

## EFFECT OF RETORTING ON WAX CRYSTALLIZATION IN UTAH SHALE OILS

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### 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 the federal lease Tracts Ua and Ub in northeastern Utah. Tract Ua is jointly owned by Phillips and Sunoco Energy Development, while Sohio holds title to Ub. This combined resource has an estimated 1.06 billion barrels of oil in place, averaging 28 gallons per ton (1).

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 necessary to reach commercial production and, ultimately, abandonment of the leases. To this end, WRSP has continued evaluating the technological progress 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 east of the Ua-Ub federal leases in a 26 square mile area known as Hells Hole Canyon. This is shown in Figure 1.

The sample was collected in two parts: the first from an approximate 12 foot interval above the Mahogany marker, and a second sample from an approximate 20 foot interval located immediately below the Mahogany marker. 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, Paraho Development Corporation, Anvil Points, Colorado, and Union Oil Co., Brea, California.

### Retorting

A. Paraho Direct Heated (DH) - Approximately 100 tons of 19 gpt Utah shale, sized 1/2" x 2", were processed in the 2 1/2 ft. I.D. pilot plant using the Paraho DH mode at a nominal rate of 1 ton per hour. In the DH mode the retorting heat is supplied by combustion, directly in the retort, of residual carbon by the oxygen in the gas-air mixture. Retort temperatures are controlled by adjusting the composition of the recycle gas return. Figure 2 gives a simple illustration of the process (2).

The oil yield for the Utah shale was 92.8 vol % of Fischer Assay, very similar to what has been reported for the Paraho DH mode on Colorado shale (3). The yield of product gas was about 8000 SCF/T of 66 Btu/Ft<sup>3</sup> gross heating value material. The overall weight balance was 98.6%. Some properties of the raw and retorted shale are shown in Table I.

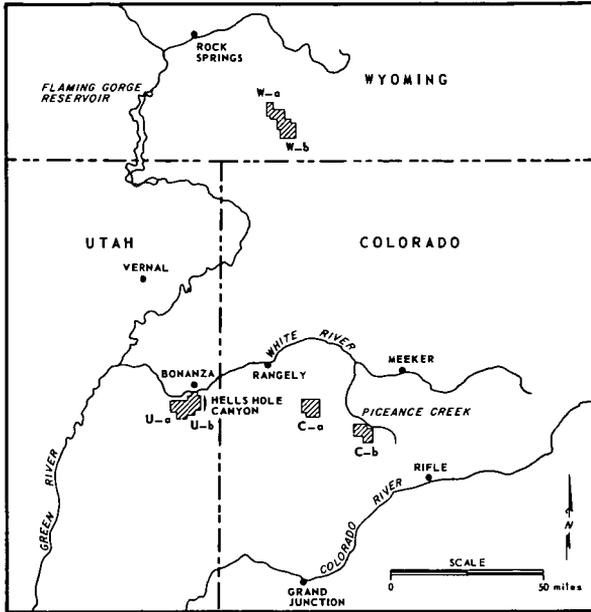


FIGURE 1. LOCATION OF  $U_a-U_b$  & HELLS HOLE CANYON

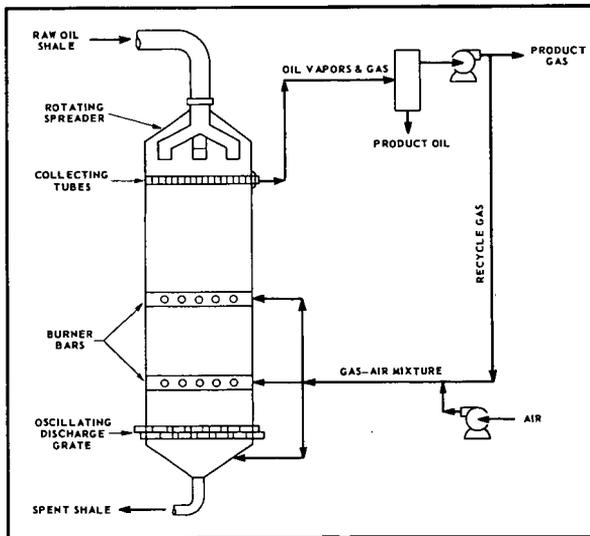


FIGURE 2. PARAHO OIL SHALE KILN

Table I  
Utah Shale Properties

	Paraho DH		Union "B"	
	Raw Shale	Spent Shale	Raw Shale	Spent Shale
Fischer Assay				
Oil, gal/ton	18.61	0.69	32.20	-
Oil, Wt %	7.11	0.26	12.21	0.0
Water, gal/ton	5.85	-	2.90	2.10
Water, Wt %	2.44	0.23	1.23	0.86
Mineral CO <sub>2</sub> , Wt %	19.83	13.39	18.96	21.93
Organic C, Wt %	-	1.93	13.68	2.83
Elemental Analysis				
C, Wt %	15.28	5.58	18.85	8.81
H "	1.46	0.11	2.05	0.35
N "	0.44	0.15	0.46	0.31
S "	0.35	0.31	0.53	0.41

B. Union "B" - The 100-ton sample of 32 gpt Utah shale was reduced to a consist of 1/4" x 1" and retorted in the Union "B" mode in their nominal 6 T/D pilot retort. Raw shale rate for these runs was around 3 T/D. The Union "B" process is an indirect heated mode where the retorting heat is supplied by externally heated recycle gas as opposed to direct combustion of shale inside the retort vessel. A unique aspect 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 diagram of the Union "B" process is illustrated in Figure 3 (4).

Oil yield was about 97 vol % of Fischer Assay (~101 vol % on a C<sub>4</sub>+ basis) for the Union "B" processing. This yield is also similar to results on Union's Colorado shale (5,6). Retort product off-gas yield was about 725 SCF/T. This material had a calorific value of about 900 Btu/Ft<sup>3</sup>. The material balance for the Utah shale runs averaged 99+ Wt %. Properties of the Utah shale processed by Union are also given in Table I.

#### Analytical Results

Practically all previously reported data from these two processes have been on Colorado Piceance Basin shales. This present effort was an attempt to obtain data on Utah oil shale and determine if Utah shale oils were any different. No major differences between Utah and Colorado shale oils were found (7). Table II presents comprehensive analytical examinations of both the Paraho and Union produced whole, raw Utah shale oils. Despite the wide variation in shale grades (19 gpt vs. 32 gpt) and the known differences between both retorting processes, the raw shale oil products appeared to be quite similar both physically and chemically.

The only major difference in the two oils was in their respective pour points, 30°F for Union "B" and 75°F for Paraho DH. Known differences between the pour points of the oils produced by these processes from Colorado shale have been reported (4). The 30°F pour point for the Union "B" shale oil was lower than expected.

Transportability of raw shale oils via pipeline is a viable option for eventual marketability. Although pour point isn't the only factor determining the pumpability of oils, it is an important variable. A naturally occurring lower pour point oil could have economic advantages when compared to oils requiring additions of available, chemical pour depressants. Therefore, this observed low pour point

of 30°F for the Union "B" Utah oil is certainly an interesting and serendipitous phenomenon. On closer examination, however, it was observed that the wax in the two oils crystallized differently.

Table II  
Physical and Chemical Properties of Raw Utah Shale Oils

Properties		Union "B"	Paraho DH
Gravity	°API	20.2	19.6
Carbon	Wt %	84.27	84.21
Hydrogen	"	11.68	11.82
Oxygen	"	1.23	1.89
Sulfur	"	0.55	0.50
Nitrogen Total	"	1.93	2.09
Nitrogen Basic	"	1.26	1.19
Ash	"	0.3	0.05
Conradson Carbon	"	4.3	3.1
Pour Point	°F	30	75
Viscosity @ 100°F	CS	35.3	60.9
Viscosity @ 210°F	"	4.83	5.95
Arsenic	W ppm	49	19
Chloride	"	15	6
Chemical Structure by ASTM D-2007			
Paraffins	Wt %	9	7
Naphthenes	"	10	10
Olefins	"	7	5
Aromatics	"	45	44
Polar Aromatics	"	24	29
Pentane Insols.	"	5	5
Distillation ASTM D-1160			
IBP		152	220
10		345	503
30		633	690
50		799	827
70		919	952
90		1078	-
EP		1100	1100
% Recovery		92	87

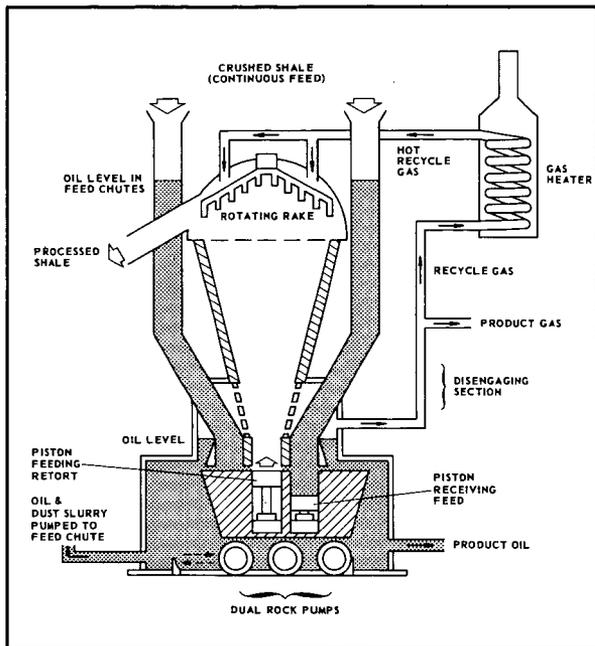


FIGURE 3. UNION "B" OIL SHALE RETORT

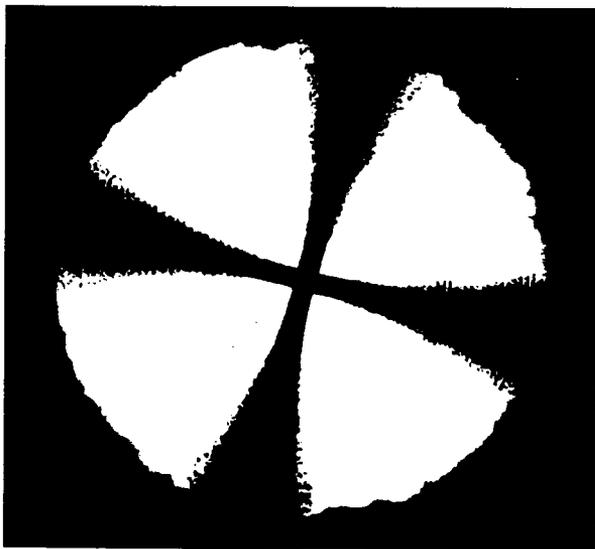


FIGURE 4. SPERRULITE OF ANISOTROPIC CRYSTALS BETWEEN CROSSED POLARS

## Wax Spherulites

In the polarizing microscope at room temperature, the wax crystals in the Paraho oil appear as the expected needles and plates, but the morphology of the crystals in the Union oil is quite different. While needles are also present, most of the crystals exhibit properties characteristic (8) of spherulites of anisotropic materials. The particles are round and, between crossed polars in parallel light, display a black maltese cross which remains stationary on rotation of the stage. This is shown schematically in Figure 4 and in photomicrographs in Figure 5. X-ray examination of the oil gives only the pattern for paraffinic wax. Although pure spherulites have not yet been isolated and examined, they are believed to be formed by wax needles arranged radially. Analogous structures are seen commonly in polymers including polyethylene but, to our knowledge, this is the first time spherulites of wax have been observed.

Two questions immediately occur. Why do the spherulites form in the Union oil, and is there a connection between their formation and the lower pour point?

### Cause of Spherulite Formation

Three aspects of the two oils were examined -- the wax, the mineral, and the effect of various fractions.

A. Wax - These were isolated by removing the pentane-insolubles from the 650°+ fractions, precipitating the crude waxes in methylethylketone-toluene, and deoiling these waxes in ethylene dichloride. The yields, based on total oils, were 5.0% and 4.7% from the Paraho and Union oils, respectively. Although the melting points were different (109 and 140°F), the fingerprints by gas chromatography were quite similar, so that the primary factor in formation of spherulites is not wax composition. This conclusion is further supported by the blending data reported in section C below.

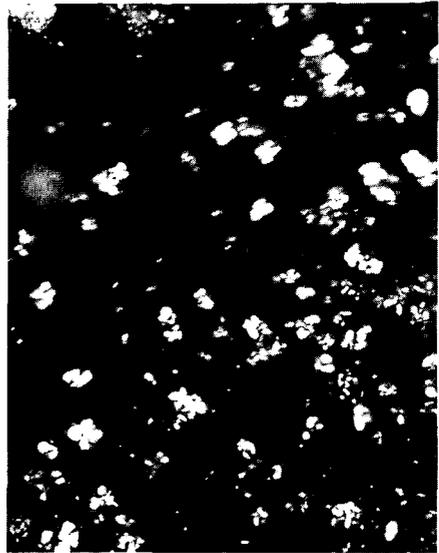
B. Mineral - As could be anticipated from the larger ash content reported in Table II, many mineral particles are observed in the Union oil. These were removed by running the hot oil through a 1.5 micron filter. Removal of the mineral appeared to have no major effect on the spherulites. Heating up the mineral-containing oil on the microscope hot stage causes the spherulites to melt, leaving the mineral. Upon cooling, the wax does recrystallize around the mineral. After filtration the mineral is not present, but the recrystallization of the wax into spherulites does not seem to be appreciably slower. Thus, mineral is not the controlling factor in spherulite formation.

C. Effect of Fractions - Both oils were distilled into I-425-650-850-1050 and 1050°F+ fractions. These fractions were blended in many different ways and the blends observed with the microscope at 77°F to see if spherulites were present. It was found that:

- Paraho Oil
  1. Adding or substituting Union 1050°F+ bottoms gives spherulites as shown in Figure 5D. Also, adding or substituting the pentane-insolubles from the Union bottoms yields spherulites, although perhaps not as well-formed.
  2. No other blends show spherulites.
- Union Oil
  1. Spherulites are formed if the 650-1050°F or 850-1050°F fractions from Paraho oil are substituted. Also, spherulites are present after removing the pentane-soluble bottoms.



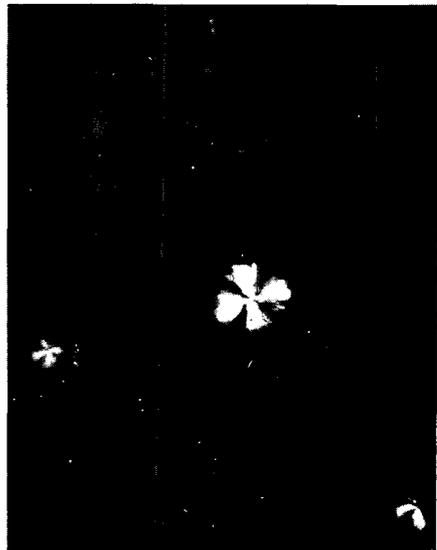
A. PARAHO SHALE OIL



B. UNION SHALE OIL



C. UNION SHALE OIL



D. PARAHO SHALE OIL SUBSTITUTE UNION  
1050° F+ FRACTION

SCALE:  $30\mu$

FIGURE 5. PHOTOMICROGRAPHS OF WAX CRYSTALS

2. Only needles are observed if either the 850-1050°F fraction or pentane-insoluble residuum is removed. Also spherulites are absent if Paraho pentane-insoluble, pentane-soluble, or whole 1050°F+ bottoms are substituted for the Union bottoms.

These facts lead to the conclusion that something in the Union 1050°F bottoms, probably in the asphaltenes, causes spherulites to form. The 850-1050°F fraction is necessary but is not unique for the Union oil.

#### Pour Points

Data measured on the Mectron Autopour are listed below in Table III.

Table III  
Pour Points

<u>Oil</u>	<u>Crystal</u>	<u>Pour Pt., °F</u>
Whole Union	Spherulite	27
Whole Paraho	Needle	77
Union, Substitute Paraho 1050+	Needle	58
Paraho, Substitute Union 1050+	Spherulite	21
Union + 9% I-425	Spherulite	36

Substituting Paraho 1050°F+ bottoms into Union oil changes the spherulites to needles and increases the pour point from 27 to 58°F. On the other hand, changing the needles in Paraho oil to spherulites by substituting Union 1050°F+ bottoms lowers the pour point from 77°F to 21°F. Doubling the I-425°F fraction in Union oil, which should lower the viscosity, seems to increase the pour point. While a viscosity study, soon to be made, is needed for confirmation, these data indicate strongly that there is a correlation between spherulite formation and pourability of these oils. It appears in the microscope that the wax changes from a three-dimensional, irregular network of needles to spheres which have less particle-to-particle interaction. Work is continuing in an effort to achieve better understanding and control of the phenomenon.

#### Acknowledgements

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