

~~SELF~~

10-64-015

Volume Seventeen

Number Four

Tell Erti Repository
Arthur Lakes Library
Colorado school of Mines

BL-8
Q 8

ECT IV
PDF Nil

QUARTERLY

OF THE

COLORADO
SCHOOL OF MINES

OCTOBER, 1922

SUPPLEMENT A

Issued Quarterly by the Colorado School of Mines
Golden, Colorado

Entered as Second-Class Mail Matter, July 10, 1906, at the Postoffice at
Golden, Colorado, under the act of Congress of July 16, 1894.

BL-8
Q 8

Volume Seventeen

Number Four

**Tell Ertl Repository
Arthur Lakes Library
Colorado school of Mines**

QUARTERLY

OF THE

COLORADO
SCHOOL OF MINES

OCTOBER, 1922

SUPPLEMENT A

Issued Quarterly by the Colorado School of Mines
Golden, Colorado

Entered as Second-Class Mail Matter, July 10, 1906, at the Postoffice at
Golden, Colorado, under the act of Congress of July 16, 1894.

QUARTERLY

OF THE

COLORADO SCHOOL OF MINES

Vol. Seventeen

OCTOBER, 1922

Number Four

Preliminary Study of the Organic Matter of Colorado Oil Shales*

By

Arthur J. Franks and B. D. Goodier

The history of industry throughout the ages shows that practice and technique are generally ahead of science. We observe the result first and seek the reason afterward, if at all. This is quite human. Perhaps in no industry has the science lagged so far behind practice as in the oil shale industry. Although Young demonstrated that oil could be produced from shales as early as 1850, and shale oil manufacture has been well established in Scotland for more than seventy years, our knowledge of the nature and the actual composition of the organic matter from which the oil is formed is but little richer than it was seventy years ago. Only very recently has progress been made in any direction, even toward an understanding of the processes of transition through which the pyrobituminous substances pass in their transformation to oils. Yet these fundamentals may be of vital importance to the success of the oil shale industry in America.

The general purpose of our investigation, the results of which are here presented, was to secure as much information as possible concerning the organic portion of a typical, high grade, Colorado oil shale and to study the mechanism of the transition from this material to oil. In considering the problem, it seemed that the following steps would be necessary to the accomplishment of our purpose:

- 1) The determination of a method for the separation of the organic matter, or "kerogen"¹, per se and in toto.
- 2) The separation of the kerogen in its original form without effecting any change in its composition, if possible.
- 3) A study of the composition and properties of the kerogen.
- 4) A study of the reactions which occur in the transition of kerogen to oil, with the object of testing the validity of present hypotheses which attempt to explain the formation of oil from shales.
- 5) The utilization of the facts obtained in determining the most suitable conditions and procedure for retorting the shale to secure the maximum yields of the best products.

Obviously, the success of this plan of attack depends entirely on the feasibility, as well as possibility, of executing the first step.

The nature and composition of the organic portion of oil shales has been widely discussed, especially in connection with theories of origin. Comparatively little has come from these discussions except a great difference of opinion. Thus far our knowledge is quite unsatisfactory

* Revised by the senior author from a thesis by B. D. Goodier for the degree of Engineer of Mines at the Colorado School of Mines.

¹ The term kerogen, as used in this paper, means the whole organic portion of the shale and not merely the oil-forming constituents. That there should be such a distinction between these terms will be evident from what comes later in the paper.

because it is composed largely of deductions from geological examinations of deposits, rather than of direct evidence from chemical studies of the material itself. Microscopic investigations have shed almost no light on our problem, which is a very complicated one. The shales which have been thoroughly examined under the microscope are not from Colorado. However, we shall discuss the important phases of the available information because of their association with our work.

The general opinion, based upon studies which have been made of shales of the Colorado type from various deposits of the world, is that the major part of the organic matter is of vegetable origin. The present properties are explained by different types of metamorphism which might have occurred, both during and subsequent to the time of deposition. We do not question this explanation, even though the probable *modus operandi* of the hypothetical metamorphism is not at all clear. The results of geologic and microscopic studies, together with the properties of the material, especially that of insolubility in ordinary solvents, furnish a sound basis for such a conclusion. Aside from geologic evidence against the animal theory of origin, it is highly improbable that animal life was ever so abundant, prolific, and concentrated in certain regions as to account for the enormous amounts of organic matter in the oil shale deposits of the world. Neither is it easy to explain how the animal remains, mainly fats and waxes, could have changed into substances with such properties as those usually observed today. Furthermore, our deductions are corroborated by examinations of the original shale and extracts therefrom, which fail to show the presence of either fatty acids or their esters.

Cunningham-Craig's hypothesis that the kerogen is a residue from the inspissation of petroleum previously absorbed and adsorbed by former clay strata, is not at all tenable for Colorado and numerous other shales, because of their structures, as well as their location and properties. It is impossible to reconcile the distinctly laminated structure and banding observed in Colorado and similar shales, and the occurrence of barren sandstone seams between rich strata, with a theory of origin that requires a seeping in of a petroleum oil and the subsequent evaporation of its light fractions. The great variations in richness between adjacent strata, even though these be very thin, is positive evidence against the inspissation theory as it stands. Additional weighty evidence against the theory is available,² but this we need not discuss here. Consequently we may confine ourselves to a study of the problem with the vegetable mode of origin as a starting point.

From the work that has been done with the microscope in the hands of skilled investigators we have the choice of three main forms of vegetable substance to account for the body of the organic matter: algae³ spores,⁴ and resins⁵. Whether any one or all of these are actually the main original, or raw material from which the kerogen of Colorado shales was formed is still very much a question, because the evidence is in each case far from conclusive. Certain specimens examined by C. A. Davis² plainly showed fossil algae, pollen, and spores, but these are present in too small amounts, and the number of specimens examined are too few, to justify the conclusion that kerogen was produced from any one or all of these forms of life. Yet even if such a conclusion could be proved beyond a doubt, our problem would still remain unsolved because metamorphism by time, pressure, and decay has so changed the original substances that they are widely different from the remains we now find. Hence there is no aid to be expected from this quarter in determining the actual composition of the kerogen or explaining the reactions through which it passes in the transition to oil. The experiment of

² U. S. Geol. Survey Bull. 691-B, pp. 35 and 46; 1918.

³ Bertrand and Renault, Bull. Soc. Hist. Nat. Autun, V, p. 159. Davis, U. S. Geol. Survey Bull. 691-B, pp. 35 and 46.

⁴ D. R. Stewart, Mem. Geol. Survey Scot., 1912, part III, pp. 164-5, "The Chemistry of the Oil Shales". Reinhardt Thiessen, Ec. Geology, XVI, 239-300; 1921; "Origin and Composition of Certain Oil Shales".

⁵ H. R. J. Conacher, Trans. Geol. Soc. Glasgow, XVI, part II, 177-80; 1916. "A Study of Oil Shales and Torbanites".

Steuart,⁴ in which he prepared a product similar to certain shale oils by the distillation of a mixture of 25 per cent lycopodium spore dust and 75 per cent Florida fuller's earth, by no means proves that the spores are the source of the oil. Other organic materials, if distilled under the same conditions, would probably yield oils of similar characteristics.

Therefore, it seems that even though the origin of the shale were known, it would help but little in the solution of the problem before us, since we are interested not so much in the substances from which the pyrobituminous material may have originated, as in the nature of this substance we now find. From our consideration of the various opinions of others and our study of Colorado shales, we are inclined to agree with Conacher⁵ that the nature of the major part of the kerogen is more or less resinic. This view seems to be most in accord with a rational consideration of the facts as far as they are known. We are not at all prepared to state at present what the rest of the kerogen or organic matter may consist of, or what its origin may have been.

To Engler and Lederer⁶ belongs the credit for the first attempt to separate the kerogen from oil shales and offer an explanation for some of the unusual phenomena associated with the operation. They first completely extracted the powdered shale with benzene, dried the insoluble residue, heated it in a closed tube at temperatures between 200 and 400° C., and extracted again. The drying, heating, and extracting were then repeated until no further soluble material was obtained. In this manner they were able to separate from various shales considerable amounts of a very viscous, tarry substance from which lighter oils could be produced by distillation. Later, Engler and Tausz⁷ demonstrated that the amount of kerogen soluble in benzene could be much increased if the extractions were performed under pressure, and therefore at higher temperatures. Engler and his coworkers explained the transition from insoluble pyrobitumen to soluble bitumen by assuming a depolymerization during the heating process. However, they did not submit proof that such a reaction actually occurred but came to their conclusion by reasoning from the analogous behavior of certain resins and gums. Since there has been considerable doubt in our minds that depolymerization accounted for the change in solubility of the organic matter in oil shales it became one of the minor objects of this investigation to secure evidence, either in favor of, or in contradiction to, this hypothesis.

Although Engler and his colleagues have shown that the kerogen may be made soluble by heating to temperatures between 200 and 400° C., they did not determine the relation between the temperature, the time of heating, and the amount of soluble material formed. They did not analyze the extracts and neglected to ascertain whether the products from successive heatings and extractions at the same and different temperatures varied in their composition; neither was it demonstrated that all the oil forming constituents were extracted. No examination was made of the original shale, or the residue after the extraction was supposed to have been completed; and this residue was not compared with that obtained from the ordinary destructive distillation of the original shale for its oil yield. Therefore, they could not show the relation between the total yield of bitumen by heating and extraction, the yield of oil by distillation, and the total organic content of the shale. All these observations are of vital importance to a clear understanding of the phenomena under investigation. Yet in spite of the incompleteness of Engler's studies, the work is the only known record to date of successful attempts to extract comparatively large portions of the kerogen from shales at temperatures below which destructive distillation occurs.

The recent work of McKee and Lyder⁸ on the thermal decomposition of oil shales is intimately connected with the results of our investigation because their work was also done on Colorado shale. In their preliminary experiments they heated finely ground shale from Grand Valley in a closed, rotary furnace for periods of time ranging

⁴ Engler-Höfer, "Das Erdöl", 1913, p. 30. Petroleum, 7, 399-403; 1912.

⁵ Zeit. f. angew. Chem., 34, 308-9; 1921.

⁶ Jour. Ind. Eng. Chem., 13, 613 and 678; 1921.

from one to six hours and at temperatures between 390 and 398° C. After this heating process, the shale was removed from the furnace, examined, and then extracted.

"It was found that in some cases when the shale was heated for six hours at about 390° C., no apparent change occurred. Little gas was given off, as was indicated by the fact that the pressure remained at about 25 or 30 lb. per sq. in. *Slight increase in solubility was noted,** but the shale in general maintained its hard, rubber like texture. In other experiments only a few degrees higher (394 to 398°) and in one case at the same temperature, decided changes were noted. The pressure suddenly rose after the shale became heated up, and remained around 100 lb. per sq. in. The product was a black tar like mass with the shale residue suspended in it. Upon extraction with benzene this yielded 30 to 40 per cent of soluble material, as compared to 1.5 to 2.9 per cent on the original shale.

"It was not possible in these experiments to keep the tubes entirely tight, and *some gas and vapors usually escaped.** This rendered the results inconclusive. Although a heavy product was obtained, as was expected, it could easily have been the result of the light vapors having been lost by distillation, but the results did show that a decided change was taking place in the shale. and this at a quite definite temperature.

"The pyrometer used in these determinations was of the ordinary base metal type and was, unfortunately, equipped with a low resistance indicator, *which rendered the results somewhat questionable.** On this account other means of studying the changes that were taking place were adopted."⁹

The method eventually adopted by McKee and Lyder was to distill the finely divided shale at atmospheric pressure in a small, brass retort, immersed in a lead bath which was electrically heated. The shale was maintained at constant temperatures which, however, differed in respective experiments. The range of temperature was from 374 to 425° C. and the period of heating one hour after the desired temperature had been reached throughout the mass of shale. Any oil that distilled during the process of heating was condensed and weighed. After the heating, the shale was extracted with carbon disulfide which was later evaporated. The weight of the extract was then determined. Their results from five "runs" are reproduced below in table I. We shall refer to them later. We also quote their conclusions.¹⁰

"It has been shown that the pyrobitumens do not decompose to form petroleum oils as a primary product of decomposition, but that the first substance obtained is a heavy solid or semi-solid bitumen. This bitumen is formed at *quite definite temperature, the formation taking place between 400 and 410° C.,** in the case of this particular shale. The petroleum oils formed from the shale are the result of the decomposition or cracking of the heavy bitumen."

TABLE I¹¹

Run	Temp. °C	Light Oil		Heavy Oil		Total Oil	
		G.	Per Cent	G.	Per Cent	G.	Per Cent
1	374	0.85	3.4	1.45	5.7	2.30	9.1
2	385	1.30	5.3	1.52	6.2	2.82	11.5
3	399	1.70	7.0	1.90	7.9	3.80	14.9
4	425	4.20	16.8	4.93	19.6	9.13	36.4
5	410	2.55	10.2	6.40	25.6	8.50	35.8

The results of certain preliminary experiments of McKee and Lyder are not in harmony with the data from most of Engler's work on foreign shales. It is difficult to understand why "no apparent change occurred" after heating the shale for six hours; and why only a "slight increase in solubility was noted," in spite of the increases in solubility, of

* The italics are ours.

⁹ Quoted from preceding reference.

¹⁰ Ibid.

¹¹ Ibid.

more than 300 to 400 per cent, which were produced by later heatings at lower temperatures and for shorter periods of time (see table I). The fact that in the first experiments the heating was done in a closed tube under pressure (which was not great) should not have exerted such a tremendous influence on the results. Engler also heated the shale in closed tubes; yet he usually observed considerable increases in the amounts of soluble material formed, even at lower temperatures. Also, the fact that "some gas and vapors usually escaped" shows that some change was taking place and that there must have been some decomposition of the kerogen or there would have been no vapors formed except, perhaps, those of water. We have always observed the distillation of small amounts of "light oil" while heating Colorado shales from the same deposit at temperatures as low as 325 to 330° C. We believe, therefore, as do McKee and Lyder, that there may have been errors, very probably high readings of the temperatures as shown by the pyrometer, in some of the preliminary work.

Studies¹² of residua of crude oils from Colorado shales have also yielded strong, yet indirect evidence to corroborate the theory that a heavy, unstable bitumen is the first product of the thermal decomposition of the kerogen in its transition to oil. Botkin¹³ has recently presented highly interesting data which show a remarkable resemblance to exist between these heavy residua and gilsonite. But the actual composition of the major part of gilsonite is still unknown. Furthermore, it is yet to be proved by direct evidence and actual experiments that a heavy bitumen is the primary decomposition product of the kerogen of Colorado shales, and that all the oil subsequently formed is produced from this intermediate product. We shall soon present such evidence and experiments, and demonstrate that the present theory of oil formation is, in general, correct. Perhaps we may also be able eventually to explain the nature of the reactions which occur in the processes of decomposition.

The kerogen of Colorado shales is so intimately associated with the inorganic constituents that a complete separation of one from the other presents a problem of numerous difficulties. In our early preliminary experiments we attempted to remove the kerogen without effecting any chemical changes therein. Extractions with the ordinary solvents, such as benzene, ethyl alcohol, ethyl ether, petroleum ether, pyridine, and even a strong solution of potassium hydroxide were tried three years ago,¹⁴ but with small success. Only minor amounts of the organic matter were dissolved by these solvents even after twenty hours' extraction. Since the kerogen could not be thus removed from the shale, it was thought possible to dissolve away the mineral matter by repeated treatments of the very finely divided shale, ground to pass a 200 mesh screen, with hydrofluoric acid, followed by washing with water, boiling with sodium carbonate solution to decompose any insoluble fluorides which might have been formed, and again washing with water. The carbonates were then decomposed with hydrochloric acid and the residue washed thoroughly with water.¹⁴ Much inorganic material was dissolved in this way, but even after a number of treatments the product still contained sufficient ash to justify us in discarding this method as a failure. Although it may be possible to remove most of the mineral constituents in this or a similar manner, we do not believe that a complete separation can be made. Then there is always the uncertainty and lack of positive knowledge that the reagents did not effect some unobserved and indeterminate chemical change in the kerogen during the process of treatment.

For this reason we abandoned this method of attack and decided to study the effect of heat on the shale at temperatures below which the kerogen decomposed to form oil. We hoped that the separation and

¹² Arthur J. Franks, *Chem. Met. Eng.* 25, 49, 731 and 778; 1921. C. W. Botkin, *Ibid.*, 26, 398; 1922.

¹³ *Ibid.*, 26, 445; 1922.

¹⁴ From unpublished work of the senior author.

study of the primary product of decomposition would throw light on the nature of the kerogen itself, as well as on the decomposition reactions.

If Engler's depolymerization theory is correct, the kerogen should depolymerize to a large extent and become soluble in carbon disulfide, if the shale were heated to a temperature just below that at which oil is produced by destructive distillation. We expected the temperature at which the reaction occurred to be definite within a few degrees, and that a relatively short time would be required for this reaction to go to completion.

A few rough experiments soon convinced us that our expectations were not to be realized. After heating 50 gram samples of shale, 30 to 60 mesh, for two and one-half hours at atmospheric pressure and at 25 degree increments of temperature between 300 and 375° C., and extracting the residue with carbon disulfide, we found that the amount of soluble organic matter increased considerably, especially at higher temperatures; but that most of the kerogen retained its insoluble form. We also observed that although no oil distilled at 300°, increasing amounts were formed at the higher temperatures. The total amounts of bitumen plus any oil formed during the periods of heating varied between 1.50 per cent, for the raw shale, to 6.01 per cent after heating at 375°.

These trial experiments demonstrated clearly that 1) if we were to study the effects of heat on the kerogen at temperatures below which it decomposed to form oil, we would have to begin heating at temperatures below 325° C.; 2) that the temperature was not the only factor which determined the amount of bitumen formed from the insoluble kerogen, since time apparently exerted some influence on the results; 3) if a depolymerization of all the kerogen was to take place at temperatures below 325°, more than two and one-half hours would be required for the reaction to complete itself; and 4) if a depolymerization actually occurred there was no definite temperature at which the reaction reached completion in a short time. From the last three conclusions it appeared evident that regardless of the nature of the decomposition reaction, equilibrium was attained rather slowly at the temperatures within which we were required to do our work. If this were the case, it should be possible to obtain additional amounts of soluble material from the kerogen by repeating the heatings at temperatures between 300 and 325°, and the extractions. We thought it might also be possible later to heat to higher temperatures without forming oil if the soluble portion of the kerogen, together with the bitumen produced by the heatings below 325°, were first removed.

With these ideas in mind we varied our mode of procedure. The shale was first extracted with carbon disulfide until no further soluble matter was present. After evaporating the adhering solvent and drying the extracted shale thoroughly, it was heated to 300° for two and one-half hours, then cooled, and again extracted completely with carbon disulfide. This process of heating and extraction was repeated, once at 300°, twice at 325°, and once at 350°. In no case was any oil formed during the heating process. In every case an additional amount of soluble substance was formed. The quantity of extract after heating to 350° was more than half as great as that from the original shale. The total quantity of extract was now more than twice that obtained from raw shale. Nevertheless, an examination showed that most of the kerogen was still in the shale.

Since it was desirable to heat at higher temperatures, because the kerogen was thereby converted into bitumen more rapidly, it was important to ascertain the maximum temperature to which the shale could be heated without causing a decomposition to oil. Another sample of shale was completely extracted, dried, heated to 300° for two and one-half hours, and extracted once more. The dried residue was then brought to 300° and the temperature gradually and very slowly increased. At 350° there were still no signs of oil in the condenser, but as the temperature reached 365° oil began to distill. Above this temperature oil vapors were evolved more freely and the quantity increased with the temperature.

The results of these rude experiments indicate clearly the correctness of our conclusions. The time factor is very important in determining the amount of bitumen formed since the decomposition reaction seems to be very slow between 300 and 325°. If there is a definite temperature at which equilibrium is reached very quickly, there is no doubt that it falls within the range of temperatures in which the kerogen simultaneously decomposes to oil. Although some oil distills from the shale at a temperature as low as 325°, the shale may be safely heated to 350° without producing any oil if the raw shale is first extracted completely, then heated to 300° for a few hours and again extracted. The rate of bitumen formation at 350° is much greater than at lower temperatures. We could think of no reason why it should not be possible to continue the production of bitumen by heating, up to and including 350°, and extracting until all the oil forming constituents of the shale were removed. With these facts to guide us, we planned the more refined experiments described below.

The shale which we studied was a typical high grade specimen from the property of Joseph Bellis, in the Parachute Creek district, Grand Valley, Colorado. Three pounds of this shale were ground to minus 30, plus 60 mesh, and then well mixed. After a thorough air drying at 110° C., the sample was transferred to a tightly stoppered bottle. The uniformity of the sample was ascertained by the closely checking results of proximate analyses of small portions taken from different parts of the large sample. Our analysis, which is an average of these duplicate determinations, appears in table III.

The shale was heated in a retort constructed from a short length of three inch pipe, into the bottom of which was welded a piece of one-fourth inch wrought iron plate. The cover was of cast iron, one fourth of an inch thick, and was fastened tightly to the retort by means of four small bolts which passed through a companion flange that had been machined to a thickness of one-fourth of an inch. An asbestos gasket insured a tight joint. A piece of thin brass tubing was fitted into the center of the cover so that a thermometer could be inserted, if desired. A small side neck was brazed to the brass tube to conduct any vapors from the retort to a piece of glass tubing which served as a condenser. Fairly uniform temperatures, measured by a 500° nitrogen filled thermometer, were secured by the use of a lead bath held in a brick furnace. Two large gas burners furnished the necessary heat. With this apparatus a 300-gram sample of shale could be maintained at temperatures which were usually constant to within 5° C.

We used *c. p.* carbon disulfide as the solvent in all our experiments. The extractions were made in a simple, continuous apparatus. It had a capacity of 300 grams of shale and consisted of a copper cylinder, a basket of 100 mesh brass gauze, and a tightly fitting cover in the form of a hollow cone. Practically complete condensation of the solvent was obtained by passing cold water through the cover. A slow boiling of the solvent was maintained by heat from a steam cone. Extraction was continued in each case until the soluble organic matter was completely removed from the shale in the basket. The solution was then transferred to a weighed casserole, the carbon disulfide slowly evaporated on a steam cone, and the last traces removed by careful heating to about 200° on a hot plate. The casserole was finally cooled and weighed.

The residue as it came from the basket always contained a considerable amount of carbon disulfide. This was distilled away by heating on a steam cone. The residue was finally heated to about 110° C., with frequent stirring, in order to remove the last traces of solvent and any water that may have been absorbed. The dried residue was then placed in a tightly stoppered bottle, cooled, and weighed.

Our plan of procedure was quite simple. We first extracted all the soluble substances from a 300-gram sample of the air dried shale. The quantity of extract was determined and the residue freed from carbon disulfide. The dried residue was then heated to 300° C. for four hours, the bitumen extracted and weighed, and the process of drying the residue, heating, and extracting was repeated.

In the remainder of the work the heatings and extractions were repeated with only a small number of variations. In a few cases the period of heating was increased in order to determine the effect of time on the amount of bitumen formed. We found that eight hour heats gave the most favorable results and were convenient periods to adopt for the remaining experiments. After the first two heatings the temperature was raised to 325°, and after the seventh heating, to 350°. When no further bitumen was formed at 350°, the residue was subjected to a temperature of 375° and 400° for two eight hour periods of time to determine whether any additional bitumen would be produced. Only a small trace was found in each case. The results of all the heatings and extractions are presented in table II.

TABLE II
DATA FROM HEATINGS AND EXTRACTIONS OF 300 GRAMS OF SHALE

Temperature, Degrees C.	Time of Heating, Hours	Weight of Extract, Gms.	Bitumen Extracted, Per cent	Total Bitumen Extracted, Per cent
...	0	5.24	1.75	1.75
300	4	1.01	.34	2.09
300	4	1.38	.46	2.55
325	16	4.60	1.54	4.09
325	9	3.50	1.17	5.26
325	8	2.79	.93	6.19
325	8	2.62	.87	7.06
325	8	2.49	.83	7.89
350	8	7.08	2.36	10.25
350	8	6.11	2.04	12.29
350	8	5.89	1.96	14.25
350	8	4.25	1.41	15.66
350	8	4.80	1.60	17.26
350	8	6.10	2.03	19.29
350	8	4.61	1.53	20.82
350	8	2.29	.76	21.58
350	8	.11	.03	21.61
375	8	trace	0 00	21.61
400	8	trace	0 00	21.61

The final residue, hereinafter designated as "R", from the series of treatments just described, was thoroughly mixed, air dried at 110° and a sample withdrawn for analysis. Determinations for volatile matter, fixed carbon, ash, nitrogen, and sulfur were made. The results of these analyses are given in table III.

The remainder of the residue was slowly distilled in a small retort in the same manner as the original shale was distilled for its oil yield. The percentages of water, gas, residue, or "spent shale," and oil were so determined. A sample of the air dried shale was also slowly distilled in order to obtain corresponding data. If our theory is correct, the spent shale from the distillation of the residue, which we shall call "R," should be practically identical with that from the distillation of the air dried shale. The data in table IV show that this is actually the case.

TABLE III
ANALYSIS OF AIR DRIED SHALE AND RESIDUE "R" IN PER CENT

Determination	Air Dried Shale	Residue R*	Residue R
Volatile matter	42.0	37.9**	10.1
Fixed carbon	3.5	8.3	12.0
Ash	54.5	53.8	77.9
Nitrogen	1.48	0.84	1.22
Sulfur	2.15	1.84	2.67

* Calculated to the basis of the original shale.

** By difference between 100 and the sum of the ash and fixed carbon.

The residue R, yielded no oil during the process of distillation but some gas and water. The data from this distillation are presented in table IV, together with the results of the distillation of the air dried shale for the yields of oil, water, gas, and residue, or spent shale, and the determinations for nitrogen and fixed carbon in this spent shale and the residue R_d.

TABLE IV
DATA FROM DISTILLATIONS OF AIR DRIED SHALE AND RESIDUE "R", IN PER CENT

	Air Dried Shale	Residue R*	Residue R
Oil	20.0	None	None
Water	5.6	3.5	5.0
Gas**	13.4	3.0	4.4
Residue	61.0	62.5	90.6 (R _d)
Extracts	21.6
Vol. and lost	9.4
Totals	100.0	100.0	100.0
Nitrogen†	1.20	0.76	1.21
Fixed carbon‡	12.4	8.3	13.2††

All the bitumen formed during the different periods of heating at any one temperature, was combined, giving us three extracts to correspond with the three temperatures: 300°, 325°, and 350°. Each of these extracts, which we shall call "B", "C", and "D" respectively, and that from the original shale, which we shall call "A", were dried at about 110° C. and cooled in a desiccator.

In order to determine whether the extracts A, B, C, and D were of the same composition, we analyzed each of them for nitrogen by a modified Kjeldahl-Gunning method¹⁵. The data from these analyses appear in table V. We thought that the percentages of nitrogen would suffice to show whether the extracts varied considerably in their composition, in which case it would not be necessary to make a complete elementary analysis for this preliminary study.

TABLE V
PERCENTAGES OF NITROGEN IN EXTRACTS

Extract	Nitrogen
A	0.70
B	1.13
C	1.69
D	2.23

Since only a few grams of extracts B and C remained after samples were taken for analyses, it was not possible to compound a large enough sample from the four extracts, in their proper proportions, for a satisfactory distillation. But, if we are to submit positive evidence that the sum of these bituminous extracts is the source of the oil, and the intermediate product in the formation of oil, it is necessary to show that the extracts yielded oil when distilled. Therefore, we distilled to dryness 10 grams of the combined extracts, in their proper proportions, in a small pyrex flask. As closely as we could determine, the material yielded about 70 per cent oil, 20 per cent coke, and ten per cent gas.

* Calculated to the basis of the original shale.

** By difference between 100 and the sum of the ash and fixed carbon.

† In the spent shale and the residue, R_d.

†† Calculated from fixed carbon in R by dividing by 90.6 per cent.

¹⁵ Chem. Met. Eng. 25, 50; 1921.

The series of treatments resulted in a gradual but definite change in the shale. We observed no difference in appearance after the extraction of the original shale; but after the first heating (at 300°) and extraction, the shale was a slight shade darker and the color deepened after each heating. The final residue was quite black and friable but most of it still retained its granular form. The final weight of the residue was 207 grams, which represented 69 per cent of the original shale.

We always observed the evolution of small quantities of gas, which had a very disagreeable, sulfurous odor, and water during each heating of the shale. In no case did any oil distill and no signs of oil were detected in the shale after the heating. Most of the gas was evolved at the higher temperatures. The quantities of gas and water produced during each heating were not measured in these experiments, because we were interested only in the total which, together with the insignificant mechanical losses due to handling, amounted to 9.39 per cent of the original shale. This was much greater than we had anticipated.

The extract A, from the original shale, was a very dark brown solid at ordinary temperatures, but it melted to a mobile liquid on the steam bath. When cold it had a greasy appearance, a slight, dark green fluorescence, and was sticky. It possessed the peculiar odor which we always associate with the raw shale. Extract B was a little darker than A, but otherwise similar to it. Extract C was much darker and had more of a tarry appearance, but it was quite like A in other respects. Extract D was a lustrous black, sticky, semi-solid bitumen which looked like a soft asphalt. It was also a mobile liquid at the temperature of the steam bath and had the distinctive odor of the heavy residua of Colorado shale oils. All the extracts exhibited a strong, green fluorescence when in solution with carbon disulfide. The determination of other properties was left for ultimate study.

We now have at hand sufficient data to indicate clearly the direction in which our investigation is proceeding and to guide us in our final work. Although we believe most of this data to be sufficiently accurate for quantitative considerations, we prefer at present to consider their qualitative significance mainly, because only one sample was studied. In either case, the results of these preliminary experiments are conclusive enough to settle a number of important questions and to define others.

There can no longer be doubt that it is possible to separate all the oil forming constituents of a Colorado shale without producing oil. Data in tables II and IV prove this conclusively. We have also demonstrated that the heavy bitumen is an intermediate product in the process of transition of kerogen to oil, because we distilled from this bitumen an oil which had all the external properties of a typical, crude, Colorado, shale oil. This part of the theory of oil formation, advanced by Engler and his coworkers^{6, 7}, and confirmed by McKee and Lyder,⁸ and the senior author¹² is, therefore, correct.

After careful consideration of our observations, we cannot agree with Engler, Lederer and Tausz,^{6, 7} that the reaction which occurs in the transformation of the insoluble portion of the kerogen to bitumen, is a depolymerization. The evidence from our work is all opposed to such a hypothesis, but indicates that the reaction is a decomposition which is identical with, or at least resembles, a slow "cracking". We shall submit proof of this contention after we have discussed what occurred during the formation of the bitumen from the kerogen.

We cannot reconcile the data in table II with the conclusion of McKee and Lyder⁸ that "This bitumen is formed at a quite definite temperature, the formation taking place between 400 and 410° C., in the case of this particular shale." Since we succeeded in forming all the bitumen by heating our shale, which came from the same deposit, at temperatures between 300 and 350° C., we believe their statement is not correct, or else its meaning is not clear to us. From the behavior of the shale at the latter range of temperature we conclude, as do Engler and Lederer,⁶ that the bitumen can be formed at temperatures as low as 200° C., but of course more slowly. Therefore, it cannot be said that the decomposition temperature is definite to within 10° C. However, we can

conceive certain specific conditions under which the qualified statement might be true.

It is evident from the data in table II, that the rate of bitumen formation increases with the temperature. The average rate of formation, in grams per hour of heating, was 0.299 at 300°, 0.326 at 325°, and 0.643 at 350°. This shows that the rate increases quite rapidly as the temperature approaches that at which the kerogen decomposes to form oil.

Time is a very important factor in the conversion of kerogen to bitumen, as table II clearly discloses. Within certain limits, the amount of bitumen produced varied almost directly with the time. The quantities formed during the eight hour periods of heating were fairly constant in some cases, but less so in others. This may have been due in part to occasional temperature fluctuations during the heating process. There seemed also to have been a general tendency for the rate of bitumen production to decrease after each heating at 325 and 350°. This was expected. The curve in figure I illustrates very well the relation between the time and the percentages of bitumen formed.

The phenomena observed during the formation of the bitumen, the properties of its components, and the character of the residue R do not support the supposition that the transition of insoluble kerogen to bitumen is due to a depolymerization. On the contrary, the results of our experiments point in another direction. We believe the following evidence is sufficient to disprove the depolymerization hypothesis:

1) A considerable quantity of gas was evolved during the process of heating. In a depolymerization of such a complex substance as kerogen, none should have been formed. The fact that some of the gas, evolved during heatings at 350°, was inflammable and burned with a luminous flame, indicates that it contained ethylenes. These are always produced in cracking reactions.

2) A small amount of water distilled from the shale during each heating. Although this may have been either water or hydration, held in the inorganic constituents of the shale, hygroscopic water, or both, it is quite possible for this water to have been produced by the decomposition of the kerogen. Water is usually produced during the decomposition or cracking of complex bitumens and pyrobitumens.

The comparatively large percentage of fixed carbon in the residue (cf. table IV) is strong evidence that a cracking, and not a depolymerization of the kerogen, occurred in the formation of the bitumen.

4) The percentage of nitrogen in the original shale was 1.48, and the sum of the percentages in the residue and the extracts was only 1.27, calculated to the basis of the original shale. Therefore, the decomposition was attended by a nitrogen loss. The total weight of nitrogen in the original shale was 4.44 grams, and the sum of that in the residue and extracts was 3.82 grams. Hence, the nitrogen loss was 0.54 grams, or 12.36 per cent of the nitrogen in the original shale. This loss, and the large quantity of nitrogen in the residue help to prove that no depolymerization, but a cracking occurred. In spite of the large loss of nitrogen, the odor of ammonia was not detected in the gases evolved from the shale. This indicates that the nitrogen escaped in its elementary form.

5) If the kerogen had depolymerized during the decomposition to bitumen, the percentages of nitrogen in the bitumen and kerogen would have been the same. Of course, this cannot have been the case, because the residue R contains 57.9 per cent of the original nitrogen, that in the original kerogen is 3.48 per cent, calculated from the nitrogen in the shale, and the average percentage in the bituminous extracts is 1.90. Although it may be argued that a part of the kerogen depolymerized simultaneously with the cracking of the remainder, the widely differing percentages of nitrogen in the extracts (cf. table V) do not support such an argument. All these observations and deliberations convince us that this decomposition is a cracking process.

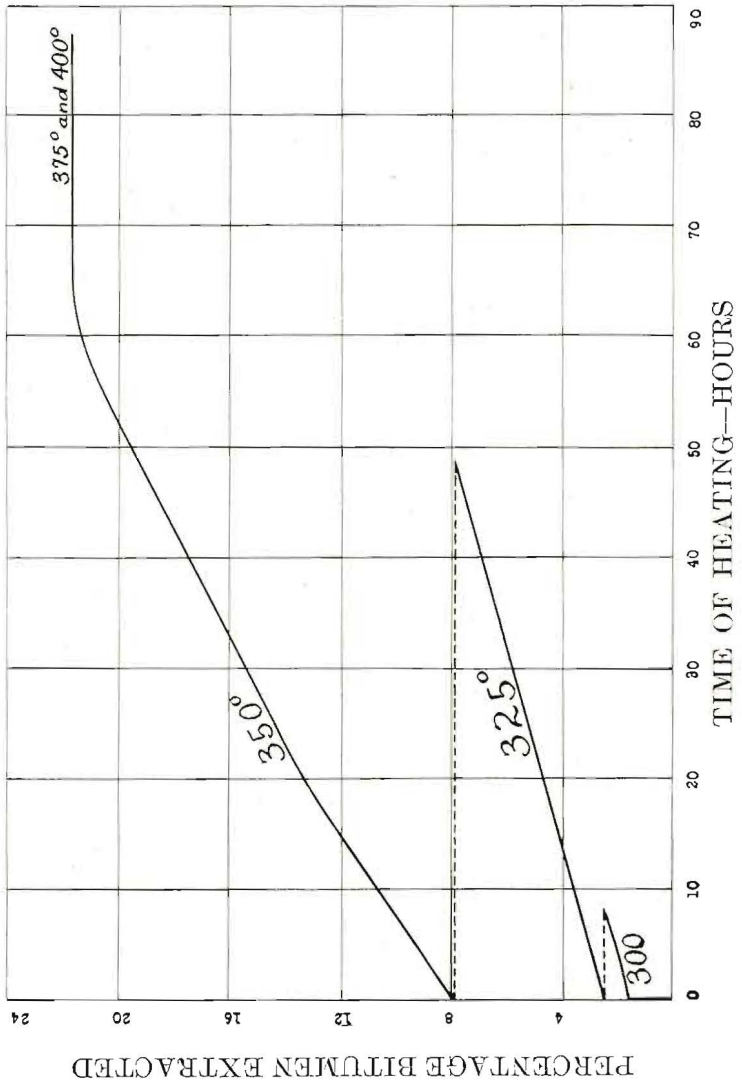


Fig. 1

In reviewing the phenomena which attend this decomposition, we were impressed by the influence of time and temperature on the quantities of bitumen formed and the fact that the amounts generally decreased after successive heatings at the same temperature. These phenomena and the apparent decrease in the rate of bitumen production after a certain period of time, indicate that equilibrium and the theory of mass action may play an important role in the decomposition of the kerogen.

Our study of the decomposition has brought to light a few general facts relative to the nature and composition of the kerogen. The data from the distillation of the residue R. (cf. table IV) and the analysis of R_d suggest that the kerogen, or the organic matter of the shale, consists of two distinct types of material: 1) the oil forming constituents, of which the bitumen is the primary decomposition product; and 2) the coke-forming constituents which yield the fixed carbon of the residue. There is no doubt that the carbonaceous matter is produced by the decomposition, because microscopic examinations of thin sections of the original shale do not show the presence of any appreciable quantity of such substance. Although it is possible that the fixed carbon was produced by the decomposition of the kerogen as a whole, the variation in composition of the extracts and the large amount of nitrogen (5.52 per cent) in the organic portion of the residue R, indicate that this is not the case, but that the coke forming constituents form a separate part of the kerogen.

It is also clear that that part of the kerogen which yields the oil cannot be a single substance or compound, but must be a complex mixture. If this were not true, the oil forming temperature would not have been raised by the extraction of a part of the kerogen, as we demonstrated in our early experiments; and neither would the composition of the extracts have varied to the extent shown in table V. The low percentage of nitrogen in extract A indicates that the soluble portion of the kerogen is different from the bitumens formed during the decomposition.

Very little, if any, sulfur must have been lost during the decomposition, as the percentages of sulfur in the residue R, and the original shale show (cf. table III). Extract D, which contained 1.46 percent of sulfur was the only one analyzed. If the sulfur in D is added to that in the residue, the percentage which can be accounted for is 2.01, calculated to the basis of the original shale. Since the residue R contains 85.7 per cent of the sulfur, it seems that most of this element is in the shale in the inorganic, rather than the organic form. This may have an important bearing on retorting problems.

In concluding our discussion, we wish to mention the possibility of applying the methods used in this investigation to a study of the tar forming constituents of coal. By a few rough experiments we convinced ourselves that the kerogen of oil shales bears a resemblance to that of coal, since we were able by heatings and extractions to produce a considerable amount of bitumen from a sample of Routt county coal from which the soluble substances had been previously extracted. We regret that we could not continue these experiments long enough to secure data worthy of presentation, because they should yield information of value and interest.

We have now succeeded in demonstrating the general mechanism of the transition of the kerogen of a Colorado shale to oil. The kerogen has been shown to consist of oil forming and coke forming constituents. A part of the former is soluble, and the remainder insoluble in carbon disulfide. During a decomposition the oil forming constituents first yield a series of heavy bitumens, the intermediate products from which the crude oil is produced by destructive distillation, while the coke forming substance yields the fixed carbon of the spent shale, and gas.

Our work shows that these decompositions are not depolymerizations, but apparently cracking reactions; and that they do not occur at a definite temperature, as formerly supposed, but within a wide range of temperatures. The rate of decomposition is much greater at higher temperatures, as would be expected.

We have yet to show more specific relationships between the probable origin of the shale and the composition of the kerogen, the various extracts and the carbonaceous matter in the residue. It would also be desirable to repeat this work on other Colorado shales of greater or lesser richness, and shales of different types from other regions. A number of refinements could be made in both our apparatus and technique. We hope to make further studies, in which such improvements will be made, and secure additional data, especially on the yields of volatile constituents during each heating process and the composition of the gases evolved.

SUMMARY:

1. The theories of the origin of oil shales were discussed in attempt to throw light on the nature of the kerogen.
2. The work of Engler, Lederer and Tausz, McKee and Lyder, and others, was reviewed critically.
3. A preliminary study has been made of the kerogen, or organic matter of a typical Colorado oil shale, of the mechanism of the thermal decomposition of this material, and of the liquid and solid products formed.
4. The kerogen was found to consist of two main types of organic matter: the oil forming and the coke forming constituents.
5. About eight per cent of the oil forming constituents were soluble in carbon disulfide. The remainder may be decomposed to a series of heavy bitumens from which the crude oil is obtained by destructive distillation. The coke forming constituents decomposed simultaneously to form fixed carbon and gas.
6. It was demonstrated that the primary decomposition does not occur at a definite temperature, as formerly supposed, but within a wide range of temperatures. In this work all the primary products were formed between 300 and 350° C. without producing any oil. The rate of decomposition was much greater at the higher temperatures.
7. Conclusive evidence was submitted to show that the primary decomposition is not a depolymerization, as was previously assumed, but that the reaction resembled a very slow cracking.
8. The bitumens produced at the different temperatures were apparently not of the same composition.
9. The oil forming part of the kerogen was found to be a complex mixture.
10. It has been suggested that the methods used in this investigation might profitably be applied to a study of the tar forming constituents of coal.

Chemistry Laboratory,
Colorado School of Mines,
Golden, Colorado.

