The Thermal Decomposition of Shales.   I—Heat Effects [1,2]

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The methods of recovering oil from oil shales are discussed in so many recent articles that they need not be repeated here. Suffice it to say that, at present, the only known methods involve the principle of destructive distillation.[1,2,3,*] This being the case, some of the factors involved in the thermal decomposition of shale have been studied. The results of this research will be published in two papers. The present one deals with the manner in which the shale decomposes under the influence of heat, while the subsequent article describes a method for the determination of the heat of reaction involved when the organic material of the shale decomposes to form oil.

ORIGIN OF OIL SHALES

DEFINITION—Oil shale is defined[4] as an argillaceous or shaley deposit from which petroleum may be obtained by distillation but not by trituration or treatment with solvents. The term is also applied to those shaley deposits which are saturated with asphalt or petroleum and from which the bituminous matter can be removed by such solvents as carbon bisulfide and benzene, but the term, as ordinarily understood and in the sense in which it is used throughout this paper, excludes the oil-bearing shales and applies only to those which contain little or no bitumen soluble in the ordinary organic solvents.

The chemical composition of the oil-forming materials from which the oil is produced is little understood. Professor Crum Brown has given the name "kerogen" to the material in Scottish shale which, on destructive distillation, yields oil.[4] He defines it as neither petroleum nor bitumen, but a substance yielding petroleum and ammonium compounds on distillation.

NOMENCLATURE—Some confusion is apt to arise as a result of the designations of the various products formed one from the other. A bitumen is usually defined as a natural or pyrogenous hydrocarbon which may or may not contain oxygen, nitrogen, or sulfur, and which is largely soluble in carbon bisulfide. Abraham[5] calls the insoluble compounds, such as are found in shales, pyrobitumens. Engler[6] classifies as bitumens the whole series of products which are formed from the decomposition of vegetable or animal fats, waxes, or residues. This latter definition would include the insoluble substances, such as kerogen and pyrobitumens, as well as the soluble ones. Since the terms "kerogen" and "pyrobitumen" have been used to designate the insoluble substance, the word "bitumen" in this paper will be restricted to the soluble hydrocarbons.

INSPISSATED PETROLEUM—Little is known as to the origin or nature of kerogen or other organic material in the shale. That all of the organic or carbonaceous matter does not produce oil is known.[7] E. H. Cunningham-Craig attributes the origin of kerogen to inspissated or dried-up petroleum. He concludes that the oil shale stratum is a former oil-bearing formation which, under the action of heat, has evaporated and dried up, leaving petroleum residues which have become insoluble by polymerization.[4] Other authorities are not inclined to accept this theory, as they see no substantial evidence of petroleum having passed through the formation.

RESIN THEORY—H. R. J. Conacher,[8] on the basis of microscopic examination, describes the organic matter in the shale as (1) carbonaceous bits of plants with occasional small spores, (2) yellow bodies believed to be algae, spores, or oil globules, (3) shells of minute crustaceans, and bones, teeth, and scales of fish, and (4) sand grains. Shale portions rich in animal remains give small yields of oil. Those rich in vegetable remains give a greater yield of oil. The yellow bodies in the foregoing tests are considered vegetable matter. New Brunswick, Colorado, and Utah shales do not contain many of these yellow bodies. They are thought to be fragments of resins set free by decay and oxidation of materials of which they were once a part. Solubility of resins decreases with age; therefore the theory that failure to extract them by solvents proves that these bodies are not resins is of no value. Resinous materials from coal yield on oxidation the same products as obtained from torbanites.

Jones and Wheeler[9] report that by extraction of common coal with pyridine and reëxtraction of this extract with chloroform, coal can be resolved into cellulosic and resinic parts. On distillation of the former they obtained phenols, while the latter gave paraffins, olefines, and naphthenes.

ANOTHER THEORY—D. R. Stuart[10] is inclined to think that the kerogen may come from different kinds of organic matter, either animal or vegetable, by the action of microbes under special conditions, the product depending upon the microbe and the starting material. The kerogen, on the other hand, may be the remains of certain kinds of vegetable matter, like pine pollen or lycopod spores. He actually prepared oils very similar in properties to shale oil by the distillation of a mixture of 75 per cent fuller's earth and 25 per cent lycopodium spore dust.

ORGANIC REMAINS—Engler[11] chooses to fit the origin of the pyrobitumens of shales into the whole scheme of bitumen and petroleum formation from organic remains, successive polymerization and decomposition playing a very important part both in the character of the petroleum and in the bitumen formed.

By the decay of fats, waxes, and other animal and plant remains there are produced free fatty acids, wax esters, and hydrocarbons of the type of adipocere, montan waxes, and, perhaps, ozokerite. These are soluble in benzene, carbon bisulfide, etc. Part of this material may condense and polymerize to form what Engler chooses to call polybitumens. These are infusible and insoluble, and are found in nature as the insoluble part of the Scottish, Austrian, and Autun shales. These, under the action of heat, may go over to soluble bitumens, small amounts of which are always found in the shale, and which may also be found in nature as malthas, etc. Disintegrating further under the action of heat and pressure, these compounds go over to natural petroleum as we find it in wells, and this, on polymerization, yields the heavy asphalts.

CLASSIFICATION

Shales differ considerably among themselves. Upon destructive distillation, they yield products differing in character even though they be produced under similar conditions. It is estimated that Elko Nevada shales will produce paraffin wax to the weight of 35 per cent of the total oil recovered, whereas the New Brunswick shale oil contains but little paraffin. The oil from the latter resembles California crude. An attempt to classify the various hydrocarbons in these shales leads to some confusion, but a partial

classification on the basis of solubility in organic solvents and chemical composition is possible.

The pyrobitumens, which form bitumens on heating, may be further subdivided into one class which contains little or no oxygen and another which does contain oxygen. Those in the first class are called asphaltic pyrobitumens because they resemble asphalts, which contain but little oxygen. They are infusible and insoluble, and include elaterite, wurtzellite, albertite, imposinite, and asphaltic pyrobituminous shales. The New Brunswick, Nova Scotia, and Quebec shales are of this type.

The nonasphaltic pyrobitumens are those which contain oxygen and oxygenated bodies, but are also insoluble and infusible. Into this class fall cannel coals, lignites, torbanites, and shales containing torbanite material. The Scottish shale belongs in this category.

DISTRIBUTION

Oil shales occur in various parts of the world in apparently unlimited quantities. In Scotland the shale oil industry dates back to 1850.[12] France began to develop shales in Autun even before the Scottish industry existed. New Zealand has several times attempted to use them.[13] In Australia several large deposits and some very rich shales occur.[14] In Tasmania there are extensive deposits.[14] In Africa there are shales in the Transvaal and in Portugese East Africa.[15] Spain and Serbia also have oil shales.[13] In the western hemisphere they are to be found in various parts of South America,[13] in Canada,[16, 17, 18] and in the United States.[19] None of these enormous deposits, except the Scottish oil shales, have, as yet, been worked with complete success.

The oil shales of the United States rival in quantity the known coal deposits. There is sufficient oil obtainable from the shales of Colorado, Wyoming, and Utah to supply the United States for several generations.[20] Colorado alone has enough shale to produce 58,000,000,000 barrels of oil.[21] When it is remembered that less than 8,000,000,000 barrels of oil have been taken from wells in this country since the first well was drilled in 1859, the quantity of oil available from these shales begins to be appreciated.

Although attention is, at present, centered on the oil shales of Colorado, Utah, Wyoming, and Nevada, it is only because these are exceptionally rich in oil-forming material. Other deposits exist,[22] and as methods are perfected for working shales the poorer ones will, no doubt, be utilized. In Kentucky there are quite extensive shale beds which, though not quite so rich as the Colorado shales, yield more oil than those being worked in Scotland at present.

The enormous quantities of shale available for oil production is the factor that continually encourages investigation in the face of all the difficulties surrounding the problem.

THE PETROLEUM SITUATION

In view of present-day statistics it must be admitted that the future of petroleum in the United States is not encouraging. The figures for 1920 show that some 110,000,000 barrels of oil were imported to make up the deficit in home production. Fig. 1 illustrates the situation as it stands.

While as yet the maximum production of petroleum in this country has not been reached, it will be seen that the consumption is much greater than the production, and the consumption is expected to increase. It was in 1895 that the first commercially practical automobile was demonstrated, and at the beginning of 1920 there were 8,000,000 automobiles, 1,000,000 trucks, and 300,000 tractors in use. Further, it is expected that by the end of 1921 there will be 9,000,000 automobiles and trucks, and 450,000 tractors in use. Aerial navigation is yet ahead, but may be expected
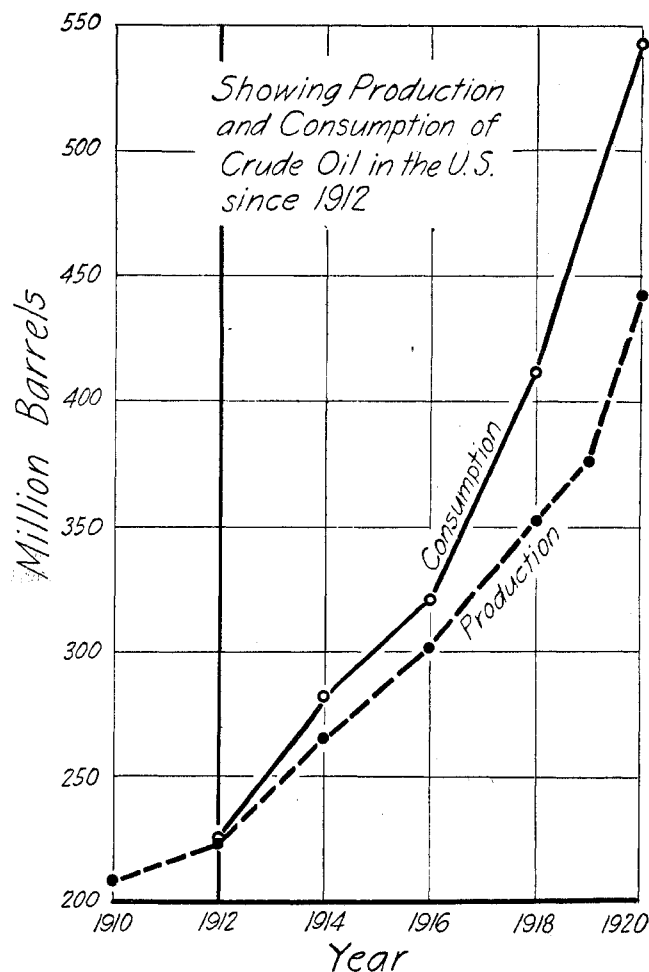

FIG. 1

soon to consume large quantities of particularly high-grade motor spirit.

That oil shale can be utilized to make up the deficiency caused by the increased consumption of petroleum is the opinion of our best authorities on the subject. In this connection we may quote Dr. Dean E. Winchester,[23] formerly of the U. S. Geological Survey:

After spending nearly five years in studying the oil shales of the western part of the United States, I am thoroughly convinced that the day is not far distant when these very shales that the cattlemen and farmers of the Rocky Mountain region have sworn at so often because they make neither good farm land nor good range, will yield oil in sufficient amounts to prevent the rapid decline on our total production which is imminent if no new source of petroleum is developed. There seems to be every indication that in the near future (perhaps ten years) there will be established in Colorado and Utah an industry for mining and distilling of oil shales which will rival in size any mining or manufacturing industry in the United States.

FIELD OBSERVATION

An inspection trip to the Colorado, Utah, and Nevada districts during the summer of 1920 revealed the fact that considerable work of a certain nature is being done toward the development of these shales. Several retorts have been built in the field, but none of them are operating in any regular way. Some are small one-unit plants operated for demonstration and experimental purposes only. Some of the schemes will probably never work and are intended more for promoting purposes and the sale of stock than for actual production of oil. Others are making every effort to produce a retort which will successfully distil these shales. Almost all of the development seems to be toward the perfecting of a retort which will produce oil, without

consideration of the character and quality of the oil produced. None of the oil is, as yet, being refined, and when refining operations are begun it is quite probable that the oil will be found deficient in quality, and some of the retorts that are furthest advanced, at present, may have to be redesigned completely to meet the necessity of producing a marketable oil. Let it be said that this does not apply to all of the plants in the field. Some are studying all of the conditions, each one in its proper relation to the other, and are making definite progress.

THERMAL DECOMPOSITION OF SHALES

Oil shales are but little soluble in organic solvents, as has been pointed out. They are not, therefore, hydrocarbons of the type of gilsonite,[24] grahamite,[24] ozokerite,[24] or asphalt. Shales must be distilled to recover the oil and ammonia products from them. The oil is said to come from a specific pyrobituminous material, and not from the entire organic remains in the shale. From Scottish shale, oil is said to come from kerogen. In any case, upon destructive distillation of a number of different kinds of pyrobituminous substances, hydrocarbons of the nature of paraffins, olefines, and aromatics are produced.[7, 25]

The hydrocarbons, when distilled off and fractionated, yield low-boiling, intermediate, and high-boiling fractions, just as do naturally occurring petroleums. Many retorts have been designed to distil these shales, and each is based on the designer's conception of the manner in which the shales decompose. For the most part the idea seems to be prevalent that, upon breaking down, the kerogen or other pyrobitumens yield, directly, petroleum oils. Many think that they yield, first, gasoline-like products; second, heavier products, such as kerosene; next, gas oil; and so on as the temperature increases. Others believe they yield a wide range of products directly, that is to say, each molecule of kerogen will decompose into gasoline, kerosene, etc., in essentially one step. In this case the gravity of the oil should not appreciably increase as the temperature rises. It has been demonstrated in this work that neither of the above conceptions is correct. The first product of decomposition was found to be a heavy semisolid or solid bitumen which is soluble in benzene and carbon bisulfide, and it was found that the formation of the petroleum oil is a result of the cracking of this heavy bitumen. This is in accord with Engler's deduction[26] that certain pyrobitumens, when heated to certain temperatures, become soluble in organic solvents. Table I shows some of the results of the decomposition of materials of this nature.[27]

TABLE I—INCREASE IN SOLUBILITY OF SHALE UPON HEATING

SOURCE	Before Heating Per cent	Temp. ° C.	Duration	After Heating Additional Per cent	
Posidonomya shale from Reutlingen	0.6	250	24 hrs.	0.34	
		300	Additional 24 hrs.	3.24	3.58
		400	Additional 24 hrs.	0.00	
Menilite shale from Strzytki, Egst. Glacia	0.85	300	0.5 hr.	1.21	
		350	Additional 24 hrs.	0.70	2.31
		350	Additional 24 hrs.	0.40	2.06
Shale from N. S. Wales, Australia	1.40	250	2 days	1.33	
		250	Additional 8 days	0.73	
Shale from N. S. Wales, Australia	1.40	300	2 days	28.50	
		300	Additional 8 days	7.80	36.3
Shale from N. S. Wales, Australia	1.40	400	1 hr.	4.90	
		400	Additional 2 hrs.	44.90	
		400	Additional 2 hrs.	5.40	55.2
		400	Additional 2 hrs.	0.00	

If this deduction is correct it is of considerable importance, and if proved experimentally would define methods for shale distillation superior to the ones now used. Experimental work was carried out as follows:

EXPERIMENTAL METHODS—The finely ground shale, 60-mesh, was placed in a 2-in. iron tube, 20 in. long. The tube was capped at both ends and fitted with a pressure

gage. The whole was placed in a rotary-type, gas-heated furnace in which it was possible to control the temperature very accurately. A base-metal thermocouple was also placed in the tube with the shale. The shale was heated in this apparatus for periods of time ranging from 1 to 8 hrs. It was then taken out and examined, and the amount of soluble material in it was determined. Observations were made on the temperature and pressure as the heating progressed.

It was found that in some cases when the shale was heated for 6 hrs. around 390° C., no apparent change occurred. Little gas was given off, as was indicated by the fact that the pressure remained around 25 or 30 lbs. 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 lbs. 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 relatively low resistance indicator, which rendered the results somewhat questionable. On this account other means of studying the changes that were taking place were adopted.

The final method was to distil the finely pulverized shale under atmospheric pressure in a small, electrically heated, brass retort, shown in Fig. 2. This apparatus had the advantage that the temperature could be controlled accurately and could be measured to within the experimental error of the mercury thermometer. Also, it was desirable that the distillation be made under atmospheric pressure.

The run was made as follows: About 25 g. of shale were placed in the retort. After the temperature of the metal bath had reached that at which it was desired to make the run, the retort was set in place and allowed to heat for 1 hr. 20 min. The temperature was measured by means of a 500° C. nitrogen-filled mercury thermometer placed in the bath. In one run thermometers were placed both in the retort and in the metal bath in order to determine the temperature lag through the shale. It was found that the center of the retort attained the temperature of the bath within 20 min.; hence, in order that all the shale might stay at the desired temperature for an hour, the heating was continued for 1 hr. 20 min. Preliminary tests had shown that if the shale did not decompose at a given temperature within an hour it could be heated at that same temperature for several hours with no apparent change. During the determination the thermometer was not used in the retort, as shown in the figure, but was placed directly in the bath. It was only the highest temperature that was of interest and, of course, this could be more easily obtained in the bath than elsewhere. The oil that distilled over was caught and measured.

After the shale had been heated for 1 hr. it was removed from the retort and extracted in a Soxhlet extractor with carbon bisulfide to remove the heavy oil or bitumen which had formed but had not distilled over. This bitumen was
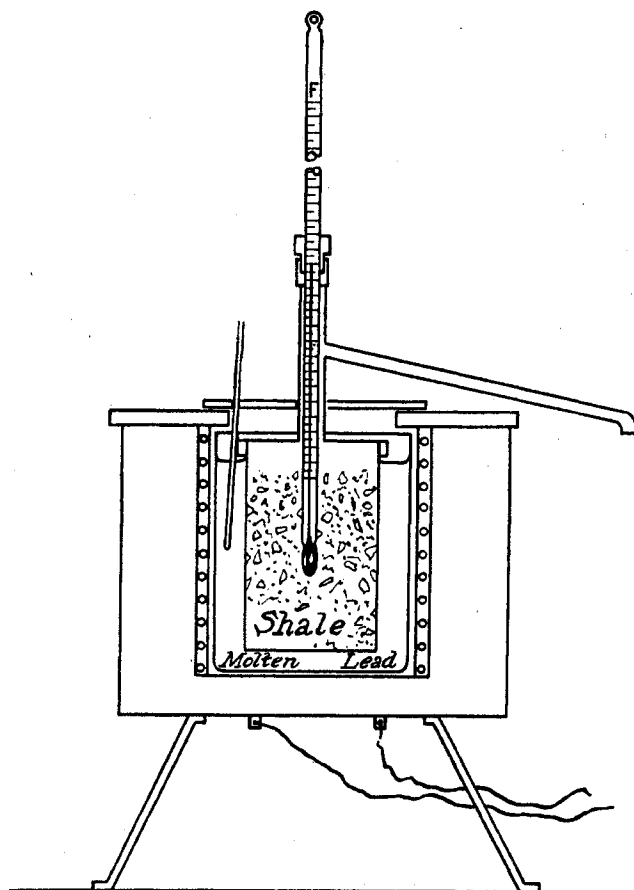
FIG. 2

freed from carbon bisulfide by evaporation, and weighed. Several runs were made, varying the temperature by small increments each time.

DETERMINATIONS—The shale used was from the Parachute Creek district near Grand Valley, Colorado. It had the following properties.

MASSIVE TYPE SHALE

Specific gravity	1.60
Specific heat	0.25
Moisture, per cent	0.13
Volatile matter, per cent	53.90
Ash, per cent	47.00
Oil yield per ton, gal	63.50
Solubility in CS₂, per cent	1.96

Run 1—This run was made as described above, with the bath kept at from 373° to 375° C. Eighty-five hundredths of a gram of oil distilled over and 1.45 g. of heavy bitumen were extracted from the residue. The shale was but slightly changed in appearance, and had not lost its hard massive texture.

Run 2—This run on 24 g. was like the previous one, except that the temperature was kept at 384° to 386° C. One and three-tenths grams of light oil were obtained, with 1.52 g. of heavy bitumen. Little change was seen in the general appearance of the shale; it was, however, slightly darker.

Run 3—This run was made at 398° to 400° C. One and seven-tenths grams of light oil were collected and 1.9 g. of bitumen. No noticeable difference had occurred in the appearance of the shale.

Run 4—A run at 425° C. yielded 4.2 g. of light oil and 4.93 g. of heavy bitumen. The character of the residue was decidedly changed. It was a dry coke-like mass which could be easily pulverized with the fingers to an impalpable powder, the original hardness and general character of the shale having been entirely destroyed. The specific gravity of the bitumen recovered was about 1.

Run 5—This decided change within 25° suggested that valuable information might be gained by taking an intermediate step. In a run made at 410° C., the amount of light oil was 2.55 g., and the amount of bitumen was 6.4 g. This bitumen, when extracted and dried, was of a rather rubber-like texture. The residue left in the retort before extraction was not a dried coke mass as in Run 4, but a sticky, tarry conglomeration which held together quite tenaciously. The following are the tabulated results of the five runs:

RUN	Temp. °C.	Light Oil G.	Per cent	Heavy Oil (Bitumen) G.	Per cent	Total Oil 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

No correction has been made in these figures for the original 1.96 per cent soluble in carbon bisulfide before heating. The figures would, of course, bear the same relation to each other as is shown above. Fig. 3 is the graph of these various factors.

INTERPRETATION OF RESULTS—The interpretation of the results of the experiments just described is plain and important. As the temperature rises in each successive determination, increasing amounts of oil are produced, but the quantity is rather small. At between 400° and 410° C. the curve suddenly rises, showing a complete destruction of the insoluble kerogen bodies in the shale. The temperature limits are seen to be close. This would indicate that the kerogen has a decomposition temperature which is definite to within 10° C.

Although it is seen from the curves that light oil is always produced, more of the heavy bitumen than light oil is produced at the lower temperatures. At the temperature of decomposition, *i. e.*, where the curve starts abruptly upward, by far the largest part is heavy bitumen, and during decomposition large quantities of heavy oil are produced, with no corresponding increase in light oil. If light oil had been directly produced from the kerogen, its curve would have followed the heavy bitumen curve.

CRACKING OF SHALE OILS

Another item of importance in connection with these decompositions is that the shales decompose at temperatures above the point where cracking will take place to a limited extent. It is seen that even at 375° C., where the decomposition of the kerogen was relatively slow, some light oil was formed, but cracking became rapid at almost the same temperature as that at which the shale decomposes.

The break and descent of the bitumen curve with no change in the total quantity of oil show conclusively that the heavy bitumen is decomposing to form light oils.

Another important point is noted here. Various distillations of this Colorado shale, either in 2-lb. lots or 20-lb. charges, under the most careful conditions, yielded 63 gal. of oil per ton. The oil obtained had a specific gravity of 0.921, which means 480 lbs. of oil. Add to this 20 lbs. of gas obtained, and we have 500 lbs., or 25 per cent of product per ton of shale. The amount of product obtained when the shale was heated just to its decomposition temperature was 36 per cent, or 720 lbs. per ton. If all this could be converted into oil of 0.921 specific gravity, it would yield 91.5 gal. of oil per ton. There would, of course, be a cracking loss if the tar were converted into light oils after its removal by solvents. This calculation is included to show that the maximum hydrocarbon yield is not produced by the present method of distillation and that it is the phenomenon of cracking that produces the light oils with which the industry is familiar.

These deductions place shale oil on the same basis as cracked products from naturally occurring petroleum. It has been shown that little or no gasoline is obtained from

shale as a primary product. The gasoline and other light cuts from shale oil are in many respects similar to gasoline obtained by cracking petroleum. They are highly unsaturated; the boiling point is low for a given gravity compared with that of paraffin hydrocarbons; they are a mixture of paraffins, olefines, and aromatics.[7,25] This would indicate that shale oil must compete with cracked products as to supplying gasoline. If these heavy residua can be cracked
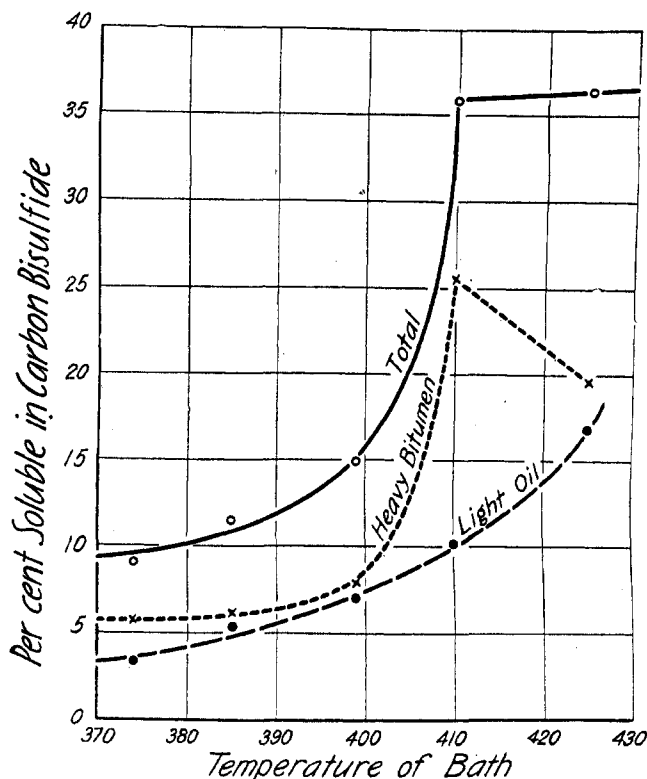

FIG. 3

to produce motor fuels, other heavy residua can also be utilized for the same purpose. Development will be along the lines of improvement of cracking processes adaptable to such oils.

Another phase of the situation is that, although gasoline is the product most in demand and the tendency is to convert other fractions into it, all of the crude cannot be used in this way, because other fractions, such as kerosene, gas oil, lubricating oil, fuel oil, and wax, are also needed. Consequently, it is the shortage in crude, and not that of gasoline, which threatens. As high-grade oils (those containing large percentages of gasoline) decrease, more gasoline will have to be produced by the cracking of heavy fractions of low-grade oils. As cracking processes improve and heavy oils are more in demand, shale oil will compete favorably as a product which can be worked up into motor fuel.

This conception has an important bearing on the commercial distillation of oil shale. It shows that there is a certain minimum temperature (which will probably vary with each shale) below which it is useless to heat and expect to recover oil at any reasonable rate. Also, when the temperature is held within the decomposition range, no gasoline is produced as a primary product. It is fallacy to say that a certain retort will yield a given amount of gasoline as a primary product. The retort should be looked upon as an apparatus for the production of heavy residua, while its efficiency as a gasoline producer should be based on its adaptability to convert these heavy oils to motor fuel. It is not meant to convey the idea that this bitumen or primary product should be removed by solvents before cracking;

in fact, it is more than probable that the most effective way to crack it is while it is yet mixed with the shale residue, but the whole problem of the production of light oils should be approached from the point of view of the cracking of heavy oils.

With this information as a guiding principle, a conclusion may be reached as to the relation that shale oils will bear in making up the shortage due to the increased consumption of petroleum.

It has been shown that the light oil is obtained by the cracking of heavy products which are formed when the shale is heated to a quite definite temperature. This means that the shale retort of to-day which produces light oils is being used as a cracking still. A little consideration will show that it may be made a very efficient one.[28]

Here is a hydrocarbon formed from the decomposition of microscopic particles of material disseminated throughout a mineral mass, and this hydrocarbon is formed near the temperature at which it is subsequently cracked to form light oils. This insures uniform distribution of heat not usually met with in ordinary processes. Further, one of the most difficult problems attending the cracking of oil is the removal of the carbon formed and deposited in the still. In the Rittman process it is continually scraped down by the revolving of chains. In the Burton still it is caught on the false bottoms of the still and thus prevented from caking on the heated zone. In the case of a shale retort such, for instance, as those used in Scotland, it is being continually removed by means of a mass of mineral matter so great that the amount of carbon is insignificant.

Without the use of steam in these retorts a high oil-yielding shale will yield about 12 per cent of carbon, which will remain in a perfectly dry, finely divided condition disseminated throughout an equally dry mineral mass. This moves through the retort without difficulty, and no carbon troubles are encountered.

It is not necessary to limit the amount of bitumen passing through the retort to that which is contained in the shale. Other heavy residua, such as bottoms from previous runs or from petroleum oil, could be injected into the retort and cracked to light oil along with the shale residua. The carbon residue would be materially increased, which is desirable because it could then be used in the production of water gas or as a fuel direct. Shale residues from the straight distillation of shales are, at present, used in a gas producer for the production of fuel for retorting.[21] They are also being used as solid fuels. It need not be emphasized that additional carbon would make them more valuable.

CONCLUSIONS

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 semisolid bitumen. 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. The petroleum oils formed from the shale are the result of the decomposition or cracking of the heavy bitumen.

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Studies on the Toxicity of Wood Preservatives—III[1,2]

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Since the date of our last publication[3] on this subject, petri-dish tests have been conducted on a number of wood preservatives. These preservatives have, in many instances, been prepared by the Section of Derived Products of the Forest Products Laboratory with the idea of throwing further light on the relation existing between their toxicity and chemical and physical properties.

METHOD

The petri-dish method used was essentially that described in former articles[4] on this subject.

The petri-dish cultures were placed in an incubator kept at approximately 25° C., and records of the rate and nature of growth were made every week for 6 wks. For each set of concentrations a check culture, consisting of 17 cc. of agar medium plus 3 cc. of distilled water, was prepared. The killing point was always verified once, and sometimes twice.

The fungus used was *Fomes annosus* Fr. This organism is a rapid wood destroyer and grows well on the medium used.

The petri-dish method has been followed in all the toxicity tests conducted at the Laboratory.[5] Other methods of test have been considered from time to time, such as the impregnation of wood or sawdust with varying dilutions of the preservatives, but these appear to offer no advantages over the petri-dish method, using an agar substrate, except possibly in the case of such substances as copper sulfate and zinc chloride, which may react with the agar medium.

The petri-dish method has the following advantages over other laboratory methods considered:

1—It is simple and rapid.

2—It requires little space for carrying on a large number of simultaneous tests.

3—It permits of successive growth measurements of the fungus to determine the *retarding* effect of the preservative on the organism, which data are essential in deriving mathematical equations to express the relation between toxicity and fungus growth.

4—It gives a more uniform mixture of preservative and substrate in many cases.

5—No organic solvent (diluting agent), such as alcohol, ether, etc., is necessary in order to secure the desired concentration.

In interpreting all laboratory tests on toxicity it should be kept in mind that they show only the *relative* antiseptic values of the preservatives and give an *indication* of the minimum amount necessary to prevent fungus growth.

The commercial value of a preservative depends upon a number of factors, the two more important from the standpoint of decay prevention being (1) toxicity, and (2) permanence in the wood under service conditions. Under approved impregnation methods used commercially, in order to obtain the necessary penetration the antiseptic requirements are several times fulfilled by a good preservative, such as coal-tar creosote, so that minor differences in toxicity would be overshadowed by the larger quantity of preservative introduced.

RESULTS OF THE TESTS

Table 1 gives a comparison of the toxicity of beechwood creosote, both crude and distilled, and also a comparison between the phenolic and neutral portions of fractions of the same oil.

TABLE 1—TOXICITY OF CRUDE AND DISTILLED BEECHWOOD CREOSOTE AND ITS NEUTRAL AND ACID PORTIONS

DESCRIPTION	Distillation Limits ° C.	Killing Point between (Per cent)	SOURCE
Commercial beechwood creosote, Sample 3359	....	0.12 and 0.24	
Total distillate[1] of above, Sample 3459	150°–260°	0.05 and 0.1	Distilled in laboratory
Portion of total distillate soluble in KOH, consisting of phenolic bodies, Sample 3460	180°–260°	0.025 and 0.05	Prepared in laboratory
Neutral portion of 195°–200° fraction, insoluble in KOH	195°–200°	0.2 and 0.5	Prepared in laboratory
Phenolic portion of 195°–200° fraction, soluble in KOH	195°–200°	0.075 and 0.1	Prepared in laboratory

[1] The chemical work involved in the preparation of the different fractions was done by the Section of Derived Products of the Forest Products Laboratory under the direction of Dr. S. F. Acree. In this connection see article

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