Viscosity, SUS @ 38°C	37.2	34.5