The Organic Matter in Oil Shales[1]

By Ralph H. McKee and Ralph T. Goodwin

COLUMBIA UNIVERSITY, NEW YORK, N. Y.

THE fundamental problem of the shale-oil industry is to produce from shale an oil that will compete favorably in a physical, chemical, and economic sense with petroleum from wells. The solution of this problem must be based on exact information attained by systematic research. This fundamental information involves the values of all the physical constants, a knowledge of the manner in which oil-forming material decomposes, and information concerning the chemical composition of the organic material that undergoes decomposition to form the oil and other products.

The motor-fuel and lubricating oils of the near future will largely come from oil shale, and therefore we should determine accurately and without delay the nature of American oil shales and the methods available for the production of oil from this material. In this paper a careful study of the organic material present in oil shales has been made by the use of the action of solvents, chemical reagents, heat, and ultimate analysis.

The pyrolysis curves show unexpected exothermic and endothermic differences between shales from different localities.

The action of solvents and chemical reagents confirms previous views on kerogen, but shows that it is highly unsaturated in character.

Ultimate analyses show a variation in carbon-hydrogen ratio in shales from different formations. A rough relation exists between this ratio and the oil yield from a shale.

An intermediate, highly unsaturated, high melting product between the kerogen of the shale and the shale oil has been isolated and studied. This intermediate product on cracking gives a shale oil much more "saturated" than the material before cracking, a phenomenon without parallel in the cracking of well petroleum.

The nitrogen of shale appears to be present in several forms. A few shales carry practically no nitrogen. In retorting, a part of the nitrogen comes off at a low temperature in the form of ammonia, pyridines, and isoquinolines, while another part comes off only at a higher temperature, principally as ammonia. The use of superheated steam increases the yield of ammonia.

The carbon-hydrogen ratio of oil shales has been used by Robertson[5] to indicate the possible yield of oil from a shale. The rule, as stated, is that the yield of oil varies directly as the percentage of organic matter and inversely as the carbon-hydrogen ratio. In other words, if the organic percentage is high and the carbon-hydrogen ratio is low, then the shale will give a good yield of oil. The greater the proportion of hydrogen the larger will be the yield of oil.

CHEMICAL COMPOSITION

Oil shale varies considerably in character, both physical and chemical, in different parts of the world and in different geological formations. There has been more experimental work on Scottish oil shales than on shales from other parts of the world, but owing to the different nature of the shale in other areas, this work will not generally apply. However, there are a few essential characteristics that are common to all oil shales.

In order to determine whether the organic matter varies in composition, and, if so, what the nature and extent of the variation is, proximate and ultimate analyses were made on several different types of oil shales—that is, shales that yield products differing in character upon destructive distillation. A shale from Elko, Nevada, will yield an oil containing a high percentage of paraffin wax. A shale from Colorado gives an oil of the mixed base type, whereas certain Utah shales yield asphaltic oil.

Oil shales cannot be graded as to oil content by the method of proximate analysis. There seems to be no fixed ratio between the volatile matter in shale and the amount of oil that can be recovered by a laboratory assay. It has been demonstrated that many variable factors in retorting have a definite effect on the quantity and quality of the oil produced. Some of these factors are—rate of heating, time of heating, pressure in retort, use of steam or other atmosphere such as hydrogen, and the final temperature reached.[1,*]

In ultimate analyses the organic or combustible part of the shale was analyzed for its elemental constituents—carbon, hydrogen, nitrogen, sulfur, and oxygen—by the methods outlined by Fisher.[2] The Kjeldahl-Gunning-Arnold method[3] was employed for the nitrogen estimations. The sulfur was estimated by heating about a 1-g. sample of the dried shale with about 10 g. of Eschke's mixture, using the double crucible methods as described by Sadtler.[4]

GENERAL RESULTS OF ULTIMATE ANALYSES OF OIL SHALES

SHALE	C	H	N	S	O (by Diff.)	Ash	C:H Ratio	Oil Gal./ Ton
Scotch[5] (Broxburn)	19.51	2.48	0.69	1.36	3.31	72.65	7.9	23.3
Scotch[5] (Pumpherston)	24.88	3.67	0.68	0.80	8.07	61.90	6.8	31.0
Australian[5] (Commonwealth)	63.58	7.81	0.81	0.43	4.41	22.96	8.11	10.8
Utah[6] (Soldiers' Summit)	13.51	1.70	0.39	0.28	18.00	66.12	7.9	16.8
Nevada[6] (Elko)	37.65	5.43	0.39	1.08	10.04	46.21	7.21	86.8
Colorado (Grand Valley)	23.67	3.50	0.66	1.78	3.79	66.60	6.8	63.5
California (Ione)	50.95	5.77	0.42	2.12	18.06	22.68	8.8	51.8
Lignite[7] (Black, U. S.)	54.91	6.39	1.02	....	32.54	5.14	8.6	....
Crude Shale Oil[8] (Autun, France)	79.70	11.80	....	....	8.50	....	....	....
Crude Petroleum (P. Heavy)	84.9	13.7	....	....	1.40	....	....	....
Crude Petroleum (Calif.)	84.00	12.70	1.70	0.75	1.20	....	....	....
Asphalt[9] (Trinidad)	82.60	10.50	0.50	6.50	nil	....	....	....
Cannel[10] (English)	79.23	6.08	1.18	....	7.24	4.84	....	....

The low hydrogen content in an oil shale has been stated as a reason for the unusually high percentages of unsaturates (part of oil dissolved by 95 per cent sulfuric acid) in shale oils.[11] Analysis of Colorado shale shows a carbon-hydrogen ratio of 6.7 in the undistilled shale, while the ratio in the product obtained from this same shale under reduced pressure is 5.5. The original shale has an excess of about 18 per cent of carbon over that necessary to form an oil having a ratio as determined. It is inferred that the higher the hydrogen content of the shale, the greater will be the percentage of saturates in the oil, and cracking of the oil during the first or subsequent distillations would tend to increase the saturation of the oil if the hydrogen content of the decomposition products had a higher ratio to the carbon content. Accord-
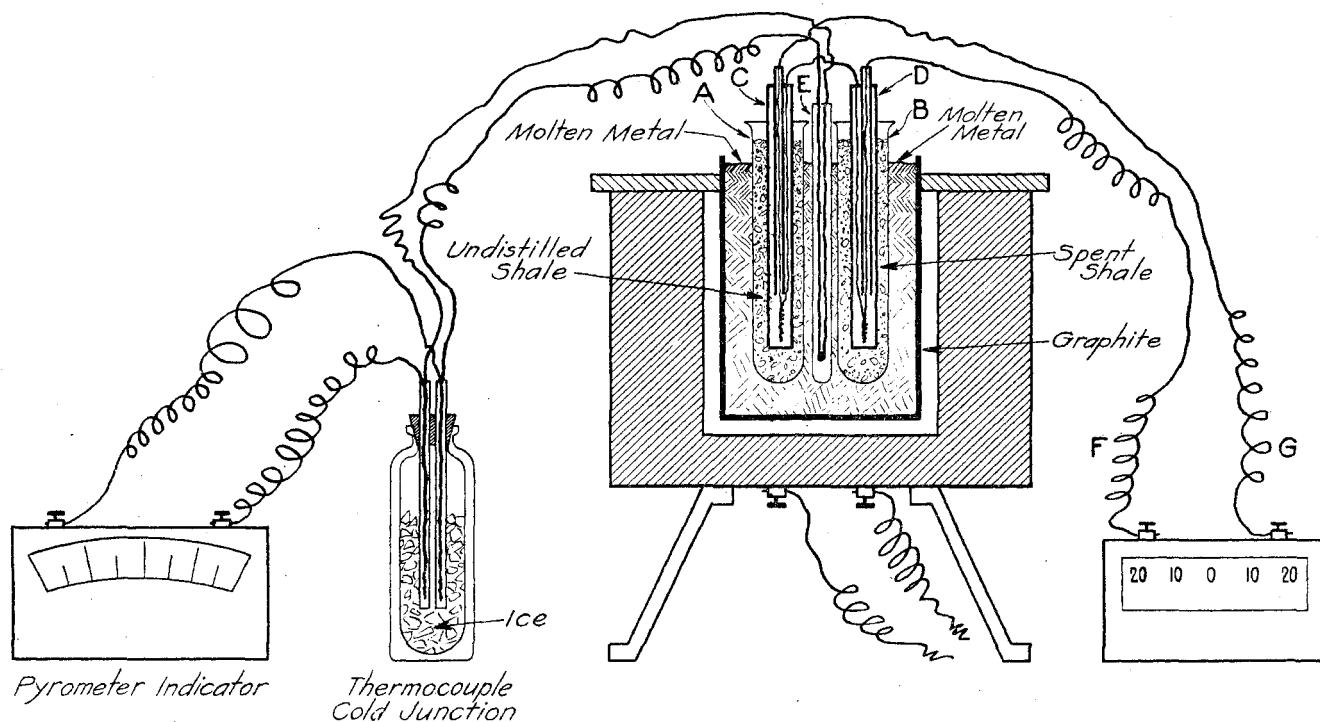
FIG. 1

ingly, if the shale is heated slowly, the yield of oil is less, but its content of saturated compounds is increased. The results obtained in this investigation agree only in part with this view.

THERMAL DECOMPOSITION OF THE ORGANIC CONTENT OF OIL SHALES

This work on pyrolysis was carried out because of the inconclusive nature of the evidence supporting the current conceptions of oil-shale distillation. McKee and Lyder[12] report quantitative results in the decomposition of shales. They determined the amount of heat involved in the conversion of the organic matter in shale to oil and other products. The reaction is endothermic and the values for three different types of shales range from 421 to 484 cal. per g. of oil and gas produced.

In this work no attempt was made to calculate the thermal balance of distillation, but simply to show that there are at different temperatures definitely exothermic and endothermic reactions, which in the complete distillation balance more or less as to quantity so that the actual heat consumed is small.

The experimental method employed consisted in heating side by side, under the same conditions, a shale that had not undergone pyrolysis and a shale that had undergone complete pyrolysis. The extent to which the temperature of the undistilled shale became higher or lower than that of the "spent" shale in the various stages of the pyrolysis was determined by means of a differential arrangement of thermocouples. The essential parts of the apparatus used are shown in Fig. 1.

The method of plotting the differential heating curve is the same as that commonly employed in metallurgical work. The galvanometer deflections are noted each 5 min. and then the differences in temperature between the new and spent shale are plotted as abscissas against the actual temperature of the metal bath as ordinates. The curves as given represent for each shale the average of four closely agreeing determinations.

Fig. 2 shows the thermal-decomposition curve for an oil shale from Green River, Wyoming. Fig. 3 shows the thermal-decomposition phenomena of an oil shale from Grand Valley, Colorado. A sample of Ione, California, shale material under thermal examinations indicates several exothermal and endothermal points. (Fig. 4, Curve II)

Hollings and Cobb[13] made a thermal study of the carbonization of coal and the evidence obtained showed that coal went through several stages of decomposition, some being accompanied by exothermic and others by endothermic heat changes. Curve I of Fig. 4 shows the thermal decomposition phenomena of such lignitic coal.

PRIMARY REACTIONS IN THE DECOMPOSITION OF OIL SHALE

When oil shale is heated with exclusion of oxygen, chemical reactions occur that are highly complex and a variety of new substances appear in place of the original kerogen. The yield and character of these products may be varied widely by changing the factors in the process of retorting, such as temperature, pressure, time, and contact surface.[14] An examination of a large number of suggested "processes" for the treatment of oil shales, and the conflicting ideas on which they are designed, indicates the importance of a knowledge of the primary reactions in the decomposition of oil shale.

The object of this part of the present investigation was to study the primary volatile products liberated from the kerogen by heat. In order to avoid secondary reactions as far as practicable, distillation at reduced pressure was used in obtaining these primary products. It is believed that secondary reactions have been largely prevented by reducing to a minimum the temperature and the time of contact of the volatile matter with heated surfaces.

It is a generally known fact that the overheating or cracking of well petroleum will give products of lower boiling point and an increase in the percentage of unsaturated compounds. Knowing this fact regarding the action of well petroleum on overheating, it has been assumed that shale oil acts likewise under the same conditions. Many have advocated retorting in a current of steam or under reduced pressure.[15, 16]

The oil-yielding materials of different shales, and even of a single shale, differ in constitution, in their manner of breaking down when undergoing destructive distillation, in their reactions with chemical reagents, and in their decomposition temperatures. Because of these variations each shale presents a distinct problem. It is thus obvious that the refining of shale oil really begins with the retorting, and that the production of a satisfactory finished product from any one type of shale will not represent a universal solution of the retorting problems of the American shale-oil industry.
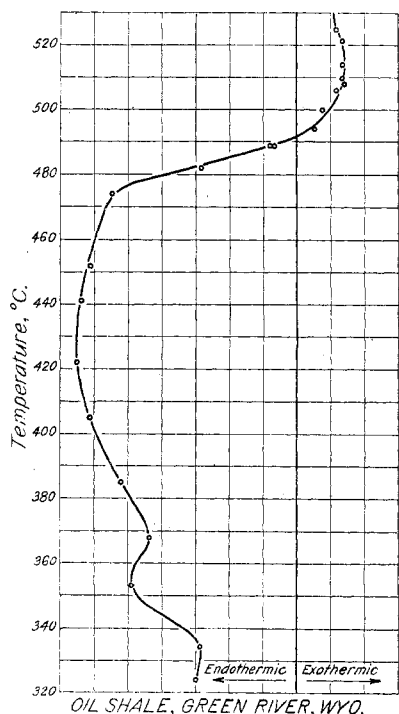

FIG. 2

DISTILLATION OF SHALE UNDER REDUCED PRESSURE—A sample of Ione, California, shale was dried and distilled under reduced pressure (8 mm.) from a metal retort (500 cc.). Up to 225° C. only a few drops of light yellowish oil collected in the receiver. From 225° to 450° C., at which temperature the distillation was complete, a straw-colored, wax-like solid collected in the condenser. This solid material constituted 90 per cent of the total distillate collected.

On account of the importance of this product, several of its physical properties were determined. It dissolves very readily in acetone and alcohol, and precipitates as a finely divided, light yellow material when the alcohol solution is diluted with water. The solid melts rather sharply at 46° C. It is completely soluble in sulfuryl chloride with the evolution of heat. When this sulfuryl chloride solution is hydrolyzed with an excess of water, a light yellow solid separates. If the material is dissolved in 95 per cent alcohol and the solution boiled with an absorbent carbon and filtered hot, a straw-colored solid separates from the alcohol on evaporation in an atmosphere of nitrogen. This material darkens readily on exposure to air, apparently because it is highly unsaturated and readily oxidized. This unsaturation is also demonstrated by its decolorization of a potassium permanganate solution and by its complete and rapid solubility in selenium oxychloride. Lehner[17] states that selenium oxychloride unites with the unsaturated hydrocarbons of the aliphatic series. On hydrolysis of the selenium oxychloride solution with an excess of water, a solid separates, but it is contaminated by the presence of red selenium.

Determination of the "saturation percentage" of this material was made in the customary way by the use of 66° Bé. sulfuric acid and Babcock cream-test bottles. After mixing with the sulfuric acid and centrifuging for several minutes there was no separation of saturated oil from the acid. The material is completely soluble in concentrated acid and therefore is composed entirely of unsaturates, as determined by this method.

An ultimate analysis of this material shows it to contain 82.83 per cent carbon and 16.79 per cent hydrogen, or a total of 99.62 per cent. This confirms the absence of nitrogen, sulfur, and oxygen, as was also indicated by qualitative tests for nitrogen and sulfur. The material contains a lower carbon-hydrogen ratio ($C:H = 4.9$) than either that of the original shale or oil distilled from the shale at atmospheric pressure.

A weighed amount of this solid was distilled at atmospheric pressure. Up to 135° C. a few drops of water and water-oil emulsion were distilled from a compound. The distillation proper began at about 290° C. and from this temperature up to 365° C. a straw-colored oil distilled over. From 365° to 380° C. there appeared to be a decomposition of the material, a light yellow semisolid collecting in the condenser. The distillation was complete at 380° C. The specific gravity of the material used for distillation was 0.913 at 15.5° C., while that of the distillate was 0.902 at 15.5° C. In the distillation 7.5 per cent of coke was formed, with a loss of 6.6 per cent by uncondensed gas. The oil obtained from this distillation was light yellow and solidified at room temperature. It contained 48 per cent by volume of unsaturates, while the product obtained by vacuum distillation was 100 per cent unsaturated compounds. This increase from 0 to 52 per cent of saturated compounds by one distillation is phenomenal.

Samples of Colorado shale (Grand Valley) were distilled under reduced pressure, using the same method as outlined above for the distillation of California shale. These distillations gave a dark-colored product, which was semisolid at room temperature. The material had a specific gravity of 0.952 at 15.5° C. and contained but 11.0 per cent by volume of saturates. By ultimate analysis the material gave a carbon-hydrogen ratio 5.5, contained 2.6 per cent nitrogen and 1.1 per cent sulfur. The saturates obtained by treating the oil with 66° Bé. sulfuric acid solidified at room temperature and were almost colorless. The material from the vacuum distillation was redistilled under the same conditions as outlined for the California shale. The distillation was slow, 5 per cent by volume distilling up to 280° C., after which the distillation was quite constant and was complete at 360° C. In the distillations 5.7 per cent by weight was lost as uncondensable gases and a residue of 10.6 per cent remained in the distilling flask. The distillate had a gravity of 0.894 at 15.5° C. and contained 38.0 per cent by volume of saturates. The saturates were liquid at room temperature. The distillation at atmospheric pressure of the vacuum product from California shale increased its saturates 52 per cent, while a similar distillation of the Colorado vacuum product increased the saturates 27 per cent. These distillations were carried on with other types of shales from Elko, Nevada, and Canada, and always with the formation of the heavy, semisolid vacuum product that gave a greater saturation per cent by redistillation at atmospheric pressure.
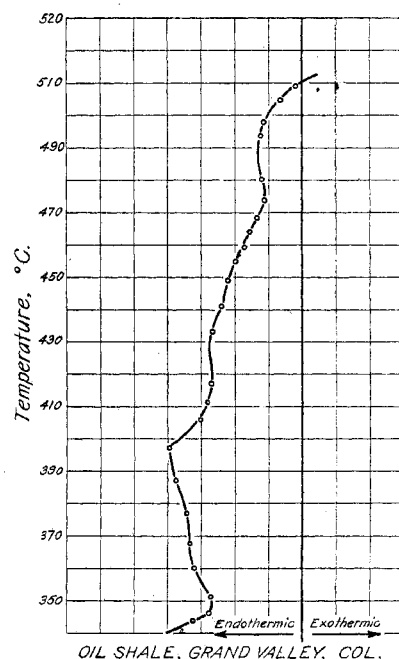

FIG. 3

Franks[18] has advanced the view that crude shale oils are not produced from the organic material in the shale by a single operation. He outlines the decomposition as occurring in two stages. The crude oils are mixtures of primary and secondary products formed during these two steps of the decomposition. This work of Franks confirms the theories of McKee and Lyder[12] on the decomposition of oil shale. The theories of these authors are now further confirmed by different methods than those used by Franks.

The results outlined above indicate several very important facts in the distillation of oil shales. In the pyrolysis of shale it is doubtful whether any of the final products are liberated as such from the shale kerogen. The authors believe that this solid, waxy material obtained by vacuum distillation of the crude oil shale represents the intermediate product between kerogen as such in the shale and the oil as obtained by pyrolysis. The decomposition of kerogen to form the oil products tends to occur in two stages. A primary decomposition takes place in which the insoluble kerogen is changed into a soluble solid, or semisolid. This intermediate product is not of the same composition as the kerogen, as indicated by analyses and by the ready solubility of the product. It is unstable toward heat, and a second decomposition by heat changes it into oils of the petroleum type of greater stability and higher saturation. It has been established that the less the decomposition of this "intermediate" product during the distillation of the shale the more unsaturated, unstable, and heavy is the oil. The saturates of the shale oil are increased in amount by distillation at atmospheric pressure.

The decomposition or "cracking" of well petroleum under the influence of temperature and pressure, to produce a more volatile product, is accompanied by a change in the products of higher molecular weight to form those of lower molecular weight. This cracking causes a decrease in the amount of saturates in the lower boiling product formed. In the heating of a highly unsaturated shale oil, results are obtained that are just the reverse of those obtained from well petroleum. Under the influence of heat an unsaturated material of high molecular weight from shale decomposes to form an increased percentage of saturated products.

ACTION OF SOLVENTS ON OIL SHALES

The understanding of the composition of the kerogen would be greatly simplified if any considerable part of it were found to show preferential solubility in any given liquid. A true solvent, as distinct from a reagent, should be chemically inert toward the substance extracted and the residue. Some of the liquids that have been employed in this investigation, notably pyridine and phenol, are open to the suspicion that they have rather more than a solvent action. The results obtained with such liquids can, however, be considered under the head of solvents, for any chemical action they initiate is of a most gentle nature.[19] The difference between a true solvent and a reagent is difficult to state, but those solvents which show a marked chemical reaction with the kerogen will be considered later as reagents.

EXPERIMENTAL PROCEDURE—The shales used were representative types from the districts in which they were collected, although not necessarily representative as regards oil yield. The oil yield from the different shales was determined by use of the standard laboratory assay method of the Bureau of Mines.[20]

About 25 g. of the moisture-free shale were placed in a paper thimble and extracted in a Soxhlet extraction apparatus. Results reported are based on two or more closely agreeing determinations. For convenience in comparing the different types of shales the solubilities are given in tabulated form. The nature of the extract is described under the discussion of the particular solvent used for obtaining it.

EXTRACTION WITH ANILINE—Aniline removed 15.60 per cent of the weight of a California shale. The high percentage of this shale soluble in aniline may be due to a partial decomposition of the organic content at the boiling point
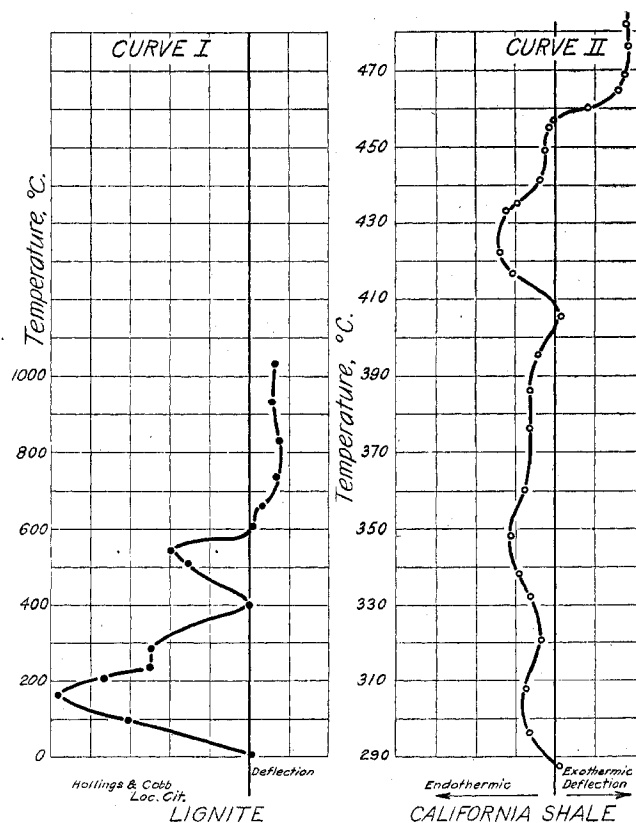

FIG. 4

(184° C.) of the solvent. A dried sample of this same shale heated 6 hrs. at 200° to 250° C. in an atmosphere of nitrogen lost 4.40 per cent by weight. If this temperature was increased to 300° C., the physical appearance of the shale changed slightly and a few oily drops collected on the cooler part of the tube and absorption bottle. This shows that the shale at this temperature undergoes a change other than just the loss of water from the hydrated mineral content, if such were present. A Colorado shale heated under the same conditions (200° to 250° C.) gave an average loss of weight of 1.82 per cent. The loss of weight of the shale does not necessarily show the total change that has taken place in the organic content, for a part of the changed material may not be volatile at this temperature. Engler[21] found that certain bitumens when heated to 250° to 300° C. became soluble in organic solvents such as benzene. Vignon[22] found that the amount extracted from the same sample of a rich coal with pyridine (b. p., 114.5° C.), aniline (b. p., 184° C.), and quinoline (b. p., 238° C.) increased in the same order as the increase in the boiling points of the solvents. Bone[23] believes that the action of these solvents on coal is primarily a

ANILINE EXTRACT

	Oil Yield by Distillation		Aniline % Soluble	Extract % of Distillation Yield	Absolute Alcohol Extract (Same Sample) % Soluble
	Gal./Ton	%			
Colorado (Grand Valley)	63.5	23.8	1.8	7.6	0.5
Wyoming (Green River)	58.8	22.0	1.6	7.3	...
California (Ione)	52.0	19.0	15.6	82.1	5.2
Nevada (Elko)	7.3	2.7	1.2	44.4	2.6
Scotch	18.2	6.8	0.7	10.3	1.0
Kentucky	18.2	6.8	1.3	17.6	...

question of temperature. In view of this evidence, the action of aniline on shale should not be considered as merely that of a solvent.

A sample of Colorado shale (Grand Valley) yielding 63.5 gal. of oil per ton was extracted with several solvents to determine the advisability of using the same solvents for other shales. It was believed that if the solvent extracted but a small per cent from a shale yielding as much oil as the Colorado type, it would be inadvisable to consider such a solvent for the other shales. It was found that shale from Ione, California, acted quite differently from the Colorado shale, so the action of solvents on this shale is given for comparison.

SOLUBILITY OF COLORADO AND CALIFORNIA SHALE IN VARIOUS SOLVENTS

	Oil Yield Gal./Ton	Abso- lute Alcohol	Acetone U. S. P.	Petrolic Ether	m-Cre- sol	Pyri- dine	Phenol	CS₂
Colorado (Grand Valley)	63.5	1.43ᵃ	1.48	1.39	0.87	2.04	0.87	1.00
California (Ione)	52.0	6.98		2.25				

ᵃ All percentages are by weight on dry weight of shale.

For comparison with the results obtained above the following table of the solubilities of oil shales in various solvents for petroleum is given.

The extraction of the California shale with absolute alcohol showed about 7 per cent of the material to be soluble. Alcohol being a *neutral solvent*—i. e., having no chemical action on the shale—it was used to dissolve the organic content in the hope of removing one constituent as it occurs in the shale. Ultimate analyses on this alcohol-soluble material from the California shale show that it contains 73.50 per cent carbon and 11.40 per cent hydrogen, or a carbon-hydrogen ratio of 6.4:1. Nitrogen was absent. The percentages of carbon and hydrogen in the original shale on an ash-free basis are 65.90 per cent carbon and 7.46 per cent hydrogen. The carbon and hydrogen percentages in the intermediate product, obtained by distilling this same type of shale under reduced pressure, are 82.83 and 16.79 per cent.

as it exists *in situ*. A distillation of this resinous material gives a viscous liquid having a characteristic petroleum odor.

From this investigation of the action of solvents on oil shale, it is evident that only a part of the kerogen of the shale can be extracted by solvents, and that the material extracted is not an oil and only resembles an oil when subjected to destructive distillation. Accordingly, we have one more proof that the shale contains no oil as such, but that it contains an organic material from which oil may be produced by destructive distillation.

Obviously, it is not commercially possible to produce oil from shale by extraction with organic solvents, because the amount of material extracted is very small, and because the material extracted is not an oil and can only be changed into a petroleum-like product by heat. Apparently, the only possible commercial method for the recovery of oil from shales is by pyrolysis—i. e., thermal decomposition.

ACTION OF REAGENTS ON OIL SHALE

Use has been made of reagents to aid in determining the constitution of coal and oil shale, chiefly by geologists and paleobotanists, who have found in the partial breakdown of the mass by concentrated acids and oxidants suitable means of isolating organized structures for examination under the microscope. Chemists have been dismayed by the complexity of such reactions, and as a rule have confined their investigations to other lines of attack. By this method of chemical attack by means of various reagents which oxidize, saturate, decompose, or otherwise alter the kerogenous substance, it was our hope to convert this organic content of the shale into recognizable derivatives—a hope not fulfilled. An attempt was made to isolate the kerogen by the action of solvents on the inorganic, ash-forming constituents. Many attempts were made to reduce the ash content by means of acids. By alternate treatments of a Colorado shale with hydrofluoric and hydrochloric acids the ash content was reduced to 13.0 per cent, but it was not possible

SOLUBILITY OF OIL SHALES IN VARIOUS SOLVENTS FOR PETROLEUM[30]

SOURCE	Yield Gal. Oil per Ton	Carbon Tetrachloride % Soluble	Distillation Yield	Carbon Bisulfide % Soluble	%ᵃ Distillation Yield	Acetone % Soluble	%ᵃ Distillation Yield	Benzene % Soluble	%ᵃ Distillation Yield	Chloroform % Soluble	%ᵃ Distillation Yield
Kentucky	18.22	0.037	0.51	0.015	1.44	....	....	0.06	0.82	0.14	1.99
Utah (Soldiers Summit)	44.60	0.74	4.45	0.76	4.57	0.53	3.16	0.91	5.47	1.05	6.32
Colorado (DeBeque)	37.75	2.04	15.42	1.85	13.97	1.33	10.04	2.23	16.84	2.41	18.22
Wyoming (Green River)	58.65	1.195	5.27	1.27	5.58	1.22	5.35	1.37	6.02	1.75	7.72
California (Ione)	52.00	7.555	33.46	5.83	29.68	10.98	55.80	....	....	10.16	51.73

ᵃ Represents the per cent of the distillation yield soluble in the solvent.

After drying this alcohol-soluble material at 70° C., it was distilled at atmospheric pressure. The temperatures were not uniform for the distillation on account of the cracking of the material under the influence of heat. The distillate was a dark brown, wax-like solid, melting at about 80° C. This same material was returned to the distilling flask and redistilled. On second distillation the material decomposed still more, as evidenced by the vapors set free and variation in boiling points. The distillate was a straw-colored liquid having a petroleum odor. The oil was very much unsaturated, as indicated by its darkening on exposure to air and its rapid decolorization of potassium permanganate solution.

Ultimate analyses of the dried material from the alcohol extract of Colorado shale give carbon 74.25 per cent and hydrogen 11.52 per cent, or a carbon-hydrogen ratio 6.4:1, a figure identical with that of the California shale. The percentages of these elements in the original shale on an ash-free basis are—carbon 71.01 per cent, and hydrogen 10.50 per cent, or a ratio of 6.8:1. It will be noted that the percentages of carbon and hydrogen in the original shale and the extracted material are about the same, indicating that the alcohol extracts a part of the kerogen from the shale about

to reduce the ash content to near zero. This is rather a strenuous treatment, and the kerogen appears to be considerably altered by it.

LIQUID SULFUR DIOXIDE—Fischer and Gludd[24] have reported the use of liquid sulfur dioxide for the extraction of coal. Liquid sulfur dioxide has been successfully employed in the refining of petroleum because of its specific solvent reaction on unsaturated hydrocarbons. Owing to the high percentages of unsaturates in shale oil, this reagent was used on shales to determine if the unsaturates are present as such in the kerogen or if they are formed as a decomposition product.

A dried sample of California shale was extracted for 24 hrs. with liquid sulfur dioxide. The extraction apparatus was of a Soxhlet type and was constructed of iron pipe. The average loss in weight of the shale by these extractions was 4.5 per cent. The extracted material was a heavy, mobile, tar-like residue, having a disagreeable odor resembling burnt rubber.

Colorado shale gave an average extraction of 0.30 per cent after 24 hrs. extraction. The extracted matter was a dark brown to black, resin-like semisolid. These extractions

indicate that if the organic content of oil shale is unsaturated it is not the type that is dissolved by liquid sulfur dioxide.

The organic content of the shale is so slightly soluble in ordinary solvents that an attempt was made to transform it by known chemical treatment into simpler and more easily definable products, capable of separation, purification, and recognition by ordinary analytical methods. The two reagents used for this chemical and solvent reaction on the shales were selenium oxychloride and sulfuryl chloride. Lehner[17] reports that selenium oxychloride reacts slowly with the saturated paraffin hydrocarbons and that the unsaturated hydrocarbons of the aliphatic series unite with it directly.

SELENIUM OXYCHLORIDE—A California shale was treated with an excess of selenium oxychloride, allowed to stand for 3 hrs. and filtered through an alundum crucible. The shale showed an increase in weight of 13.5 per cent by this treatment. The excess selenium oxychloride containing the extracted matter was evaporated to dryness under reduced pressure. A semisolid material was formed which was badly contaminated with the red form of selenium. This form of selenium was also present in the extracted shale, thus increasing the weight of the extracted material. If water is added to the extracted shale before drying, or to the selenium oxychloride filtrate, a large amount of red selenium is formed. This contamination with red selenium makes impossible the identification of the extracted materials.

Samples of Colorado shales gave an average increase in weight of 20.9 per cent when treated with selenium oxychloride as outlined above. Both the extracted shale and the extract contained red selenium. An attempt was made to remove this red selenium by dissolving it in carbon disulfide, but after extracting for several hours the selenium was not all dissolved. On account of the difficulties encountered in eliminating this red selenium from the extract, further experiments were not tried with this reagent.

SULFURYL CHLORIDE—This reagent reacts with the higher olefins, amylenes, and hexylenes to yield dichlorides. If sulfuryl chloride is run rapidly into a boiling mixture of benzene and aluminium chloride, chlorination occurs almost to the exclusion of all other reactions.[25] If lignite is treated with sulfuryl chloride, it yields a dark brown resin in small quantities.[26] On account of the action of sulfuryl chloride both as a chlorinating agent and a solvent for hydrocarbons it was used on oil shales in an attempt to separate recognizable substances.

Samples of California shales were refluxed for 48 hrs. with sulfuryl chloride. The filtrate was hydrolyzed by adding it to water, and a light yellow solid separated out. This separated solid was partially soluble in alcohol, leaving a residue of inorganic chlorides formed from the ash content of the shale. The shale lost by this treatment 8.9 per cent of its weight.

California shale was refluxed for 24 hrs. with an excess of sulfuryl chloride. The shale was found to have increased in weight 37.2 per cent by this treatment. This dried shale was extracted to completion with absolute alcohol, using a Soxhlet extraction apparatus. The loss of weight by this alcohol extraction was 47.74 per cent, calculated on the original weight of the shale used.

An Elko, Nevada, shale, after refluxing 12 hrs. with sulfuryl chloride, increased in weight 6.75 per cent. A Colorado shale under the same treatment increased in weight 9.32 per cent. There appears to be no definite relation between the percentage of volatile matter in the shale and the increase in weight by the action of sulfuryl chloride. The Nevada shale contains 20.2 per cent volatile matter and increases in weight 6.75 per cent, while the Colorado shale contains 53.9 per cent volatile matter and increases in weight only 9.52 per cent.

ACTION OF CHLORINE ON SHALES—Chlorine, bromine, and iodine were found to be absorbed by different coals, showing the presence in them of different proportions of compounds containing unsaturated groupings.[27] When lignite is treated with chlorine or bromine without external heating, the temperature increases to 90° to 100° C.[28] If this reaction product is extracted with carbon disulfide, a halogen-containing resinous substance is obtained. Cross and Bevan[29] have shown that coal is attacked by chlorine with the production of a chlorinated derivative similar to that previously obtained by them from lignified tissue. A shale oil obtained by distillation often contains 50 to 75 per cent of "unsaturates;" so these chlorination experiments were performed to see if the unsaturation is present in the organic content of the shale, or if it is produced by decomposition, and to see if it is possible to obtain less complicated chlorine products than those obtained with sulfuryl chloride.

Colorado shale was suspended in carbon tetrachloride and chlorine gas was passed through the solution for 36 hrs. The solution was filtered through an alundum crucible, and the residue dried and weighed. The increase in weight after this chlorine treatment was 0.59 per cent. This same sample of shale was then extracted with absolute alcohol in a Soxhlet extraction apparatus until the siphoning liquid was colorless. The absolute alcohol extracted from the chlorinated shale 6.23 per cent, calculated on the weight of the original shale. Absolute alcohol extracts 1.43 per cent from this shale before chlorination.

California shale, treated with chlorine in a carbon tetrachloride suspension for 24 hrs., filtered, and dried, increased in weight 6.5 per cent. This sample was also extracted with absolute alcohol. The loss in weight by this extraction was 26.8 per cent. This shale after extraction with absolute alcohol and drying was again suspended in carbon tetrachloride and rechlorinated. It was found that the shale increased in weight 8.28 per cent by this second chlorination. The shale was dried and again extracted with absolute alcohol until the extraction was complete. The alcohol dissolved 14 5 per cent of soluble matter from the rechlorinated shale. The solubility of this California shale in absolute alcohol before chlorination was 6.9 per cent, while its solubility in this solvent after two chlorine treatments was 41.5 per cent.

The organic constituent of shale, kerogen, is highly unsaturated, as evidenced by the increase in weight on chlorination and by the high chlorine content of the product resulting from its treatment with sulfuryl chloride. This unsaturation is present in the shale before it has undergone any heat treatment other than drying at 104° C. In the distilled oil itself unsaturation is not caused by the heating during distillation, as it has been shown that heating and cracking of the oil result in *higher* rather than *lower* saturation.

CONCLUSIONS

Different oil shales give different products under similar treatment. The commercial extraction of such shales by solvents is not feasible. The organic content of the shales studied is highly unsaturated. Pyrolytic decomposition at atmospheric pressure is accompanied by a marked decrease in the unsaturates. The retorting of each shale is a separate problem. The problem of refining of the oils begins with the retorting of the shales.

BIBLIOGRAPHY

1—Gavin and Sharp, "Some Physical and Chemical Data on Colorado Oil Shale," *Bur. Mines, Report* 2152 (1920).

2—Fisher, "Laboratory Manual of Organic Chemistry," J. Wiley & Sons, Inc., New York, 1920, p. 217.

3—Sherman, "Organic Analysis," Macmillan Co., New York, **1919**, p. 291.

4—Sadtler, *J. Am. Chem. Soc.*, **27** (1904), 1188.

5—Robertson, *Proc. Royal Soc. Edinburgh*, **34** (1914), 190.

6—Winchester, "Oil Shales of Northwestern Colorado," *U. S. Geol. Survey, Bull.* **641F**, 161.

7—*U. S. Geol. Survey, Professional Paper* **48**.

8—Sainte-Claire-Deville, *Compt. rend.*, **66** (1868), 442.

9—Peckham, *J. Soc. Chem. Ind.*, **16** (1897), 727.

10—Groves and Thorp, *Chem. Tech.*, **1** (1917), 55.

11—Botkin, *Chem. Met. Eng.*, **26** (1922), 398.

12—McKee and E. E. Lyder, THIS JOURNAL, **13** (1921), 613.

13—Hollings and Cobb, *J. Chem. Soc. (London)*, **107** (1915), 1106.

14—Gavin, "Analytical Distillations of Typical Shale Oils," *Bur. Mines, Report* **2332** (1922).

15—George, "Oil Shales of Colorado," *Colorado Geol. Survey, Bull.* **25** (1921).

16—Redwood, "Treatise on Mineral Oils and Their By-products," p. 52.

17—Lenher, *J. Am. Chem. Soc.*, **43** (1921), 33.

18—Franks, "Studies of Colorado Shale Oils," *Colorado School of Mines Quarterly*, **16** (1921), 73.

19—Lewes, *Progressive Age*, **29** (1911), 1030.

20—*U. S. Geol. Survey, Bull.* **641**, 148.

21—Engler, "Das Erdol," **1** (1917), 35.

22—Vignon, *Compt. rend.*, **158** (1914), 1421.

23—Bone, "Coal and Its Scientific Uses," London, **1918**, p. 82.

24—Fischer and Gludd, *Ber.*, **49** (1916), 1469.

25—Dunans, *J. Chem. Soc. (London)*, **121** (1922), 44.

26—Badische Co., *J. Soc. Chem. Ind.*, **31** (1912), 151.

27—Hart, *Chem.-Ztg.*, **30** (1906), 1204.

28—German Patent 313,875 (1919).

29—Cross and Bevan, *Phil. Mag.*, **5**, Sect. 13, 328.

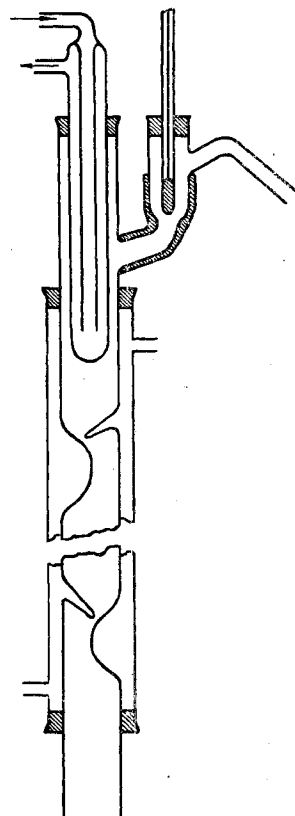30—Gavin and Aydelotte, "Solubility of Oil Shales in Solvents for Petroleum," *Bur. Mines, Report* **2313** (1922).

A Laboratory Fractionating Column[1,2]

By H. T. Clarke and E. J. Rahrs

EASTMAN KODAK CO., ROCHESTER, N. Y.

THE PRINCIPAL desiderata for a laboratory fractionating column are, after efficiency, simplicity of construction, strength, and absence of movable parts. The column here described, while undoubtedly less efficient than one constructed with wire-gauze plates, has been found satisfactory in the remaining respects; and since metals are entirely absent, it is suitable for the fractionation of corrosive liquids.

The column consists of a Pyrex tube 90 cm. in length and 20 mm. in internal diameter. Beginning 15 cm. from the upper end a series of semi-bulbs (25 mm. longitudinal diameter, 10 mm. transverse diameter, and 12 mm. depth) are sucked in, and points sloping downward from the opposite side of the tube are poked in (by means of the butt end of a small file or the "lead" of a pencil) to within about 1 mm. of the upper part of the convex surface of each bulb. Below every set of bulb and point, and as near as possible to it, is placed a similar set arranged at an angle 90 degrees on the periphery of the tube; in this way every fourth set occupies a corresponding position. This series is continued until finally 10 cm. of the unaltered tube remain at the lower end. At 8 cm. from the upper end a side arm is placed, similar to that of a Claisen distilling flask; the delivery tube, situated at the mid-point of its vertical portion, is so bent as first to ascend for a short distance before descending to the condenser. This side arm, in which is fitted the thermometer, is 15 mm. in internal diameter, and may profitably be lagged with asbestos over its lower portion, in order to minimize errors in temperature readings due to radiation from the bulb of the thermometer. At the top of the tube forming the column is stoppered a Pyrex tube 16 cm. in length and 15 mm. in external diameter, through which cold water can be passed. The entire length of the column below the side arm to within 8 cm. of the lower end is jacketed with a stout glass tube 30 mm. in internal diameter, tubulated at top and bottom, and secured with India-rubber stoppers.

In fractionating, distillation is carried out at the usual rate of one drop of condensate for every 3 to 5 sec., the size of the flame and the distance to which the water-cooled tube projects with the column below the side arm being so regulated that condensed liquid returns to the distillation flask 10 to 15 times as rapidly as it collects in the receiver.[3] For liquids of high boiling point the cooling tube may have to be withdrawn until only its lower end is level with the side arm, while for those of low boiling point, not only will it be necessary to expose its maximum length to the vapor but to pass a downward current of cold air at a regulated rate through the jacket. In fact, for very low-boiling liquids, such as acetaldehyde, it is advantageous to jacket the column with water at a suitable temperature. For liquids boiling above 70° C. the tubulations should be closed, so that the jacket acts as a heat insulator.

The column has been found to act satisfactorily in fractional distillation under reduced pressure without material modification. In such an operation it is well to dispense with a capillary tube, if possible, in order to avoid the entrainment of vapors by the gas thereby admitted.

As an example of the operation of the column the following table shows the results obtained on distilling a mixture of 1000 cc. each of commercial benzene and toluene from a 3-liter flask:

RANGE °C.	VOLUME Cc.	TIME
72–81	15	5 min.
81–83	455	6 hrs. 30 min.
83–85	180	2 hrs. 45 min.
85–88	240	3 hrs. 40 min.
88–91	90	55 min.
91–95	185	3 hrs. 15 min.
95–100	95	1 hr. 45 min.
100–105	95	1 hr.
105–109	185	2 hrs. 55 min.
109–110	400	25 min.
Residue	40	

[3] The authors are greatly indebted to Prof. W. K. Lewis for drawing their attention to the principle of refluxing from the top of the column.