

EFFECTS OF THERMAL HISTORY ON OIL SHALE PYROLYSIS PRODUCTS

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Abstract

This laboratory study determined the effects of mild thermal treatment of oil shale on quantity and quality of subsequently produced Fischer assay oil. It was determined that heating oil shale, at 70 to 180°C in air, reduced Fischer assay oil yield as much as 58 percent. Similar thermal histories in oxygen-free atmospheres gave unchanged Fischer assay oil yields. Specific gravity of product shale oil was increased when oil shale was preheated in an oxygen-containing atmosphere.

Introduction

Production of oil from oil shale requires that the kerogen in the oil shale undergo thermal decomposition. All retorting processes, above ground or in situ, produce a great deal of waste heat, generally used to preheat oil shale before it actually reaches retorting temperatures. A knowledge of the effects various preheating conditions have on product oil is fundamental to proper design and operation of an oil shale preheating system. These studies were undertaken at temperatures in the range of 70-180°C at which oil shale is generally believed to be unreactive.

Previous investigators have studied effects of temperature and preheating in the temperature range of 200 to 525°C. These studies have included kinetics of kerogen decomposition and effects of heating rate and preheating on oil yields. Johnson and others (1975) studied the effect of heating

rate on oil yield of 30 gpt (0.14 m³) shale when retorting with a terminal temperature of 470°C under inert atmosphere. They reported that, when the heating period was shortened from 14 days to 40 minutes, oil yield increased from 70 to 100 percent of Fischer assay by weight.

A series of experiments by Hubbard and Robinson (1950) showed the effect of terminal temperature on oil yield. Samples containing 13.9 percent by weight of kerogen were rapidly heated to terminal temperature under an inert atmosphere and held at temperature for various lengths of time. A modified Fischer assay of this shale sample gave 26.7 gallons (0.12 m³) of oil per ton of shale, or an 83.4 percent conversion of kerogen to oil plus gas. Rapid heating to terminal temperature resulted in kerogen conversions of 71 percent in 150 minutes at 400°C, and 83.4 percent in 7 minutes at 525°C. It was also determined that kerogen conversion continued for 24 hours when shale was heated to 350°C.

Hubbard and Robinson's results (1950) were verified in a series of experiments by Hill and others (1967) using 35 gpt (0.16 m³) shale. Hill determined that only 34 percent of Fischer assay oil yield could be obtained by heating the shale to 350°C, after heating for 425 hours.

Stout and others (1976) determined the effect on oil yield of interrupting the Fischer assay heating profile for a hold period of isothermal heat soaking. At holding temperatures of 250°C or below, little

effect on oil yield was noted. At holding temperatures between 300 and 425°C, a significant decrease in oil yield was noted, up to a maximum of 19 percent. Robinson and Hubbard (1951), and Stout and others observed that if sufficient quantity of inert sweep gas is passed through the shale during an isothermal soaking period, oil yield upon subsequent Fischer assay is not affected. Oil yield loss, noted in non-sweep experiments, was attributed to thermal degradation of liberated oil and not to the thermal history of the kerogen.

Robinson and Hubbard (1951) also noted that if oxygen were present in the sweep gas, oil yield decreases would be observed. Oil yield decreases were dependent on heating temperature, heating time, shale particle size and oxygen content of heating gas. Heat soaking temperatures studied ranged from 200 to 350°C, for periods of 15 to 240 minutes. Oil losses of up to 26 percent, compared to Fischer assay of untreated shale, were observed and were attributed to oxidation of the kerogen. This effect was noted for oxygen content in sweep gas as low as 1 percent.

The literature shows that various thermal factors have definite effect on decomposition of kerogen and quantity of oil produced in a Fischer assay. Experiments reported in this paper examined the effects of thermally treating oil shale at 70 to 180°C, in air and nitrogen atmosphere, on the quantity and quality of oil produced by subsequent Fischer assay. These temperatures are much lower than those used in previously reported studies. According to Cumming and Robinson (1972), these conditions are too mild to cause significant conversion of kerogen to bitumen and oil. Raw shale weight and organic carbon content were monitored during preheat; any changes noted were small. Fischer assay product yields of shale, preheated in a nitrogen atmosphere, were unchanged. Oil yields from subsequent Fischer assay of air preheated shale were as low as 42 percent of Fischer assay, while gas and water yields were increased. Quality of oil

was altered by this mild air preheating treatment, as determined by an increased density compared to Fischer assay oil of untreated shale.

Experimental

Shale Sampling - The oil shale used in this research was 32 gpt (0.145 m³) shale from the Colony Mine, Piceance Creek Basin area, Colorado. With the exception of shale used in a particle size study, all shale was processed through a jaw crusher and Raymond mill to minus 65 mesh size before preheating. As shown in table 1, the shale sample was characterized by the following analyses: mineral carbon, organic carbon, oxygen, and Fischer assay.

Fischer assay determinations were performed on samples that were minus 65 mesh in particle size. The procedure used at Tosco has been previously described by Goodfellow and Atwood (1974). This procedure allows all product gas to be collected and analyzed by gas chromatography. Gas analysis, along with recovery of oil, water and spent shale, allows complete material balances to be made around the Fischer assay procedures.

Shale samples for particle size studies were obtained by crushing and then fractionating the shale into various particle sizes by screening. Size ranges selected for study were: U.S. Mesh sizes -1/4"+8m; -8m+20m; and -65m. Samples for control Fischer assay determinations were taken from each fraction and assayed in the normal manner before preheating treatments.

Procedure - Shale to be preheated in air was spread in a thin layer (5 mm) on aluminum trays and placed in an oven for the required length of time. Shale to be preheated under an inert atmosphere was placed in a sealed container with fittings that allowed a nitrogen purge. This container was sealed and purged before and during the preheat period. The shale was not stirred during preheating. When preheating was complete, samples were split for various analyses. Fischer assay was performed, as described by Goodfellow and Atwood (1974).

Bitumen content was determined by a 24-hour benzene Soxhlet extraction. Benzene was removed from bitumen by reduced pressure, rotary evaporation.

Carbon analysis was used to determine amount of hydrocarbon volatilized during the heating period, since no significant weight losses were observed. Losses in organic carbon, during preheating, were expressed as oil losses by dividing by 0.85. These oil losses, called preheating losses, were added to actual Fischer assay oil yields of preheated samples to give reported total oil yield values.

Results and Discussion

Samples were heated in air at 120°C for up to 25 days. Analyses of these samples at days 5 and 25 are given in table 2. Samples preheated in a nitrogen atmosphere showed no change or were within experimental error of the analyses. After five days of 120°C treatment in air, samples had oil yields of only 81 percent Fischer assay. At 25 days, oil yield was 66 percent of Fischer assay, while gas and water yields had increased to 164 percent and 217 percent, respectively, of those determined for fresh shale. Weight changes, during 120°C preheat, were within experimental error, and organic carbon losses during preheat were small, when compared to loss of oil yield by Fischer assay.

Although not shown in the table, the amount of organic carbon in the Fischer assay residue increased 90 percent with 25 days of heating. When fresh shale was assayed, spent shale accounted for 84 percent of the material balance. Spent shale, from shale preheated 25 days at 120°C in air, accounted for 87 percent of the material balance. The increase can be entirely accounted for as unretorted or carbonized organic carbon on the spent shale. Table 2 also shows that oxygen content of the raw shale increased from 17.8 percent for fresh shale to 21.5 percent in shale heated for 25 days. Using the value of 5.8 percent given by Smith (1961) for organic oxygen in oil shale, and, assuming that oxygen gained

during heating is organic, there was a 64 percent increase in organic oxygen at 25 days.

When shale was preheated and then stored at ambient temperatures for six months, the same Fischer assay products were obtained as for shale promptly assayed after preheating. The necessity of oxygen for altered yields, and the irreversibility with time suggest a partial oxidation of the kerogen during the preheat process. Heat of combustion, as determined by a Parr bomb calorimeter, confirms that shale is partially oxidized during preheating. Heat of combustion of shale, preheated for 25 days at 120°C, is 88 percent of that of fresh shale (1440 versus 1630 cal/g, table 8). It is concluded that a non-volatile, partial oxidation product of kerogen is formed during the preheating treatment.

There were significant differences in the character of Fischer assay oils from fresh oil shale and preheated oil shale. As shown in table 3, specific gravity of oil increases after treating oil shale only 5 days at 120°C. Initially, the increase in specific gravity was thought to be due to a loss of light ends during preheat treatment, even though no weight losses were observed. Microdistillations on Fischer assay oils

Table 1. - Characterization of oil shale.

<u>Analysis</u>	<u>Value</u> ⁽¹⁾
Mineral Carbon	5.6
Organic Carbon	14.8
Oxygen	17.8
Bitumen	1.28
Fischer Assay	
<u>Product</u>	<u>Yield</u> ⁽¹⁾
Oil ⁽²⁾	12.0
Gas	2.8
Water	1.2

(1) Expressed as weight percent of raw oil shale

(2) Specific Gravity, 0.9071

Table 2. - Analysis of shale preheated in air at 120°C.

<u>Product Yield</u> ⁽¹⁾	<u>Fresh Shale</u>	<u>Preheated</u>		<u>Preheated</u>	
		<u>5 days</u>	<u>(% of Fresh)</u>	<u>25 days</u>	<u>(% of Fresh)</u>
Fischer Assay Oil	12.0	9.2	(77)	5.4	(45)
Preheating Losses	---	0.5	(--)	2.5	(--)
Total Oil	12.0	9.7	(81)	7.9	(66)
Fischer Assay Gas	2.8	3.6	(129)	4.6	(164)
Fischer Assay Water	1.2	1.6	(133)	2.6	(217)
Bitumen on Raw Shale	1.3	0.6	(46)	0.4	(31)
Oxygen Content Raw Shale	17.8	---		21.5 ⁽³⁾	
Organic Oxygen	5.8 ⁽²⁾	---		9.5 ⁽³⁾	

(1) Given as weight percent of raw oil shale

(2) Smith (1961)

(3) Additional oxygen content at 25 days assumed to be organic

Table 3. - Microdistillation inspection data for Fischer assay oil.

<u>Oil Fraction</u>	<u>Oil Source</u>				
	<u>Fresh Shale</u>		<u>Preheated Shale</u>		
	<u>Wt%</u>	<u>Gravity</u>	<u>(5 days - 120°C)</u>		
			<u>Wt%</u>	<u>Gravity</u>	
Whole Oil	--	0.907	--	0.933	
IBP - 200°C	12	0.772	14	0.777	
200 - 315°C	17	0.858	18	0.870	
315 - 425°C	25	0.918	22	0.930	
425 C +	46	0.973	46	0.991	

from fresh and preheated oil shales proved that light ends were not lost. The specific gravities of various fractions were determined, and are also reported in table 3. The data show that the relative amount of material in each temperature range is approximately the same for each oil, and that the specific gravity of each fraction, throughout the boiling range, has increased with preheating. The microdistillation technique, developed at Tosco, provides distillation curves and data in agreement with those obtained by ASTM D-2892, but requires only 50 ml of oil.

A fluorescent indicator analysis (FIA), ASTM D-1319, was made on oils from fresh and 25-day, 120°C, preheated shales. These data, given in table 4, show increased concentrations of aromatic or polar materials, and

Table 4. - FJA analysis* of oil product.

<u>Component (vol%)</u>	<u>Oil Source</u>	
	<u>Fresh Shale</u>	<u>Preheated Shale</u>
	<u>(25 days - 120°C)</u>	
Saturates	26	22
Olefins	48	46
Aromatics	26	32

* ASTM D-1319

decreased concentrations of saturated or non-polar materials with preheating. This analysis is consistent with the increased specific gravity of oils formed from preheated shale.

An elemental analysis of oils from fresh and 25-day, 120°C, preheated shales supports the contention that oils from preheated shales are more polar. Analyses, given in table 5, show a significant increase in oxygen content for oil from preheated shale.

It may be concluded from the oil analyses that oil from preheated oil shale is of a lower quality than oil from fresh shale. This is shown by increased specific gravity throughout the entire boiling range which may be due to increased concentrations of aromatic compounds, oxygenated compounds,

Table 5. - Elemental analysis of shale oil.

Element	Oil Source	
	Fresh Shale (wt%)	Preheated Shale (25 days - 120°C) (wt%)
Carbon	84.7	83.7
Hydrogen	11.6	11.0
Oxygen	1.0	1.8
Nitrogen	1.8	1.6
Sulfur	<u>0.6</u>	<u>0.5</u>
Total	99.7	98.5

or both.

Product gas, formed by Fischer assay of fresh and 25-day, 120°C, preheated oil shale, was analyzed by gas chromatography (GC). GC analyses are given in table 6. Preheating oil shale causes significant changes in Fischer assay product gases: hydrogen and hydrogen sulfide are decreased; carbon monoxide and carbon dioxide are increased. The decrease in hydrogen and hydrogen sulfide may be due to a hydrogen deficiency caused by increased formation of water (table 2). More than 60 percent of the sulfur that did not form hydrogen sulfide in the preheated shale Fischer assay product gas was accounted for as other unidentified forms of gaseous sulfur products. Total sulfur content of Fischer assay product gas was determined by microcoulometry. The increased gas production of preheated shale is essentially accounted for by increased amounts of carbon monoxide and carbon dioxide.

The greatly increased concentrations of carbon mon- and dioxides, and water, suggest that an oxidation reaction, begun during preheating, was either completed or the combustion products released during Fischer assay. These products result from normal combustion or oxidation; their increased yields support the hypothesis that kerogen is partially oxidized in air at relatively low temperatures.

Apparently, oxidation of kerogen can take place at temperatures approaching those attainable on shale exposed to the summer sun, or generated by spontaneous combustion in stockpiled raw oil shale. For example,

Table 6. - GC analysis of Fischer assay gas product.

Component	Gas Source			
	Fresh Shale (mole %) (kg/t)		Preheated Shale (25 days - 120°C) (mole %) (kg/t)	
H ₂	28	0.6	9	0.2
CO	4	1.1	8	3.1
CO ₂	23	10.5	53	31.4
H ₂ S	7	2.3	1	0.6
C ₁	18	3.0	15	3.2
C ₂	8	2.5	7	2.6
C ₃	5	2.3	3	2.0
C ₄ ⁺	7	5.6	4	2.9
Total	100	27.9	100	46.0

Table 7. - Effect of low temperature heating on oil yield.

Length of Preheat	Oil Yield % of Fischer Assay
1 mo	94
2 mo	90
3 mo	84

* -65 mesh shale @ 70°C

when samples of -65 mesh oil shale were heated in air to 70°C for 1, 2 and 3 months, product oil yield was lowered. Fischer assay oil yields of these preheated oil shales are shown in table 7. After 3 months, preheating at 70°C Fischer assay produced only 84 percent of the oil produced from identical fresh shale.

Oil shale samples were preheated in air at various temperatures from 100 to 180°C for five days in order to determine temperature effects. Results of these experiments are shown graphically in figure 1. While there was essentially no change in oil yield after five days preheat at 100°C or less, at higher temperatures, oil yield decreased rapidly. At 180°C preheat for five days, oil yield was only 42 percent that of fresh shale.

The effect of particle size on Fischer assay oil yield losses due to preheating was examined in a series of 28-day experiments at 140°C. Results of these experiments are shown in table 8. It was determined that greatest losses were associated with smallest particle size (or greatest surface

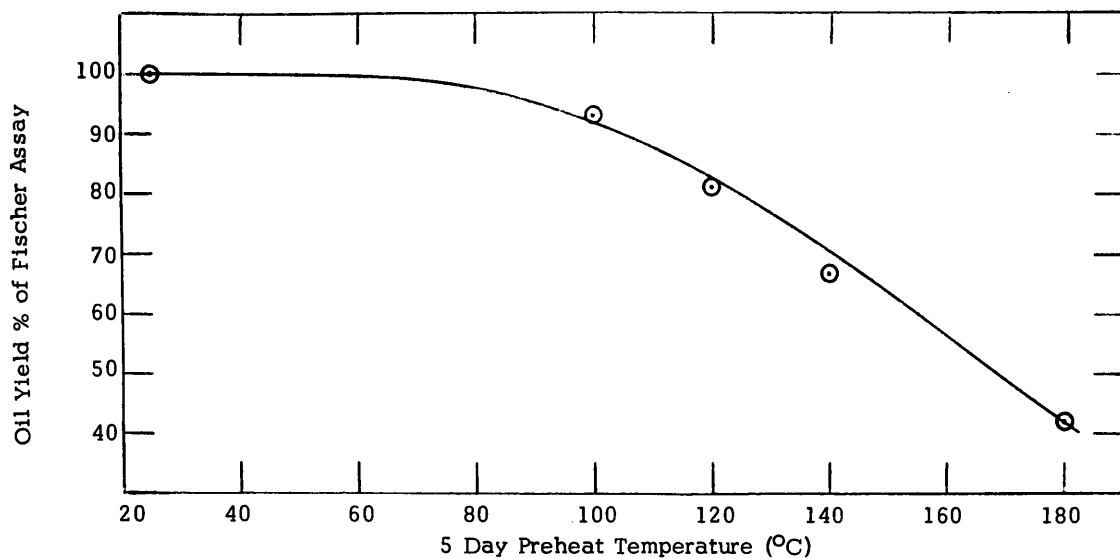


Figure 1. - Effect of preheat temperature on oil yield.

Table 8. - Dependence of preheating effect on particle size.

<u>Mesh Size (U.S.)</u>	<u>Oil Yield (wt% Fischer Assay)</u>
-1/4" + 8m	81
-8m + 20m	65
-65m	50

area). The direct relationship with surface area also supports the hypothesis that kerogen is partially oxidized under these mild preheating conditions.

Page (1967) has shown that oil yield is related to particle size. When a sample of shale is ground, the larger particles are richer in kerogen than the finer particles. For this reason, special precautions were taken in these particle size experiments. Individual Fischer assays were performed on each particle size fraction, with and without the preheating. The values in table 8 are comparisons of fresh and preheated shales of identical particle size, and obtained from the same grinding operation.

Conclusions

When oil shale is exposed to relatively mild thermal conditions in the presence of oxygen, a partial oxidation of kerogen occurs which is detrimental to subsequent oil production. A summary of data, supporting a partial oxidation hypothesis, is given in table 9. The decline in Fischer assay oil yield, noted with preheating in air at temperatures of 70 to 180°C, is accompanied by increased production of combustion products: CO₂ and water. Factors affecting this oxidation are: preheating temperature, preheat time, surface area, and presence of oxygen. Conditions need not be severe before a significant oil loss is noted. In addition to lower oil yield, quality of oil also decreases. Both of these factors would affect the economics of commercial oil shale processing.

Factors affecting oil yield and quality should be considered in the design of preheat systems for above ground retorting operations, where the presence of small amounts of oxygen could have an adverse effect on oil yield and quality. In in-situ

Table 9. - Evidence for partial oxidation.

	<u>Fresh Shale</u>	<u>Preheated Shale (25 days - 120°C)</u>
Raw Shale		
Fischer assay oil yield (wt%)	12.0	5.4
Oxygen content (%)	17.8	21.5
Heat of combustion (cal/g)	1630	1440
Fischer Assay Products		
CO ₂ (kg/t)	10.5	31.4
Water (kg/t)	12.2	26.4

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operations, where large amounts of shale are exposed to varying thermal conditions for long periods of time before retorting, there is also cause for concern. Above ground storage of shale from in-situ or stockpiling for above ground retorting, where summer sun can provide necessary thermal input, can result in oxidation of kerogen and may be an important factor in subsequent retorting operations. In the storage, handling and drying of shale samples for Fischer assay, it is necessary to remember that mild thermal conditions affect oil yield.

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