THE THERMAL DECOMPOSITION OF OIL SHALES

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The Thermal Decomposition of Oil Shales

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE, COLUMBIA UNIVERSITY

BY

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The Thermal Decomposition of Shales. I—Heat Effects

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

* Numbers refer to bibliography on page 18.

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, impsonite, 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.[13] 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.[14] 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 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,[22] formerly of the U. S. Geological Survey:

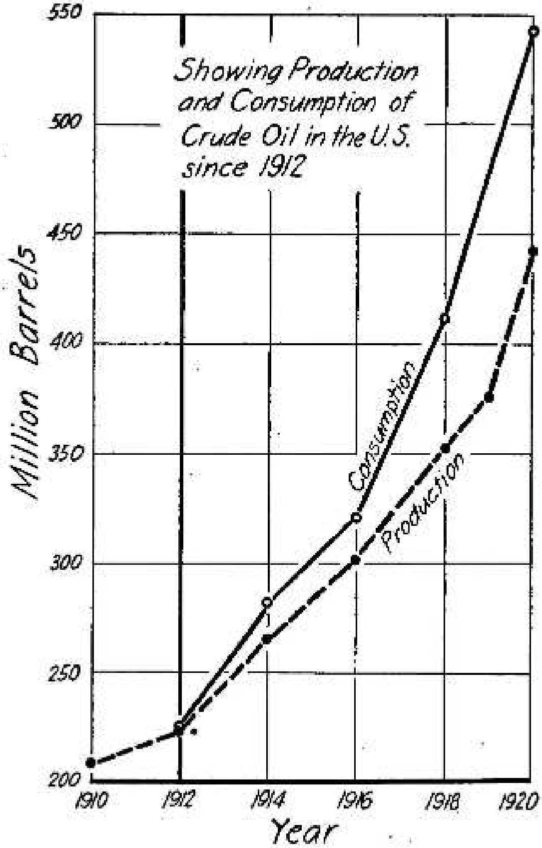

Fig. 1

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)