

PRODUCTION OF UTAH SHALE OILS BY THE PARAHO DH AND UNION "B" RETORTING PROCESSES

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ABSTRACT

Uinta Basin oil shale from the Hells Hole Canyon outcrop in eastern Utah has been retorted by both the Paraho direct-heated (DH) and Union "B" processes for the White River Shale Project. Despite wide variation in the shale grades respectively retorted and the known retort differences, the raw shale oil products appeared to be quite similar both physically and chemically. Comparisons with existing data on Piceance Basin Colorado shale oil from these two processes are also quite similar. The one unexpected difference was the 30°F (-1°C) pour point for the Utah "B" oil. There are potential economic advantages in pipeline handling if this anomaly is a naturally-occurring phenomenon.

INTRODUCTION

The White River Shale Project (WRSP) was formed in June, 1974, by Phillips Petroleum Company, Sunoco Energy Development Co., and Sohio Petroleum Company. The purpose of the project was to develop jointly the oil shale resource on federal lease Tracts U-a and U-b in northeastern Utah. Tract U-a is jointly owned by Phillips and Sunoco Energy Development, while Sohio holds title to U-b. This combined resource has an estimated 1.06 billion barrels (168 g m³) of oil in place, averaging 28 gallons per ton (117 l/metric ton) (WRSP 1976).

To abide by the lease terms, WRSP prepared and issued a detailed development plan (DDP) in June, 1976. This DDP included the various phases of development needed to reach commercial production and, ultimately, abandonment of the leases. To this end, WRSP

has continued technological evaluation of the various retorting processes. In February, 1976, the WRSP mined several hundred tons of Uinta Basin, Utah, oil shale from an outcrop formation on patented lands about 3 miles (4.8 km) east of the U-a and U-b federal leases in the 26-square mile (6734 ha) area known as Hells Hole Canyon (fig. 1).

This work reports comprehensive, analytical data on the shale oils produced from this Utah shale by the Paraho DH and

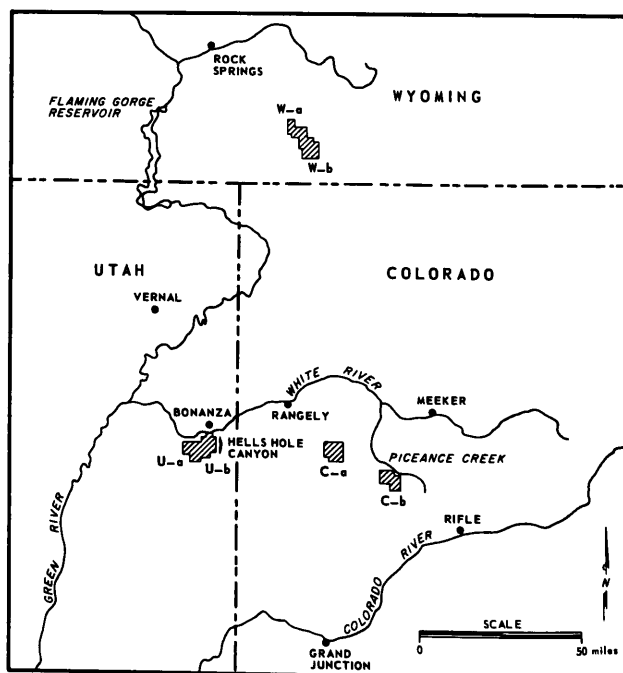


Figure 1. Location of Hells Hole Canyon.

Union "B" retorting processes. Emphasis is placed on the physical and chemical description of the two oils; no attempt is made at process comparisons.

MINING

There were two primary concerns in planning the mining of these bulk samples: the first centered upon the desire to obtain reasonably unweathered samples, but it was unknown as to what depth weathering had an effect; the second was to be sure of the stratigraphic interval of the samples so that they would correlate with the equivalent position on the tracts.

The Mahogany marker was located and traced to the sample location, thus satisfying the stratigraphic problem. An arbitrary depth of 10 ft. (3 m) into the face was chosen to offset possible weathering effects.

Mining began with some grading out of the access road down the canyon, a road previously used only by sheepherders in the area. As much dirt and loose rock as possible was dozed from above the outcrop to reduce contamination of the samples.

Using a wagon drill and steel, a pattern of nominal 2" (50 mm) holes was drilled. The holes were loaded with ANFO, and the face was shot. This first round removed the 10 ft. (3 m) of weathered material. This was dozed across the road and used to build a pad for loading the trucks with the final samples. Additional drilling and blasting produced the two final samples, which were loaded on small trucks for haulage out of the canyon, then transferred to highway trucks for final shipment.

The ore body was not pre-assayed at Hells Hole Canyon. Therefore, the grades of the samples were unknown until they were received and Fischer assayed by the respective toll processors.

Approximately 100 tons (90 metric tons) of raw oil shale were delivered to each retort facility. The sample taken from above the Mahogany marker, which eventually assayed an average of 19 gpt (79 l/metric ton)

went to Anvil Points, Colorado, for Paraho processing; and the shale taken from below the Mahogany marker, which later assayed an average 32 gpt (133 l/metric ton), was sent to Brea, California, for Union "B" processing.

The mine area was subsequently cleaned up; final grading removed most traces of activity.

RETORTING

Paraho Direct Heated (DH)

Approximately 100 tons (90 metric tons) of 19 gpt (79 l/metric ton) Utah shale, sized 1/2" x 2" (13 mm x 50 mm), were processed in the 2 1/2 ft. (75 cm) I.D. pilot plant, using the Paraho DH mode at a nominal rate of 1 ton/hr (0.9 metric ton/60 sec). In the DH mode, the retorting heat is supplied by combustion, directly in the retort, of residual carbon by oxygen in the gas-air mixture. Retort temperatures are controlled by adjusting the composition of the streams fed to each set of burner bars and adjusting the composition of the recycle gas return. Figure 2 gives a simple illustration of the process (Jones 1977).

Oil yield for the Utah shale was 92.8 percent by volume of Fischer Assay, very similar to what has been reported for the Paraho DH mode on Colorado shale (Sladek 1975). The net yield of product gas was about 8000 SCF/T (227 m³/T) of 66 Btu/Ft³ (2.5 Mj/m³) gross heating value material. Comparable gas yields have been reported by Jones (1977) on 28 gpt (117 l/metric ton) Colorado shale. The overall weight balance was 98.6 percent. Some properties of the raw and retorted shale as produced are shown in table 1.

Union "B"

The 100-ton (90-metric) sample of 32 gpt (133 l/metric ton) Utah shale was reduced to a consist of 1/4" x 1" (6.5 mm x 25.4 mm) and retorted in the Union "B" mode in their nominal 6 T/D (5.4 metric

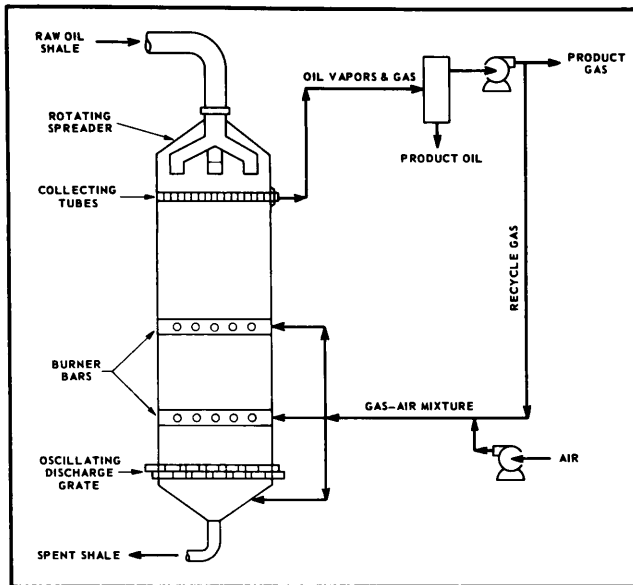


Figure 2. Paraho oil shale kiln.

Table 1. Utah shale properties - Paraho DH Retort.

	Raw Shale	Spent Shale
Fischer Assay		
Oil, gal/ton	18.61	0.69
Oil, Wt.%	7.11	0.26
Water, gal/ton	5.85	
Water, Wt.%	2.44	0.23
Mineral CO ₂ , Wt.%	19.83	13.39
Organic C, Wt.%		1.93
Elemental Analysis		
C, Wt.%	15.28	5.58
H "	1.46	0.11
N "	0.44	0.15
S "	0.35	0.31

tons/D) pilot retort. Raw shale rate for these runs was around 3 T/D (2.7 metric tons/D). The Union "B" process is an indirect heated mode where retorting heat is supplied by externally heated, recycle gas as opposed to direct combustion of shale inside the retort vessel. Another unique concept of the Union process is the upflow of raw shale using a reciprocating "rock pump" rather than gravity downfeed of the raw shale. A simplified, conceptual diagram of the Union "B" process is illustrated in figure 3 (Atwood 1977).

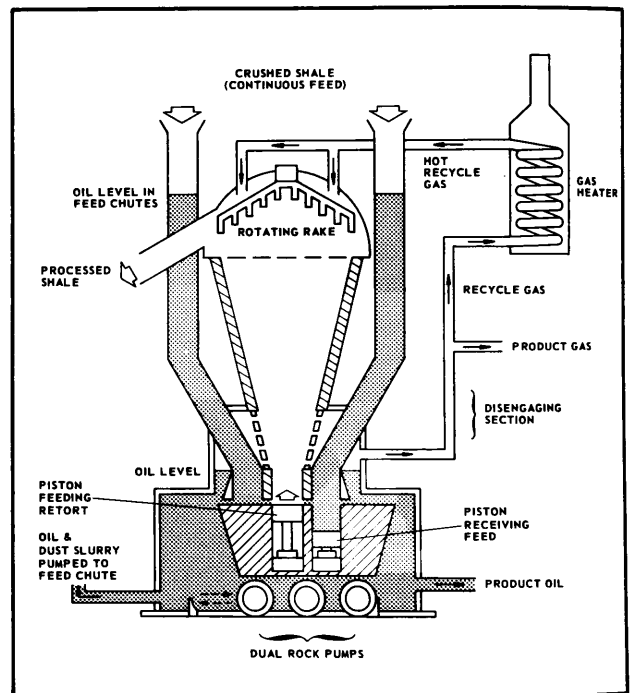


Figure 3. Union "B" retort.

Oil yield was about 97 percent by volume of Fischer Assay (~101 percent by volume on a C₄+ basis) for the Union "B" processing. These yields are similar to results on Union's Colorado shale, reported by Hopkins and others (1976) and Duir and others (1977). Retort product gas yield was about 725 SCF/T (20 m³/T).

This material had a calorific value of about 900 Btu/Ft³ (33.5 MJ/m³). The material balance for the Utah shale runs averaged 99+ percent by weight. Properties of the raw and spent, dry Utah shale processed by Union are given in table 2.

Table 2. Utah shale properties - Union "B" retort.

	<u>Raw Shale</u>	<u>Spent Shale</u>
Fischer Assay*		
Oil, gal/ton	32.20	
Oil, Wt.%	12.21	0.0
Water, gal/ton	2.90	2.1
Water, Wt.%	1.23	0.86
Mineral CO ₂ , Wt.%	18.96	21.93
Organic C, Wt.%	13.68	2.83
Elemental Analysis		
C, Wt.%	18.85	8.81
H, "	2.05	0.35
N, "	0.46	0.31
S, "	0.53	0.41

*Based on 105°C dry shale

ANALYTICAL RESULTS

Practically all previously reported data from these two processes have been on Colorado Piceance Basin shales. Since WRSP has the Utah leases, this effort was an initial attempt to obtain data on Utah oil shale and see if Utah shale oils were any different. Table 3 presents comprehensive analytical examinations of both Paraho DH and Union "B"-produced whole, raw Utah and Colorado shale oils. Despite the wide variation in shale grades [19 gpt (79 l/metric ton) vs. 32 gpt (133 l/metric ton)] for the Utah rock and the known differences between both retorting processes, all the raw shale oil products appeared to be quite similar both physically and chemically. Tables 4 and 5 present some

fractional analyses of the two Utah shale oils which are helpful in understanding the concentration of types of compounds as a function of the boiling range.

Generally, it can be stated that shale oils have a narrower boiling range than most conventional crude oils. The same is the case with the Utah oils, as shown graphically in figure 4. The shale oils contain less naphtha boiling material [$<400^{\circ}\text{F}$ (204°C)], less residua [$\geq 1050^{\circ}\text{F}$ ($565^{\circ}\text{C}+$)], and more middle distillate range material than typical crudes. A distillation curve for Kuwait crude oil is included in figure 4 for illustrative purposes.

Other significant properties considered were nitrogen, sulfur, arsenic and chemical structure. As known, the

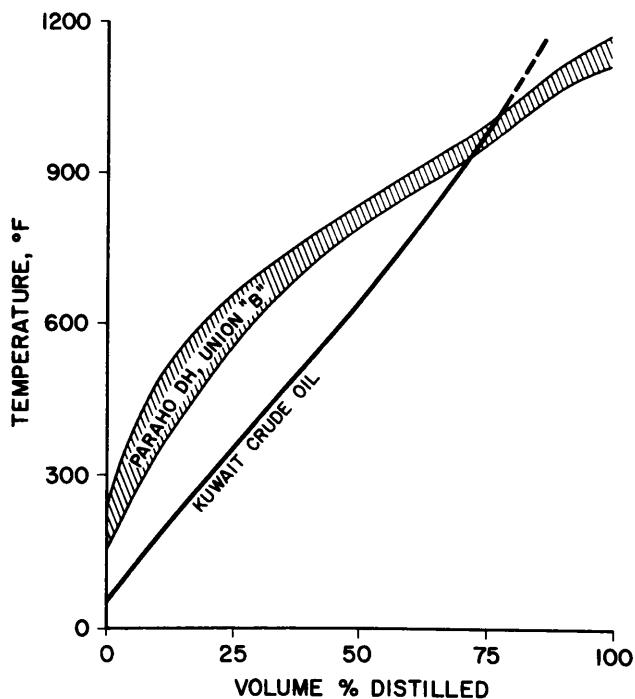


Figure 4. Distillation range for Utah shale oils.

Table 3. Physical and chemical properties of Green River formation shale oils.¹

Properties		Union "B" Colo.	Union "B" Utah	Paraho DH Utah	Paraho DH Colo.
Gravity	°API	21.2	20.2	19.6	21.4
Carbon	wt %	85.3	84.27	84.21	84.5
Hydrogen	"	11.15	11.68	11.82	11.2
Oxygen	"	1.12	1.23	1.89	1.6
Sulfur	"	0.61	0.55	0.50	0.64
Nitrogen Total	"	1.77	1.93	2.09	1.96
Nitrogen Basic	"	1.04	1.26	1.19	1.27
Ash	"	0.03	0.3	0.05	0.08
Conradson Carbon	"	ND	4.3	3.1	1.4 ^R
Pour Pt.	°F	60	30	75	72
	°C	15	-1	24	22
Viscosity @ 100°F	cst	33.5	35.3	60.9	38.0
Viscosity @ 210°F	"	4.88	4.83	5.95	5.3
Arsenic	W ppm	52 ²	49	19	28
Chloride	"	5	15	6	2
Chemical Structure by ASTM D-2007					
Paraffins	wt %	9	9	7	11
Naphthenes	"	8	10	10	7
Olefins	"	7	7	5	6
Aromatics	"	48	45	44	46
Polar Aromatics	"	24	24	29	26
Pentane Insols.	"	4	5	5	4
Distillation ASTM D-1160					
IBP		145	152	220	145
10		397	345	503	442
30		660	633	690	660
50		797	799	827	794
70		903	919	952	912
90		1037	1078	-	1050
EP		1100	1100	1100	1100
% Rec.		97	92	87	94

R = Ramsbottom Carbon

- 1 All analytical data determined by Sun on "as received" oils directly from the respective retorts; no further processing done or implied.
- 2 As content of Union "B" Colorado shale oil is reduced to about 20 ppm during solids removal.

Table 4. Physical properties of Utah shale oils.

Fraction	UNION "B"						PARAHO DH									
	IBP	-375°F	-425°F	-500°F	-650°F	-850°F	-1050°F	1050°F+	IBP	-375°F	-425°F	-500°F	-650°F	-850°F	-1050°F	1050°F+
Property																
TBF Distillation																
Wt. %	8.0	2.8	6.0	15.5	22.2	30.1	15.4	7.0	2.4	3.0	7.0	15.4	23.0	26.3	22.9	
Mid-Cut Wt. %	4.0	9.4	13.8	24.6	43.4	69.6	92.3	8.9	1.2	3.9	8.9	20.1	39.3	64.0	88.6	
Cum Wt. %	8.0	10.8	16.8	32.3	54.5	84.6	100.0	12.4	2.4	5.4	12.4	27.8	50.8	77.1	100.0	
Vol. %	9.2	3.1	6.5	16.0	21.9	29.7	13.6	7.7	2.8	3.4	7.7	16.1	23.1	25.7	21.2	
Mid-Cut Vol. %	4.6	10.8	15.6	26.8	45.8	71.6	93.2	10.1	1.4	4.5	10.1	22.0	41.6	66.0	89.4	
Cum Vol. %	9.2	12.3	18.8	34.8	56.7	86.4	100.0	13.9	2.8	6.2	13.9	30.0	53.1	78.8	100.0	
API Gravity @ 60°F	45.8	38.7	34.4	27.3	21.0	20.1	5.3	32.8	42.6	36.4	32.8	26.1	19.4	15.2	6.7	
Kinematic Viscosity, cs																
30°F	3.30	14.41	27.63	---	---	---	---	36.15	4.11	9.87	36.15	---	---	---	---	
70°F	1.09	2.32	3.23	---	---	---	---	3.53	1.23	1.92	3.53	---	---	---	---	
100°F	---	---	---	6.71	57.7	---	---	2.40	---	1.41	2.40	7.40	67.7	---	---	
160°F	---	---	---	2.93	13.57	87.3	---	---	---	---	---	3.20	---	94.4	---	
210°F	---	---	---	1.79	5.94	24.6	2249.	---	---	0.70	0.97	1.90	6.35	25.6	985	
275°F	---	---	---	---	---	---	228.6	---	---	---	---	---	---	---	143.9	
Pour Point, °F	---	-48	-38	+13	+79	+93	120+	-38	---	-55	-38	+12	+80	+84	120+	
Freeze Point, °F	---	-62	-64	---	---	---	---	-52	---	-52	-32	---	---	---	---	
Flash Point, PM°F	---	124	148	280	390	500	600+	168	---	110	168	275	390	450	600+	
Smoke Point, MM	---	15	13	---	---	---	---	15	---	15	15	---	---	---	---	
Octane Number, RON/MON	67.2/60.9	---	---	---	---	---	---	74.5/67.1	---	---	---	---	---	---	---	
Reid Vapor Press, PSIG	0.3	---	---	---	---	---	---	0	---	---	---	---	---	---	---	
Cetane Number	---	33.2	32.9	34.8	---	---	---	26.3	---	26.3	31.7	32.9	---	---	---	
*Cetane Index	---	38.5	37.0	41.0	---	---	---	29.5	---	29.5	34.3	39.5	---	---	---	
Ash, Wt. %	---	---	---	---	0.21	2.95	0.94	---	---	---	---	---	---	0.01	0.36	
Conradson Carb. Res., Wt. %	---	---	---	---	---	---	22.0	---	---	---	---	---	---	2.72	19.6	

*May not apply, correlation is petroleum based.

Table 5. Chemical properties of Utah shale oils.

Fraction	UNION "B"							PARAHO DH						
	TBP -375°F	-425°F	-500°F	-650°F	-840°F	-1050°F	1050°F+	TBP -375°F	-425°F	-500°F	-650°F	-850°F	-1050°F	1050°F+
Property														
Carbon, Wt. %	84.54	83.20	83.82	84.31	84.81	85.20	84.21	83.89	83.88	84.34	83.29	84.12	84.40	84.41
Hydrogen	13.07	12.78	12.41	12.75	11.51	11.24	10.37	12.98	12.25	12.41	11.83	11.43	11.16	10.13
Oxygen	1.33	1.99	1.88	1.38	1.27	1.07	1.28	1.67	2.20	2.05	1.92	1.52	1.43	2.06
Nitrogen, Total	0.23	0.85	1.34	1.39	2.04	2.15	3.25	0.94	0.94	1.06	1.74	1.99	2.35	2.73
Nitrogen, Basic	0.56**	1.06**	0.97	1.10	1.17	1.33	1.52	1.03**	1.20**	0.99	1.14	1.14	1.25	1.58
Sulfur	0.62	0.54	0.71	0.76	0.52	0.46	0.42	0.37	0.46	0.51	0.47	0.48	0.37	0.30
H/C, Atomic Ratio	1.86	1.84	1.78	1.81	1.63	1.58	1.48	1.86	1.75	1.77	1.70	1.63	1.59	1.44
PNOA by Mass Spec:														
Paraffins, Vol. %	24.6	21.0						19.5	19.8					
Naphthenes	7.4	4.8						6.2	6.2					
Aliphatic Monoolefins	31.0	33.1						31.0	24.2					
Cyclic Monoolefins	13.7	11.1						14.9	11.0					
Alkylbenzenes	22.0	20.8						26.1	28.4					
Alkylindans + Tetralins	1.3	8.3						2.2	8.5					
Alkyl naphthalenes	0.0	0.9						0.1	1.9					
Structure by ASTM D-2007:														
Paraffins, Wt. %	22.9*	19.3*	15.3	18.5	9.4	3.0	} 2.6	18.0*	17.9*	15.9	14.8	9.5	3.3	} 2.1
Naphthenes	7.5*	4.9*	12.7	16.1	12.8	8.7		6.2*	6.2*	11.4	10.0	16.4	11.2	
Monoolefins	43.5*	42.5*	10.4	2.2	2.3	3.5	44.3*	33.4*	11.2	6.4	1.6	2.7		
Aromatics	26.1*	33.3*	52.5	41.2	52.9	52.8	31.7	31.5*	42.5*	49.3	50.4	49.7	50.2	26.8
Polar Aromatics	---	---	8.7	21.3	21.8	32.0	38.7	---	---	11.9	17.7	22.3	31.8	52.3
Pentane Insolubles	---	---	0.4	0.7	0.8	0.0	27.0	---	---	0.3	0.7	0.5	0.8	18.8
Total Acid Number Mg/GM	4.0	7.9	6.5	2.8				3.1	4.3	4.7	3.3			
Total Base Number Mg/GM	15.8	24.2	26.0	37.1				24.7	30.0	31.0	37.4			
Arsenic, ppm	3	11		84	46***			12	6	6	14	16	19	27

* Estimated Wt. % by PNOA-MS not ASTM D-2007

** Problems with the test

*** 650°F+

high nitrogen content of raw shale oil is a distinctive and significant characteristic. So, too, with Utah shale oil. Figure 5 illustrates the distribution of nitrogen and sulfur versus boiling range. For simplicity, the data are presented as bands to bracket individual data points. Nitrogen content increases with increasing boiling range, from about 1.0 percent by weight in the naphtha fraction, to around 2.5 percent by weight in the heavy residua. This characteristic is also typical for petroleum crude oil. Conversely, for sulfur in the raw shale oil, the naphtha boiling material has the highest sulfur concentration of about 0.7 percent by weight with a rather flat decline to about 0.3 percent by weight in the 1050°F+ (565°C+) bottoms.

Metals concentrations in Utah shale oils are low, relative to petroleum crude. The most significant trace element, however,

in the Utah shale oils is arsenic, which is about 1000 times greater than in conventional crude oil. This is also the case for Piceance Basin shale oils. Table 6 presents the significant trace elements found in the Utah shale oils.

Table 6. Trace metals in Utah shale oils.

Element	Concentration, W ppm	
	Union "B"	Paraho DH
Arsenic	49	19
Iron	56	140
Nickel	<2	20
Copper	<2	<2
Vanadium	<20	<20

Table 7. Qualitative MS characterization of the polar fractions of Utah shale oils.

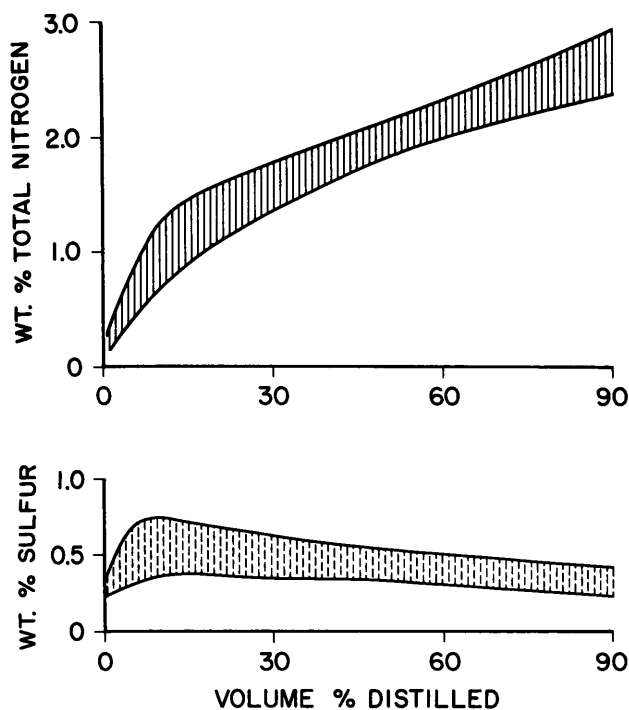


Figure 5. Nitrogen and sulfur distributions in raw Utah shale oils.

The chemical structure of the Utah shale oils again shows significant differences relative to conventional crude oil. Figure 6 shows the paraffin and olefin contents to be higher in the lower boiling fractions. Naphthene content tends to be fairly constant, while aromatics increase with boiling range. The high percentage of polar aromatics in the higher boiling range fractions indicates the presence of heteroatoms of nitrogen, oxygen, and sulfur in the ring structure of the higher molecular weight aromatics. Table 7 gives a qualitative breakdown of the polar compounds found in the two Utah shale oils.

The only major difference in the two oils was in their respective pour points, 30°F (-1°C) for Union "B" and 75°F (24°C) for Paraho DH. Known differences between the pour points of the oils produced by these processes from Colorado shale have been reported by Atwood (1977). The 30°F (-1°C)

	UNION "B"			PARAHO DH		
	425-500°F	500-650°F	650-850°F	425-500°F	500-650°F	650-850°F
QUINOLINES	M	M	M	M	L	M
CYCLOALKYLINDOLES						
NAPHTHOLS	T	M	M	T	M	S
INDENOLS						
INDOLES	M	L	M	M	L	S
INDENO-PYRIDINES						
CHROMANS	S	M	S	S	S	S
CYCLOALKYLPYRIDINES	M	M	M	M	M	M
INDANOLS	M	M	M	S	M	M
PYRIDINES	M	M	M	M	S	M
ANILINES						
PHENOLS	L	S	M	L	S	S
ACRIDINES	M	S	M	S	S	M
BENZOQUINOLINES						
DIHYDROXYPHENOLS	S	S	S	S	S	S
CATECHOL						
RESORCINOL						
QUINOL						
ALKYLCARBAZOLES	S	S	L	S	S	L
ACRIDANS						
ACENAPHTHYLENOLS	S	S	M	T	T	M
BENZINDANONES						
PHENYL-PYRIDINES	S	M	M	T	M	M
ACENAPHTHENOLS	T	S	S	T	S	S

L-LARGE, M-MEDIUM, S-SMALL, T-TRACE

pour point for the Union "B" shale oil was lower than expected.

Pipeline transport of raw shale oils is highly desirable. If it can be done, this method would lower costs and, consequently, increase sales. Although pour point is not the only factor determining whether oils can be pumped, it is an important variable. A naturally occurring, lower pour point oil would have certain economic advantages compared to oils requiring the addition of available chemical pour depressants. Therefore, this observed low pour point of 30°F (-1°C)

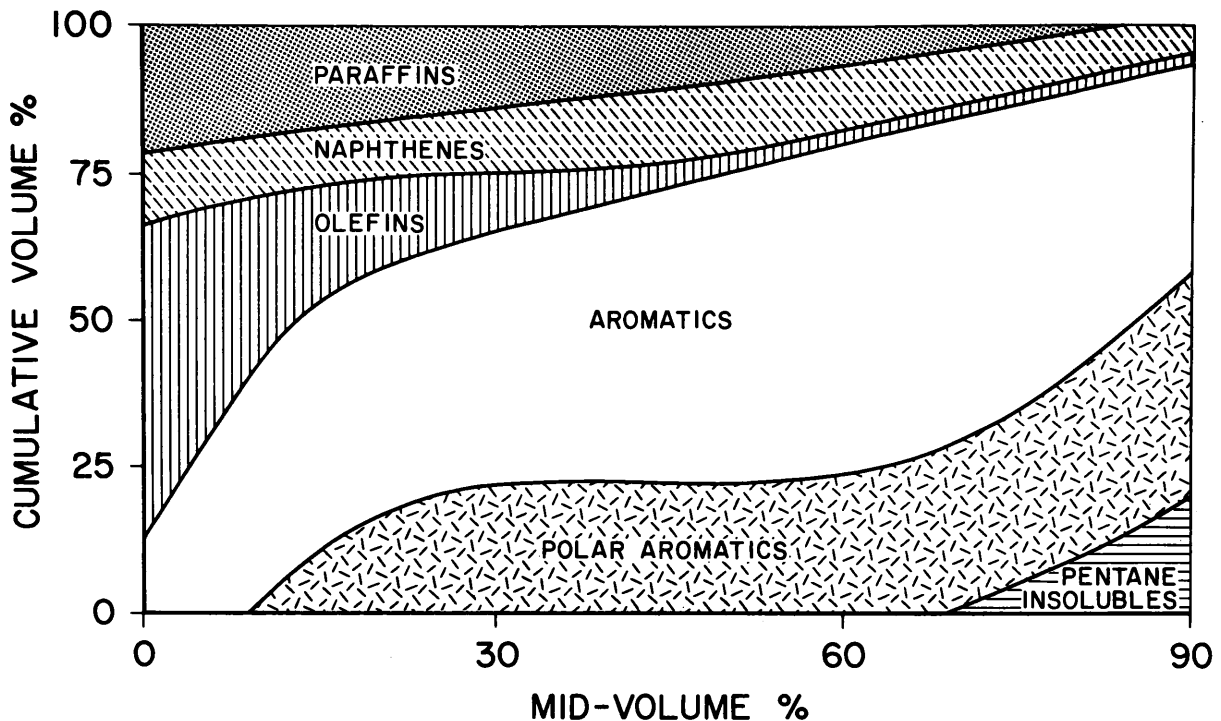


Figure 6. Graphical representation of raw Utah shale oil chemical structure.

for the Union "B" Utah oil is certainly an interesting and serendipitous phenomenon.

ACKNOWLEDGEMENTS

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