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Characteristics and Utilization of Oil Shale and Shale Oil

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This paper presents a general discussion of the properties and characteristics of oil shales, shale oils, and their products, and presents briefly the results of major phases of the research and process development work now in progress at the Laramie, Wyo., station of the Bureau of Mines. For the most part, the experimental work pertains to oil shale of the Green River formation in Colorado. The properties of products obtained by retorting the oil shale and refining its shale oil by several different processes are given. The properties of Green River oil shale and its products are also compared with those determined for several foreign oil shales.

THE term "oil shale" applies to a variety of fine-grained sedimentary rocks containing organic material which is only slightly soluble in petroleum solvents but is largely converted to oil by the application of heat. According to one theory, oil shale was formed in quiet lakes or seas by simultaneous deposition of mineral and organic matter in situ. This organic matter consisted of small plants such as algae, pollen, and spores, or a structureless jelly or sapropel derived from the plants as a result of bacterial action. Green River oil shale, particularly the rich oil shale, is a tough rock rather than a typical shale, and it is sometimes referred to as marlstone.

The Colorado oil shales are from the Green River formation and represent various grades of shale currently being mined and processed into shale oil and refined products at the Bureau of Mines oil-shale demonstration mine and plant near Rifle, Colo. The importance and extent of the Green River formation were recently described by Belser (3). He estimated that an area of 16,500 square miles exists in adjoining portions of Colorado, Utah, and Wyoming and that the portion of this formation assaying more than 15 gallons of oil per ton of shale contains 300 billion barrels of oil.

Extensive physical and chemical properties of Colorado oil shales are given by Frost et al. (11). These show the oil shales of the Green River formation to be highly laminated sedimentary rocks ranging in color from gray for a lean shale to dark brown for a rich shale. Chemical and petrographic examination of the Green River shales showed them to be composed essentially of calcite, dolomite, clay, and yellow organic material; the minor constituents are quartz, orthoclase, andesine, pyrite, marcasite, analcite, opal, black organic material, and small woody fragments.

Oil shales are commonly compared according to their oil yields by the modified Fischer retort method (19), and their properties are determined by standard analytical methods. In some instances, these standard methods are not entirely applicable to oil shales, which commonly contain both organic and inorganic materials in widely different amounts. Accordingly, improved analytical methods are required, particularly for determining the quantity and ultimate composition of the organic material in oil shale. This organic material consists chiefly of compounds of carbon, hydrogen, oxygen, nitrogen, and sulfur—elements that also occur in the inorganic portion of the shale. Some of the properties of Colorado (Green River) and several other oil shales are shown in Table I. These particular samples contained approximately 18 to 55% organic material. The total sulfur and total nitrogen contents ranged from 0.4 to 1.7% and 0.4 to 0.9%, respectively, whereas the carbon to hydrogen ratios of organic materials ranged from 6.3 to 11.1. The organic material with the highest carbon to hydrogen ratio yielded the least oil. This trend is further shown in Table II, where the data are given for shales in the order of increasing richness. In general, the richest shales from a given source showed the maximum conversion of available organic material to oil. These and other data indicated that the efficiency of the conversion to oil by the assay retorting procedure was dependent on the character of the organic material and, to a lesser extent, on the amount and character of the associated mineral matter in the shale.

Table III shows the composition of ashes from several shales. These data, together with petrographic and x-ray diffraction analyses, showed that the types and amounts of the mineral constituents varied greatly. The mineral portion of the Colorado shale consisted predominantly of calcite or dolomite, clay, quartz, plagioclase, and feldspar; in the Australian shale the mineral was chiefly quartz; and in the South African and Brazilian shales the mineral was principally clay. The Spanish shale was not examined petrographically or by x-ray diffraction, but its mineral is

TABLE I.   PROPERTIES OF VARIOUS OIL SHALES AND TORBANITES

	Colorado	Australia	South Africa	Brazil	Spain
Yield of assay oil, gal./ton	36	108	45	53	47
Yield of assay gas[a], cu. ft./ton	499	1125	960	649	943
Heating value, B.t.u./lb.	3080	9250	8610	4990	5380
Ash, %	60	44	44	64	63
Sulfur, %	0.73	0.44	1.01	0.73	1.68
Nitrogen, %	0.44	0.47	0.88	0.50	0.55
Organic material[b], %	18	55	54	35	35
C:H ratio of organic material[c]	7.1	8.1	11.1	6.3	7.7
Oil from organic material, %	75	73	33	55	50

[a] At 60° F. and 760 mm. mercury pressure; calculated to air-free basis according to oxygen content.
[b] Organic content approximated as ignition loss of shale minus its mineral CO₂ content.
[c] Calculated from ultimate analysis of raw shale by correcting for inorganic carbon in carbonates but not for hydrogen as possible water of crystallization in inorganic material.

TABLE II.   CONVERSION OF ORGANIC MATERIAL TO OIL BY MODIFIED FISCHER ASSAY

	Source of Oil Shale or Torbanite								
	Colorado			Australia			South Africa		
Sample No.	C:H Ratio[a]	Organic Content[b], %	Oil[c], %	C:H Ratio[a]	Organic Content[b], %	Oil[c], %	C:H Ratio[a]	Organic Content[b], %	Oil[c], %
1	5.6	7	55	11.5	34	25	12.4	55	24
2	7.0	15	69	8.1	55	73	11.1	57	31
3	7.1	18	75	7.8	95	78	11.1	54	33
4	7.8	32	70	..	..	..	9.8	54	49
5	7.6	33	71	..	..	..	8.7	66	58
6	7.6	39	73	..	..	..	..	..	..

[a] Of organic material by correcting ultimate analysis of shale for inorganic carbon in mineral carbonates but not for hydrogen as possible water of crystallization in inorganic material.
[b] Approximated as ignition loss of shale minus its mineral CO₂ content.
[c] From organic material in shale.

presumed to be principally clay. As shown in Table III, many minor elements, principally sodium and potassium, have also been detected in these shales.

For convenience, the organic material in oil shale is frequently called kerogen. Very little is known about kerogen, although obviously it is not a single chemical compound but a complex mixture of organic compounds which vary greatly in different oil shales. According to Cane (4, 5), kerogen is a noncrystalline substance, possibly a polymer of high molecular weight consisting of cyclic nuclei with long and short side chains and numerous cross linkages. Studies are in progress to determine the constitution of kerogen from Green River oil shale as a means of devising more suitable methods for its conversion to shale oil. An initial step in this study is the isolation or preparation of concentrated samples of kerogen from the shale. To date, methods for this purpose, which involved the removal of mineral matter by leaching the oil with acids and by gravity separations, have been only partly successful. Controlled degradation methods, such as oxidation, hydrolysis, and solvent extraction, are being used to separate the kerogen into smaller fragments. The identification of these fragments is being undertaken and may aid in determining the constitution of the original kerogen.

OIL-SHALE PROCESSING

The production of shale oil involves two essential steps in addition to mining and transportation of shale to the processing units: conversion of the solid organic material to a liquid or semiliquid and separation of this conversion product from the inorganic residue. Likewise, the conversion and separation can be accomplished in at least two essentially different ways—by heat and distillation (retorting) or by heat and extraction with solvents (thermal solution).

Probably the simplest retort is that used in the laboratory to determine the quantity of oil that may be obtained from a shale. By this Fischer-assay technique (19), in which a pot still charged with shale is heated externally, the organic matter is converted to gas, oil, and organic residue or coke; the first two distill from the

shale. A typical yield of products obtained from this retort, based on the organic material in the shale, is: gas, 10%; oil, 65%; and organic residue, 25%. Commercial retorts commonly are rated in efficiency of conversion by the percentage of the Fischer-assay yield of oil which they produce. Few exceed the assay yield; most do not equal it. Table IV shows some yields obtained in foreign retorts. Data from pilot plant retorts operating in this country are inadequate for comparison purposes. However, as most of the techniques that have been applied to retorting in the United States are represented in these foreign retorts, it can be expected that efficiencies of the same order of magnitude will be or have been obtained. As this table shows, most retorts succeed in producing 85 to 100% as much oil as is produced by assay. In other words, most commercial retorts recover only 55 to 65% of the organic matter as oil.

The reasons for this relatively low recovery of oil will not be completely understood until the mechanism of the conversion reaction has been clarified. The classical conception of this conversion reaction (12) is that it is a depolymerization reaction in which first a solid or semisolid bitumen is formed and then, by cracking of this primary product, oil, gas, and coke result. Although the basic reaction is not yet fully understood, some of the thermal characteristics of the reaction and the effects of temperature on the rate of reaction have been determined.

From a study of the heat required to retort a 28-gallon-per-ton shale, it has been found that the heat of the conversion reaction either is a negligible quantity, in comparison with the heat content of the shale, or is balanced by other heat effects. Table V shows some of the results obtained in this study.

The heat of retorting values, as determined, comprise the total quantity of heat required to raise the temperature of the raw shale from the base of 77° F. to the maximum shale temperature. This quantity includes the heat content of the mineral and other nonvolatile portions of the shale at the final retort temperature; the heat of reaction in converting the organic matter to gas, oil, and coke; the heat of decomposition of that portion of the mineral carbonates which decomposes under the experimental conditions and other heats of reaction due to changes in the mineral content

TABLE III.   COMPOSITION OF ASHES FROM OIL SHALES AND TORBANITES

	Colorado	Australia	South Africa	Brazil	Spain
			Per cent		
Ash	60	45	44	64	63
SiO₂	42.4	90.7	60.6	58.0	56.6
Fe₂O₃	4.7	0.9	3.1	8.5	9.1
Al₂O₃[a]	10.5	4.8	30.4	24.5	27.7
CaO	23.5	0.5	1.9	2.6	2.6
MgO	9.3	0.3	1.7	3.3	2.2
SO₃	2.0	0.2	0.1 −	0.7	0.5
Misc.[b]	7.6	2.6	2.2	2.4	1.3

[a] Principally Al₂O₃, obtained by subtracting the Fe₂O₃ from the R₂O₃.
[b] Principally Na₂O and K₂O, but the following elements have also been reported: Ag, As, Au, B, Ba, Be, Bi, Co, Cr, Cu, Hg, Ir, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Sr, Ti, Tl, U, V, Zn.

TABLE IV.   OIL YIELD OF FOREIGN COMMERCIAL AND PILOT PLANT RETORTS

Type Retort	Oil Shale	Assay Value of Shale, Gal./Ton	Oil Yield, % of Assay
Pumpherston	Scottish	31	85–90
Lantz	French	16–21	95–98
Marceaux	French	11–12	100–102
Davidson	Estonian	62	90
Tunnel oven	Estonian	50–60	94–99
Lurgi-Schweitzer	Estonian	50	100–111
Fuschun	Manchurian	12–15	80
Sven Bergh	Swedish	15	85–94

of the shale; the heat of vaporization of volatile products including water; and the heat content of the gas and oil vapors at the temperature of their exit from the retort.

The calculated heat content is based on the low temperature heat content determinations on several shales, extrapolated to retorting temperatures. These data are described by Shaw (15). The apparatus and method used in determining the heat of retorting are described by Sohns et al. (18).
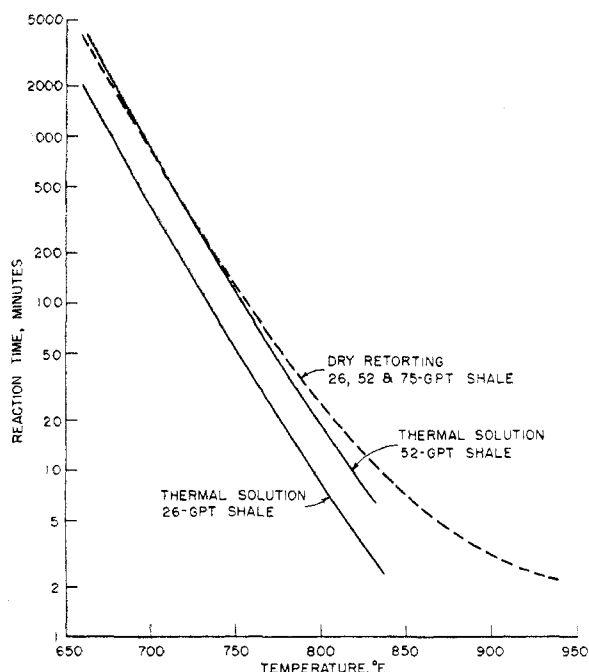

Figure 1. Reaction Time for 90% Decomposition of Kerogen in Colorado Oil Shales

The rate at which the organic matter is converted to oil and gas has been determined in two different systems: one simulates conversion conditions in a retort and the other conditions prevailing in a system in which a solvent oil is present during the conversion (14). The results of this study are shown in Figure 1. The conversion is rapid at temperatures above 850° F., 90% of the conversion taking place in less than 5 minutes. Yet, in most commercial retorts, the shale is retained at high temperatures for periods often amounting to several hours. These long retention times have been found by experience to be required to drive out all of the volatile conversion products. Several factors have made it difficult to approach in practice the retorting times indicated by these data to be adequate for the conversion. Among these are the low thermal conductivity of the shale, the low heat transfer rates attainable in some retorting processes, and the low rate of diffusion of the conversion products through large particles of shale.

Inasmuch as commercial oil-shale retorting is principally a large scale materials-handling process, practical mechanical considerations may limit the extent to which theoretically favorable conditions can be applied to design and operation of retorts. It would be desirable to use finely crushed shale from the standpoint of heat and mass transfer, but this procedure results in increased crushing costs and introduces the problem of separating fine dust from the retort products. Likewise, the richness of the shale affects the mechanics of retorting because rich shales tend to coke or become plas-

tic at high temperatures. For these and other reasons, retort design and operation necessarily may be a compromise between theory and good mechanical practice. Such considerations account in part for the wide variety of the hundreds of retorts that have been used or proposed.

One scheme which offered possibilities for shorter reaction time, lower temperature of operation, and higher recoveries of organic matter from the shale is the so-called thermal solution process. In this process, the shale is mixed with a solvent and heated to the desired reaction temperature for the time necessary to produce conversion. The solvent theoretically aids the initial depolymerization, facilitates heat transfer, and consequently permits lower temperature gradients in the system and less cracking of the conversion products. It dissolves the liquid conversion products and permits their removal from the gangue without distillation. Although any of a large number of solvents might be satisfactory, practical considerations dictate that solvents made up of fractions of shale oil be used.

This process has been investigated widely, and numerous claims are made for it. The rate of conversion obtained in this system are shown in Figure 1 with the rates obtainable in retorting. The rates of conversion in both systems are of the same order of magnitude. However, the quantity of organic material recovered as gas and oil in the thermal solution process exceeds considerably that recovered by retorting. The results reported by several investigators of this process are shown in Table VI. Although higher recoveries of organic matter are obtainable in this system than in retorting, some problems not encountered in retorting remain to be solved. Chief among these is the difficulty of separating the solvent and the dissolved product from the spent shale; this is due to disintegration of the shale particles during extraction into an extremely fine state and also to the high-boiling range and viscosity of the product which prevent separation by distillation or steaming. Filtration and washing appear to be the most suitable method of separation but would be costly because the organic matter represents only one sixth of the weight of an average oil shale. Also, close control of the thermal solution process would be required to prevent excessive cracking of the solvent.

Various retorting processes, too numerous to describe here, have been used or proposed, but it does not appear that a best method for producing shale oil from oil shale has been developed to date. Such development can only come about through research to determine the nature of the conversion reactions occurring and the effective means of controlling them. Theoretically, this research can lead to an increase in the recovery of oil from oil shale to as much as 140 to 160% of that obtainable by present methods and to production of an oil of much better quality than the usual retorted shale oil.

TABLE V. HEAT OF RETORTING ABOVE 77° F. FOR 28-GALLON-PER-TON SHALE

Maximum Shale Temp., ° F.	Heat of Retorting above 77° F., B.t.u./ Lb. of Raw Shale	Calcd. Heat Content (15), B.t.u./Lb. of Raw Shale
750	207	207
800	230	226
900	259	267
1000	323	310
1100	358	355

TABLE VI. COMPARISON OF THERMAL SOLUTION PROCESSES

	Materials Used		Thermal Solution Process Conditions		Yield of Gas and Oil, Wt. % of Organic Matter	
Reference	Solvent	Shale	Temp., ° F.	Pressure, lb./sq. inch	Thermal solution	Retorting
U. S. Bureau of Mines[a]	Shale oil–gas oil	Colorado	850	330	92	88
D'yakova (10)	Shale distillate	Russian	716–806	440–590	85–90	..
Dulhunty (8)	Benzene	Torbanite	662–752	1200	91	83
Dulhunty (9)	Torbanite oil	Torbanite	707–752	126–130	84	..
Smith and Stewart (16)	Aromatic kerosene	Scottish	752	320	63.3	55.8

[a] Unpublished.

CHARACTERISTICS AND COMPOSITION OF SHALE OIL

Shale oil normally is produced by a reaction at a temperature somewhat in excess of 750° F. Consequently, it contains materials similar to those found in substances such as tars prepared at high temperatures. It has a high content of unsaturated and aromatic materials; sulfur, nitrogen, and oxygen compounds are present in appreciable amounts. Although the crude oil is relatively stable, distillates prepared from it exhibit definite instability.

TABLE VII. COMPARISON OF AMERICAN SHALE OIL WITH OILS FROM FOREIGN SOURCES

Country and Retort	C:H Ratio	Sulfur, Wt. %	Nitrogen, Wt. %	Oxygen[a], Wt. %
United States (N-T-U)	7.35	0.74	1.78	1.64
Australia (Pumpherston)	7.14	0.56	0.52	1.62
South Africa (Salermo)	7.51	0.64	0.85	1.95
Sweden (Rockesholm)	8.97	1.65	0.68	1.71
Sweden (Lungstrom)	6.97	0.71	0.11	2.56
Scotland (Pumpherston)	6.99	0.35	0.77	1.36
Spain (Pumpherston)	7.21	0.40	0.68	1.13
France (Petit)	8.60	3.40	0.65	1.85
France (Marceaux)	7.81	3.00	0.53	1.27
France (Lantz)	7.60	0.61	0.54	1.67
France (Pumpherston)	7.60	0.51	0.90	1.71

[a] By difference.

Crude Shale Oil. Shale oils differ both because of differences in oil shale from which they are produced and because of retorting methods. The source of oil shale causes wide variations in the properties of the oil. Oils from many of the shales now being utilized are compared in Table VII. American shale oil has the highest nitrogen content and, except for French and Swedish oils, the highest sulfur content. Its degree of aromaticity, shown by the carbon to hydrogen ratio, is high (7.35) compared with petroleum (6 to 7.5), about normal for shale oils (7 to 9), and low by comparison with coal-carbonization products (9 to 18).

The retorting method has relatively little effect on the oil produced unless extreme conditions are employed. In general, retorting processes are designed for the greatest yield of oil, and the properties of the oils thus produced from a single source of shale are similar. Table VIII compares some properties of oils produced from Colorado shale by various processes. In addition, the composition of the naphtha as determined by a silica gel adsorption method (6) is particularly revealing. For all of the oils in Table VIII except the last three, the nitrogen and sulfur contents and the composition of the naphtha are similar. The amount of naphtha depends to a large extent on the recovery system of the retort. The results reported on the Hayes retort are for runs when the temperature was allowed to rise excessively. The extreme temperature conditions produced an oil of quite different properties, but at the expense of oil yield.

Crude shale oil as produced at the Rifle plant of the Bureau of Mines is a black, waxy solid at room temperature. As shown in Table IX, only 52.8% is distilled up to 300° C. under 40 mm. of mercury pressure. The deficiency in low boiling material and the presence of sulfur and nitrogen indicate some of the problems in preparing fuels. Detailed knowledge of the composition of the oil

TABLE VIII. PROPERTIES OF SHALE OILS PRODUCED BY VARIOUS METHODS OF RETORTING COLORADO SHALE

Retort	Compn. of Crude Oil, %			Compn. of Naphtha, Vol. %		
	Sulfur	Nitrogen	Naphtha	Paraffins-Naphthenes	Olefins	Aromatics
1947 N-T-U	0.74	1.78	2.7	33	48	19
1929 N-T-U	0.77	1.98	3.6	33	46	21
1929 Pumpherston	0.77	1.57	17.6	32	43	25
1945 Parry	0.87	1.81	14.9	27	48	25
1946 Royster	0.58	2.09	4.6	31	49	20
1948 Union Oil Steam retorting at 800° F.	0.71	1.89	2.7	21	55	24
	0.59	1.92	8.2	39	41	20
1946 Hayes	0.56	2.3	13.2	16	50	34
1946 Hayes	0.81	2.7	24.8	18	24	58
1946 Hayes	0.68	3.0	27.7	4	12	84

would be of great assistance in solving these problems. The complexity of the material causes difficulty in analysis, especially for unsaturates (6) and nitrogen (22), but methods have been developed which give satisfactory results in many cases. The presence of tar acids, tar bases, and wax is significant from the by-product standpoint.

Naphtha Fraction from Shale Oil. Naphthas produced from shale oils obtained from the same oil shale are very similar in composition, even though the amounts obtained may be quite different. Consequently, the analysis of naphtha from a crude oil produced in the Pumpherston retort from Colorado shale may be considered as representative.

Table X shows the breakdown by groups of the compounds found in the Pumpherston naphtha. A previous paper (2) describes the techniques used and the compounds found. The first group, that of tar acids, consists essentially of phenol and its homologs although some carboxylic acids are present. The tar bases contain pyridines, quinolines, and their homologs, as well as a portion of the pyrroles. Compounds which have been identified include phenol, p-cresol, 2-methylpyridine, 2,4,6-trimethylpyridine, quinoline, 2-methylquinoline, and pyrrole.

TABLE IX. BUREAU OF MINES CRUDE SHALE OIL ANALYSIS OF OIL PRODUCED BY N-T-U RETORT AT RIFLE, COLO.

PROPERTIES

Crude shale oil		Distillation	%	Sp. Gr.	° A.P.I.
Specific gravity	0.935	Naphtha (fractions 1–7)	2.7	0.791	47.4
° A.P.I. gravity	19.8	Light distillate (fractions 8–11)	15.7	0.872	30.8
Sulfur, %	0.74	Heavy distillate (fractions 12–15)	34.4	0.913	23.5
Nitrogen, %	1.78	Residuum	45.8	0.980	12.9
Pour point, ° F.	90	Loss	1.4		
Viscosity, S.U.S. at 100° F.	280				

ANALYTICAL DATA

Distillation at 760 Mm. Hg-Pressure

Fraction No.	Cut °C.	Cut °F.	%	Sum, %	Gravity Specific, 60/60° F.	° A.P.I., 60° F.		Naphtha Composite (Fractions 1–7), %
1	50	122	..	..	...	..	Tar acids	3.0
2	75	167	..	..	...	..	Tar bases	7.8
3	100	212	..	..	...	..	Neutral oil	
4	125	257	..	..	...	..	Paraffins and naphthenes	33
5	150	302	..	..	...	..	Olefins	48
6	175	347	..	..	...	..	Aromatics[a]	19
7	200	392	2.7	2.7	0.791	47.4		

Distillation at 40 Mm. Hg Pressure

Fraction No.	Cut °C.	Cut °F.	%	Sum, %	Gravity Specific, 60/60° F.	° A.P.I., 60° F.	Viscosity at 100° F. Kinematic, cs.	S.U.S.	Aniline point, ° C.	Cloud test, ° F.
8	150	302	3.4	6.1	0.854	34.2	2.5	34	37.4	Below 5°
9	175	347	5.3	11.4	0.864	32.3	2.1	37	37.8	10
10	200	392	7.0	18.4	0.886	28.2	6.1	48	41.6	25
11	225	437	8.3	26.7	0.894	26.8	10.6	59	..	45
12	250	482	7.2	33.9	0.905	24.8	13.6	72	..	60
13	275	527	7.9	41.8	0.920	22.3	22.7	110	..	80
14	300	572	11.0	52.8	0.929	20.8	40.8	190	..	95
Residuum[b]	..	..	45.8	98.6	0.980	12.9	..	..	..	..

[a] Including sulfur and nitrogen compounds.
[b] Carbon residue of residuum 7.5%; carbon residue of crude 3.4%; ash on residuum 0.1%; ash on crude 0.05%.

TABLE X. COMPOSITION OF NAPHTHA FROM COLORADO SHALE OIL

	Volume, %
Tar acids	0.8
Tar bases	5.6
Paraffins	21.2
Cycloparaffins (naphthenes)	8.2
Aliphatic olefins	25.9
Cyclic olefins	15.1
Aromatics	18.2
Sulfur compounds	3.4
Nitrogen compounds (other than tar bases)	0.9
Separation loss	0.7
	100.0

Among the saturated hydrocarbons (paraffins and naphthenes), the straight-chain paraffins predominate. A similar situation exists with the olefinic compounds, where more than half of the total olefins or 75% of the aliphatic olefins are straight-chain compounds. Olefins form 41% of the naphtha and aromatics are present to the extent of 18%.
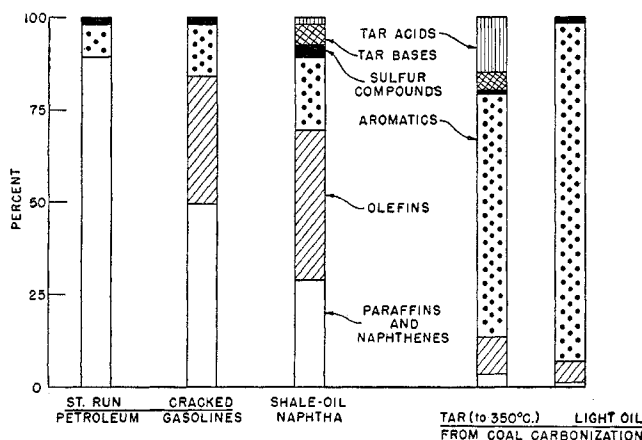

Figure 2. Constituents of Naphthas from Shale Oil, Petroleum, and Coal Tar

Sulfur compounds which are predominantly thiophenic comprise 3.4% of the naphtha. Nitrogen compounds, unextracted as tar bases, are present to the extent of 0.9%. These compounds are thought to be pyrrollic.

This analysis indicates the character of shale-oil naphtha to be intermediate between products of similar boiling range from petroleum and coal tar. Figure 2 shows this comparison.

The composition of equilibrium mixtures of isomers as required by thermodynamic considerations for various temperatures has been given by Taylor et al. (20). The composition of the C8 and C9 aromatics was determined in the study of Pumpherston naphtha. Table XI compares the relative amounts of the isomers found with the equilibrium mixtures at various temperatures. The composition appears to check closely with that postulated for 500° C. This value is not inconsistent with the temperatures expected in the eduction zone of the retort.

Naphthas prepared by cracking shale oil vary considerably depending on the conditions under which they were produced. However, thermally cracked naphthas are similar in many respects to the primary or straight-run product from shale oil.

Naphtha prepared from shale oil either by distillation or by cracking discolors within a few days until it is almost black and deposits a film of gum on the container. Table XII shows the gum content as determined by the A.S.T.M. method on a cracked naphtha (from N-T-U oil) and on various fractions prepared from it by distillation. The type compounds responsible for the gum was of particular interest. As the amount of gum increases with boiling point and the olefin content decreases, it appears unlikely that olefins are chiefly responsible. The sulfur

compounds are mainly of the residual or unreactive type. The nitrogen which was not removed as a tar base when calculated as pyrrole derivatives gave values proportional to the gum contents. Analysis of some of the gums has indicated them to be rich in nitrogen. Accordingly, much of the instability of shale-oil naphthas is attributed to pyrrole-type compounds.

Intermediate Distillates. Although complete analyses such as are given for the naphtha are not available on higher boiling materials, Table XIII indicates how the composition changes with boiling range. Modifications were necessary in order to adapt the silica gel method to the analysis of these materials (7). The increase in aromatic content at the expense of saturates and olefins is shown as is the increase in tar bases.

The next higher boiling fraction, that boiling between 625° and 1100° F., presents a much more difficult analytical problem. However, since it forms approximately one third of the crude oil and is the cracking stock for gasoline preparation, it is important to know something of its composition. A comprehensive analysis has not been accomplished, but Table XIV shows a summary of the groups present. Tar acids and bases are so slightly reactive in this range that they were not determined. The unusual thing about this fraction is the large content of nitrogen compounds. This group of compounds has been separated by florisil adsorption techniques (17). The presence of this material, the composition of which is unknown, should have considerable effect on processing methods.

REFINING OF SHALE OIL

The foregoing discussion of the chemical composition of shale-oil distillates presents a rather clear picture of the composition of the material boiling in the gasoline range and a good breakdown into types of compounds contained in the light distillate fractions but insufficient information on the higher boiling fractions to be able to make a reasonable prediction of their behavior under cracking conditions. The gas-oil fractions used as cracking stock contain hydrocarbons similar in structure to those found in petroleum but apparently not in the quantities found in most petroleums. This is evident from the lower yields of gasoline and higher yields of gas and coke which are obtained when shale-oil stocks are cracked as compared with the yields of these products from cracking petroleum stocks of similar boiling range. The analytical and experimental cracking results both indicate the presence of compounds which contribute little to the formation of gasoline during cracking but react readily to form gas and coke.

From a consideration of the physical properties of the gas-oil fraction of shale oil, it was suggested (13) that the molecular structure of a large percentage of the fraction would be represented by a partly hydrogenated polycyclic compound. This type compound may be either hydrocarbon or heterocyclic, containing sulfur, nitrogen, and possibly oxygen, and probably has relatively short side chains. In addition to this polycyclic material, high boiling shale-oil fractions contain appreciable quantities of paraffinic ma-

TABLE XI. EQUILIBRIUM ATTAINED BY SHALE-OIL NAPHTHA

Compound[a]	Pumpherston Naphtha	Thermodynamic Equilibrium			
		300° C.	400° C.	500° C.	600° C.
C8-benzenes					
Ethyl	9	5	8	10	13
p-Xylene	19	23	22	21	20
m-Xylene	46	51	48	46	44
o-Xylene	26	21	22	23	23
C9-benzenes					
Isopropyl	0	1	1	1	2
n-Propyl	0	1	2	3	4
1-Methyl-4-ethyl	11	8	11	12	13
1-Methyl-3-ethyl	22	12	17	20	23
1-Methyl-2-ethyl	25	4	6	8	10
1,3,5-Trimethyl		21	17	14	12
1,2,4-Trimethyl	42	53	46	42	36

[a] All values in volume per cent.

TABLE XII.   GUM FORMATION AND NITROGEN CONTENT OF CRACKED NAPHTHA

	Naphtha					
	Origi-nal	Tar acids and bases removed	Fraction			
			1	2	3	4
Boiling range, ° F.	....	....	Up to 250	250-300	300-350	350-400
Neutral naphtha, %						
Paraffins and naphthenes	58	....	63	50	51	54
Olefins	30	....	35	37	28	23
Aromatics	12	....	2	13	21	23
Gum, mg./100 ml.	288	164	5.8	7.4	218	540
Tar acids, %	1.0	....	2.0	0.0	0.2	2.5
Tar bases, %	4.1	....	0.7	1.6	4.9	9.4
Nitrogen, %	0.41	....	0.15	0.28	0.63	0.69
Nitrogen (after tar base removal), %	....	0.14	0.02	0.06	0.16	0.16
Calculated pyrroles mg./100 ml.	....	720	85	320	810	1115

TABLE XIII.   EFFECT OF BOILING RANGE ON HYDROCARBON GROUP DISTRIBUTION OF DISTILLATES FROM N-T-U SHALE OIL

	Naphtha	Kerosene	Light Distillate
Boiling range, ° F.	267-480	266-579	267-626
50% boiling point, ° F.	353	465	565
Tar acids, %	3.0	4.7	4.4
Tar bases, %	7.8	10.9	12.2
Neutral oil, %			
Paraffins and naphthenes	33	27	26
Olefins	48	48	33
Aromatics (including some sulfur and nitrogen compounds)	19	25	41

TABLE XIV.   COMPOSITION OF GAS-OIL FRACTION (625-1100° F.) FROM N-T-U SHALE OIL

	Volume %
Paraffins and naphthenes	20
Olefins	16
Aromatics (and some sulfur compounds)	21
Nitrogen compounds (including oxygen and remaining sulfur compounds)	43
	100

terial, as shown by the high pour points and wax content of these oils.

Additional research now in progress must be completed before the molecular composition of these high boiling shale-oil fractions will be known with certainty, but the above conception of the structure—that it consists of a large percentage of polycyclic material—explains satisfactorily the behavior of these stocks in thermal and catalytic cracking reactions. Cyclic hydrocarbons and probably heterocyclic compounds dehydrogenate and dealkylate under cracking conditions with little rupture of the ring taking place. These denuded rings then tend to condense to more complex polycyclic materials, ending eventually in coke. Lower total yields of gasoline must be taken in cracking a shale-oil stock than in cracking a petroleum stock of similar boiling range if residuals of comparable properties are to be produced. It may be possible to produce total yields of gasoline from a shale-oil stock of about the same magnitude as would be obtained from a petroleum stock of like boiling range, but in the former instance it would appear necessary to crack to coke or a much heavier fuel oil than would be produced from the petroleum stock at the same depth of cracking.

In catalytic cracking of shale-oil stocks, another factor in addition to the possible polycyclic nature of the cracking stock contributes to high coke formation and low yields of gasoline with rapid deterioration of the catalyst. This is the high nitrogen content of the oil. Shale-oil fractions in the gas-oil boiling range contain as much as 2% nitrogen. The inhibition effect of organic nitrogen compounds on cracking catalysts is well recognized in the petroleum industry. Possibly a technique can be developed in catalytic cracking of shale-oil fractions to inhibit the effect of nitrogen compounds on the cracking catalysts and consequently improve the yields obtained by this process.

Table XV shows the characteristics of thermally and catalytically cracked naphthas from a gas-oil feed stock. The much greater proportion of aromatics and olefins in the catalytically cracked naphtha produces gasoline of considerably higher octane number than that from thermal cracking. The sulfur and nitrogen contents of both untreated naphthas are high, and the tetraethyllead susceptibility consequently is low.

Hydrogenation of shale oil appears, from data so far obtained, to offer the best possibilities of producing good quality products in high yield from shale-oil stocks. This process will remove sulfur, nitrogen, and oxygen from the oil as hydrogen sulfide, ammonia, and water—all easily separable from the liquid products. It will control or entirely prevent the condensation to coke of the polycyclic compounds and will promote ring rupture with consequent formation of high yields of low boiling distillates of good refining characteristics.

TABLE XV.   CHARACTERISTICS OF CRACKED SHALE-OIL NAPHTHAS

| | Shale-Oil Gas Oil Cracking Stock | Cracked Naphtha | |
		Thermal	Catalytic
Cracking conditions			
Temperature, ° F.	....	875	900
Pressure, lb./sq. inch	....	300	Atm.
Reaction time, sec.	....	1800	....
Liquid hourly space velocity	....	....	1.0
Yield, volume % of charge	....	23.3	16.5
Properties			
A.S.T.M. distillation, vol. % (760 mm.), ° F.			
Initial boiling point	449	138	135
10	509	212	203
50	569	305	300
90	630	366	357
End point	668	410	387
Specific gravity, 60/60° F.	0.8907	0.7783	0.7808
Sulfur, wt. %	0.70	0.97	0.76
Nitrogen, wt. %	1.58	0.56	1.68
Tar acids, vol. %	....	0.25	1.0
Tar bases, vol. %	....	4.25	9.9
Composition of neutral oil, vol. %			
Paraffins and naphthenes	....	49	16
Olefins	....	35	54
Aromatics (including sulfur and nitrogen compounds)	....	16	30
Octane number, motor method (untreated sample)			
Clear	....	64	74.9
+ 1 ml. TEL	....	66.8	75.5
+ 3 ml. TEL	....	70.9	76.7

TABLE XVI.   CATALYTIC HYDROGENATION OF N-T-U SHALE OIL USING COBALT-MOLYBDATE CATALYST

| | N-T-U Shale Oil | |
	Crude	Hydro-genated
Process conditions		
Temperature, ° F.	....	825
Pressure, lb./sq. inch	....	1000
Liquid hourly space velocity	....	1.0
Liquid recovery, vol. %	....	90
Properties		
A.S.T.M. distillation, vol. % (760 mm.), ° F.		
Initial boiling point	356	116
5	479	198
10	517	273
20	646	353
50	703	518
70	a	618
90	....	751
End point	....	759
Specific gravity, 60/60° F.	0.9301	0.8272
Pour point, ° F.	90	70
Viscosity, S.U.S. at 100° F.	310	34
Sulfur, wt. %	0.69	0.03
Nitrogen, wt. %	1.91	0.44

a Cracking.

TABLE XVII. PROPERTIES OF STRAIGHT-RUN DISTILLATE FUEL OILS FROM N-T-U SHALE OIL

	Grade No. 1		Grade No. 4	
	Specification (1)	Product	Specification (1)	Product
Flash point, °F., min.	100	115	130	150
Pour point, °F., max.	0	-20	20	30
Water and sediment, vol. %, max.	Trace	nil	0.50	0.02
Carbon residue on 10% bottoms, wt. %, max.	0.15	2.3	....	....
Ash, wt. %, max.	....	....	0.10	Trace
Distillation temperatures, °F.				
10% point, max.	420	401	....	....
End point, max.	625	576	....	....
Viscosity, Saybolt Universal at 100°F., sec.				
Max.	....	....	125	45
Min.	....	....	45	....
Viscosity, kinematic at 100°F., cs.				
Max.	2.2	3.1	....	....
Min.	1.4	....	....	....
Gravity, °A.P.I., min.	35	33.6	....	....
Corrosion, copper strip, 3 hours at 122°F.	Pass	Pass	....	....
Vol. % of crude shale oil	....	17	....	38

Table XVI shows the manner in which shale oil can be improved by hydrogenation. These results do not represent the ultimate as they were obtained in the early stages of the investigation of this process. Large reductions in sulfur and nitrogen content can be obtained, the distillation characteristics of the oil improved, and a more saturated, stable oil produced.

Shale oil as produced by common retorting methods contains little material boiling in the gasoline range. However, quite large volumes of distillates, which boil in the range of commercial distillate fuel oils, can be obtained by simple fractionation. Table XVII shows the characteristics and yields of shale-oil distillates from N-T-U crude shale oil from which No. 1 and No. 4 distillate fuel oils might be manufactured. The percentages shown in this table are not the maximum quantities of these distillates that might be produced from this oil, for these quantities can be varied considerably depending on the boiling range of the fraction taken. The data show, however, the extent to which specifications for these types of fuels can be met. The specification for carbon residue of 10% residuum is the most difficult to meet for No. 1 fuel oil, indicating that additional treatment will be required. Pour point is the more difficult specification to meet on No. 4 fuel oil, and dewaxing may be required for fuels of this boiling range for some uses. Diesel fuels having cetane values of 35 to 40 can be made from distillates in this boiling range. Hydrogenation, chemical treatment, or solvent extraction, together with pour-point reduction, may be required to manufacture Diesel fuels to meet specifications for high speed Diesel engines.

As much as 85% of crude N-T-U shale oil may be utilized in the manufacture of No. 6 fuel oil, as shown in Table XVIII, whereas 100% of the oil will meet all specifications for No. 5 fuel.

SECONDARY PRODUCTS FROM SHALE OIL

Waxes. Shale oils contain considerable quantities of paraffin wax (21). A yield of 18.1% of wax was obtained from the gas-oil fraction (625° to 1100° F.) by extraction, using methyl ethyl ketone at 32° F. The wax consists of 82.5% saturates and 17.5% olefins. No aromatics are indicated by ultraviolet absorption, and the sulfur and nitrogen are very low. The wax, after solvent extraction and clay filtration, has the following physical properties: no moisture; less than 0.1% oil; Saybolt color +30; melting point of composite sample is 133° F. (a mixture of hydrocarbons with melting points ranging from 105° to 144° F.); odorless; tasteless; meets heat stability requirements for food containers but does not pass the carbonizable test owing to the presence of the olefins. A wax obtained by acid and clay treating of the solvent-extracted wax is free of olefins and meets the specifications of fully refined petroleum paraffin wax.

A microcrystalline wax which also consists of saturated and unsaturated hydrocarbons has been solvent-extracted from deasphaltized, uncracked shale-oil residuum. The shale-oil microcrystalline wax resembles that from petroleum in crystal structure and melting point, but the other physical properties are not definitely known at this time.

Asphaltic Products. Crude shale oil yields residuums which might be useful for the manufacture of paving materials and other types of asphalt. Table XIX shows a comparison of 100-penetration asphalts prepared by the vacuum distillation of N-T-U crude shale oil and two petroleum crude oils. The crude shale oil yielded 16% of 100-penetration (at 77° F.) asphalt which differed from the petroleum asphalts in several respects. As the preparation of the shale oil involved destructive distillation, the asphalt had positive spot tests and low values for bitumen and bitumen soluble in carbon tetrachloride, which were indicative of previous cracking. The shale-oil asphalt was more susceptible to hardening by the loss-on-heating test and had a lower ductility than the petroleum asphalts. It contained considerable wax but less sulfur than the petroleum asphalts and had a higher temperature susceptibility—for example, the Furol viscosities of the shale-oil asphalt at 210° and 275° F. were only approximately one third those of the petroleum asphalts.

TABLE XVIII. PROPERTIES OF STRAIGHT-RUN RESIDUAL FUEL OILS FROM N-T-U SHALE OIL

	Grade No. 5		Grade No. 6	
	Specification (1)	Product	Specification (1)	Product
Flash point, °F., min.	130	170	150	165
Water and sediment, vol. %, max.	1.00	0.2	2.00	0.14
Ash, wt. %, max.	0.10	0.03	....	....
Viscosity, Saybolt Universal at 100°F., sec.				
Min.	150	190	....	....
Viscosity, Saybolt Furol at 122°F., sec.				
Max.	40	25	300	43
Min.	....	....	45	....
Vol. % of crude shale oil	....	100	....	85

TABLE XIX. PROPERTIES OF 100-PENETRATION ASPHALTS FROM PETROLEUM AND SHALE OIL

(Estimated from properties of series of asphalts of different penetrations)

	Petroleum		Shale Oil from Colorado Oil Shale
	Oregon Basin, Wyo.	Byron, Wyo.	
Yield from crude oil, %	45	27	16
Bitumen, %	100.0	100.0	99.8
Bitumen soluble in CCl4, %	100.0	100.0	99.7
Carbon residue, %	20	25	20.7
Ductility at 77° F. (5 cm./min.), cm.	100+	100+	98
Fire point, %	655	720	695
Flash point, %	565	625	575
Furol viscosity at 210° F., sec.	1,300	1,180	403
Furol viscosity at 275° F., sec.	160	140	53
Loss on heating (at 325° F.), %	0.00	0.03	0.06 to -0.03
Nitrogen, %	.....	.....	2.84
Penetration			
32° F., 200-gram wt., 60 sec.	21	19	10
60° F., 100-gram wt., 5 sec.	30	33	19
77° F., 100-gram wt., 5 sec.	100	100	100
Penetration at 77° F. of residue from loss-on-heating test,	85	82	69
Softening point, ° F.	113	112	113
Specific gravity at 77/77° F.	1.026	1.024	1.019
Spot tests[a]	Negative	Negative	Positive
Sulfur, %	4.8	3.9	0.6

[a] By the Oliensis and modified Oliensis tests.

Tar Acids and Bases. The quantities and characteristics of the tar-acid and tar-base materials which may be extracted from the light shale-oil distillates were previously discussed. These materials will be by-products of shale-oil refining operations unless hydrogenation or other means of destroying the compounds are used. The tar acids, consisting principally of phenolics, are present in shale-oil distillates in concentrations ranging from

about 2 to 5%. Coal tar extraction and purification processes have been found applicable to shale oils, and the products should find a ready market as wood preservatives and in the manufacture of plastics and pharmaceuticals. The tar bases, consisting principally of pyridine and quinoline homologs, are present in about twice the concentration of the tar acids. No large ready market appears available for the tar bases, although their chemical structure suggests numerous uses such as insecticides, chemical intermediates, and pharmaceuticals. The octane number of several pyridine homologs is over 100; this suggests the retention of the bases in the motor fuels if their deleterious properties can be inhibited.

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SHALE OIL REFINING

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As a basic approach to the study of the refining of Colorado crude shale oil, thermal cracking and chemical treatment processes were carried out on a demonstration plant scale to explore the variability of yield and quality of finished products and of certain distillates which could be suitable as charge stocks for other refining processes. Some flexible thermal operations as topping, visbreaking, recycle cracking, and coking have been made under exploratory operating conditions, which are not necessarily optimum for the purposes intended, to produce a pipe-line crude, cracked gasolines, coker distillate, and residues.

Various gasolines and Diesel fuels, meeting most of the petroleum industry specifications for such products, have been produced by chemical treatment and by rerunning where necessary. Usage of treated cracked gasoline and Diesel fuel in local vehicles and equipment indicates excellent performance characteristics. The thermal cracking studies were made on 100- to 300-barrel-per-day fresh feed charge distillation-cracking plant of industrial type design; the data here could be expected to be duplicated in large scale equipment. This is the first exploratory study on this scale made on crude oil from Colorado oil shale.

THE increased demand for petroleum products resulting from World War II and the possibility that supplemental sources of liquid fuels may be needed in the future, led to passage of the Synthetic Fuels Act in 1944. This enabling act, of 5 years' duration, and the subsequent 3-year extension act of 1948 authorized the experimental program on synthetic fuels now being conducted by the Bureau of Mines. Under this program, coal and oil shale are being studied as sources of synthetic fuels. The oil-shale work has been divided into two sections. Research and basic studies are being conducted at the Petroleum and Oil-Shale Experiment Station at Laramie, Wyo. Larger scale pilot- and demonstration-plant work as well as mining research are being carried on at the Oil-Shale Demonstration Plant at Rifle, Colo. The project at Rifle is on the Naval Oil-Shale Reserve.

To produce shale oil, it is necessary to mine the shale, crush and screen it to size, and then convert the solid carbonaceous material of the shale to oil by retorting. To produce finished products such as motor and Diesel fuels the crude oil must then be refined. Thus,

the work naturally falls into three categories—mining, retorting, and refining.

Research and development work on mining oil shale has been done by the mining staff at Rifle. The techniques and mining methods developed have been markedly successful, and large tonnages of oil shale have been mined at low cost. Low cost mining is a prerequisite to the development of an oil-shale industry.

In the field of retorting, several experimental programs are now under way at Rifle. The first work undertaken was construction of two batch-type internally fired N-T-U retorts, each with a shale capacity of 40 tons. N-T-U retorts were selected because earlier work by the Bureau of Mines (1) in 1926–29 at Rulison, Colo., had shown them to be adapted to Colorado shales, and for initial work a process was needed that would produce oil for refining studies and serve as a starting point for a retorting program. These two units were put into operation in the spring of 1947. A substantial program of experimental operations has been completed, and the retorts now are on a production basis to supply