On the Origin of Petroleum

L. K. Osnitskaya,
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L. K. Osnitskaya

Petroleum and the products of processing it are an extremely important raw material in the modern people's economy. Several hundreds of millions of tons of petroleum are consumed annually by auto-transport, aviation, the fleet, and the chemical industry. The importance of petroleum in the country's economy was understood long ago, and therefore the study of the properties of petroleum and its origin, its formation in natural conditions, have received great attention from investigators since the times of old.

Back in 1763 Lomonosov, as if he were foreseeing the development of science and economics 150 years in the future, expressed the idea that the mother substance of petroleum is peat, which produces petroleum products under the action of high temperature.

A subsequent attempt to determine how petroleum could come into existence was made by a member of the St. Petersburg Academy of Sciences, Pallas, who decided that petroleum was formed as a result of the dry distillation of hard coal located in the bosom of the earth.

However, in 1863 the Russian academician Abikh, studying a deposit of petroleum on the Apsheronskiy Peninsula, came to the conclusion that Pallas's point of view was erroneous since the gases found with petroleum do not contain carbon monoxide, which is always found in the gases of the dry distillation of coal. The entire aspect of occurrence of petroleum deposits permitted Abikh to think that shales lowered deep into the earth could be subjected to heating which caused the appearance of vapors which rise through cracks and yield petroleum deposits in porous receptacles in the earth. However, since the processes of distillation of shales assumed by Abikh were not actually observed, Abikh did not insist on his theory, and as soon as Mendeleyev suggested a theory of the mineral origin of petroleum in 1877 Abikh immediately adopted the Mendeleyevian theory.

Mendeleyev's theory came into being on the basis of the work of the French chemists Berthelot and Boisson. In 1863 Berthelot expressed the hypothesis that the core of the earth consists of alkali metals exposed to the action of carbonic acid and carbonates, as a result of which carbides are formed; the latter, under the action of water, yield acetylene, which is condensed into liquid hydrocarbons, yielding as a result of further transformations petroleum, which soaks through cracks and accumulates in porous receptacles in the earth. Berthelot's erroneous assumption that the inner part of the earth consists of alkali metals was replaced by Boisson with the assumption that within the earth there is iron which, as a result of the action of solutions of carbonates, yields hydrocarbons, and that the latter are liquefied due to condensation or chemical processes of densification and form petroleum.

Mendeleyev analyzed the facts more precisely, and therefore the theory created by him was quite logical. On the basis of the degree of density of the earth and the properties of chemical elements he came to the conclusion that the earth's center consists of carbides. It is known that carbides are found in large quantity in meteorites, and it may therefore be assumed that when the formation of the earth from a liquid mass took place carbon could be combined with metallic iron and yield carbides, which after the formation of

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the earth's crust could yield gaseous and liquid hydrocarbons under the action of water. Subsequently additional reactions took place, as the result of which petroleum deposits appeared. The geological circumstances of the Apsheronskiy Peninsula made it possible in the light of existing views to acknowledge the correctness of such a picture. Research by chemists showed that under the action of water on carbides (cast-iron, for example) liquid and gaseous hydrocarbons are formed, which can be condensed and yield mixtures of hydrocarbons similar to petroleum. Such, in brief, is the theory of the mineral origin of petroleum, which received widespread dissemination due to the fact that it was comprehensible to chemists, on the one hand, and on the other hand gave geologists a means for searching for new petroleum deposits. According to this theory petroleum should be sought at the sites of pronounced depressions, which cause the appearance in the earth's crust of cracks along which water would move toward the incandescent center of the earth's core and petroleum would be raised to the natural receptacles in which we find it, that is, in the foothills of both existing mountain ranges and mountain ranges which once existed in ancient times. And in fact, quests for petroleum in such regions were not unsuccessful.

Thus Mendeleyev's theory was progressive and aided the discovery of new deposits and the finding of new chemical reactions.

Although Mendeleyev's theory seems to find confirmation in experimental data, a whole series of writings have also appeared which are critical of it. In these writings the following facts are adduced in opposition to the mineral theory of the origin of petroleum:

1. Metal carbides occur so deeply that the penetration of water to them is greatly hampered.

2. Metal carbides are located in the bosom of the earth at a temperature of several thousand degrees, while petroleum contains, as was determined later, extremely complex compounds of little stability (porphyrins), which break down at temperatures above 150-200 degrees Centigrade.

3. Petroleum is encountered mainly in sedimentary rocks of marine origin. Thus petroleum would have to have moved over great distances, while the majority of geologists do not consider this possible.

Mendeleyev's mineral theory was gradually supplanted by new theories of the origin of petroleum, which regarded petroleum as a product of biogenic origin.

Of such theories we shall mention first of all the theory of the animal origin of petroleum proposed in 1888 by Engler. Engler obtained products similar to petroleum as a result of the distillation of blubber at 360-420 degress Centigrade. On this basis he assumed that petroleum was formed in the process of distillation of mainly animal and partially vegetable residues buried in the earth.

At first this theory was figured on a par with Mendeleyev's theory by certain geologists, but later it acquired ever greater individual weight. However, the discovery by Walden in 1893, and again later by Rakuzin in 1904, of the optical action of petroleum, which had been observed by Biot back in 1835 and at once forgotten, and the later discovery by Treybs and Orlov (1933) of porphyrins (residues of hemin and chlorophyll synthesized by animal or plant organisms) in petroleums, and also the geological conditions of the location of petroleum contradicted Engler's distillation theory, too.

Subsequent development of study of the origin of petroleum by the work of Russian (A. A. Arkhangel'skiy, G. M. Mikhaylovskiy, K. P. Kalitskiy, L. A. Sel'skiy, and others) and American (Trask) geologists, and chemists (V. V. Markovnikov, N. D. Zelinskiy, S. S. Nametkin), rendered Engler's theory worthless.

The geological circumstances of petroleum deposits and the chemical composition and properties of petroleums, which were given detailed study by numerous schools (the V. V. Markovnikov, N. D. Zelinskiy, and S. S. Nametkin schools), and later by their adherents both here and abroad, have shown that petroleum could not be formed at the temperatures necessary for distillation of organic deposits or the products of changes in these deposits, as held by Engler, Poton'ye and their adherents. Temperatures of 200 to 250 degrees Centigrade are the limits at which porphyrins and the rotatory power (optical) of petroleums can be preserved, Sulphur compounds of certain petroleums begin to break down at still lower temperatures over the brief time-intervals of laboratory experiments. Therefore, the distillation theory can be applied only for a very small number of instances, such as for Scottish petroleum.

Inasmuch as the formation of petroleum cannot take place at temperatures exceeding 200 degrees Centigrade, scholars attempted to replace the temperature factor with the time factor, having calculated by means of extrapolation on the basis of Arrhenius' law how much time was necessary to obtain petroleum at 200 to 150 degrees Centigrade. Thus, Seyer and a number of other authors hold that the reactions necessary for conversion of waxes and fats into petroleum could be achieved at 150 degrees Centigrade, but in the course of the geological periods transpiring since the moment that the materials were buried. However it is not always possible to carry out such an extrapolation, inasmuch as products formed at 450 to 500 degrees Centigrade might show extremely essential differences from the products of reactions occurring at 150 degrees Centigrade.

In studying the conditions of occurrence of petroleum deposits, geologists have not succeeded in finding indications of the accumulation of a layer of buried animals, required by Engler's theory..

Lecret, back in 1866, designated sea-weeds as a source material for the formation of petroleum. Mikhaylovskiy, Jeffrey, Rakuzin, Ipat'yev, Watts, Sel'skiy, Arkhangel'skiy, Kreychi-Graf, Poton'ye, Kalitskiy, Lilley, Porfir'yev, Gubkin, Stadnikov, and others have been in agreement with this view (at times with an additional assumption as to the possible participation of animal remains in this process).

Certain of these investigators advance extremely weighty evidence that the basic role of the mother substance in the formation of petroleum from marine plant remains was played by sediments of vegetable remains on the floor of littoral salt-water or partially enclosed basins.

A particularly graphic picture of the original stage of formation of petroleum from marine vegetable remains was given by G. M. Mikhaylovskiy in 1906. In his opinion there took place in littoral zones a rapid precipitation of limestone-clay silt together with the remains of various organisms of the animal and vegetable kingdom; as the result of covering by succeeding layers an anaerobic decomposition of the remains of the organisms took place in the deposits under the action of bacteria. Afterwards bituminization took place under the action of solutions of mineral salts and increased temperature. Thus, back in 1906 direct indications were made as to the participation of microorganisms in the formation of petroleum. Later a number of investigators -- Arkhangel'skiy, Sel'skiy, Porfir'yev -- on the basis of the discovery by Bastin and Ginzburg-Karagicheva (1926) of bacteria in petroleums and the liquids occurring with them, developed the idea of the participation of bacteria in petroleum formation, assuming that complete transformation of vegetable material deposited in a salt-water basin into petroleum could occur in greatest part as a result of biochemical processes of reduction and hydration accompanied by the smashing of molecules, facilitated by increased pressure and temperature. The products of reduction which formed, depending on the conditions of formation of petroleum, as a result of the processes of orogenesis, migrated together with gas and water along the cavities of tectonic faults and formed secondary accumulations in the porous rocks of natural receptacles.

However, although there are data concerning the modification of fats under the action of bacteria given off by petroleum -- thus, according to Rodinova's studies the process takes place in the direction of the formation of free fatty acids, polymerization of them, increase in the quantity of unsaponifiables, and transition of the saturated fatty acids into unsaturated ones -- still, there has not been until recent times knowledge of the facts of the action of the bacteria which cause breakdown into light hydrocarbons, reduction of double compounds, hydroxyls, and ketone groups, and other processes which should take place in the conversion of the mother substance into petroleum, in other words, there are as yet no foundations to assert that the basic processes of formation of petroleum can be achieved only by bacteria. It has been established that bacteria: (a) hydrolyze cellulose, (b) convert glucose into lower alcohols and fatty acids, (c) saponify fats, (d) reduce saturated acids into non-saturated ones, (e) decompose the higher fatty acids to lower ones, (f) polymerize unsaturated fatty acids, and (g) oxidize hydrocarbons due to the oxygen of the air and sulphates. In recent times Tsobell and Yankovskiy's report has appeared, to the effect that under the influence of desulphurizing bacteria from fatty acids (propionic, butyric, caprylic, and other acids) oils containing hydrocarbons of the aliphatic series are formed.

In 1927 A. D. Arkhangel'skiy wrote that the precipitation of argillaceous sediments, which provided the foundation of petroleum-producing layers, occurred in marine basins in which deep strata were infected through hydrogen-sulphide fermentation.

Analogous pictures of the first stage of formation of petroleum were painted by Kreychi-Graf, Poton'ye, Porfir'yev, Kalitskiy, and Lilley. In their conceptions the organic mass of salt-water basins, as a result of the biochemical processes of decarboxylization (anaerobic fermentation) which occurred in the absence of oxygen, was made poorer in oxygen by comparison with the original material. In the presence of oxygen or in fresh-water basins the process of decomposition ended either with complete disappearance of the organic substance or by formation of comparatively poor-in-hydrogen fuel shales, or with the formation of various types of coal. Geologists have succeeded in checking these processes rather closely.

G. L. Stadnikov, on the basis of analysis of the behavior of vegetable remains buried in a salt-water basin, imagined the formation of primary petroleum in the following manner. Primary petroleum is a product of the decarboxylization of polymerizers of liquid acids, humus acids dissolved and dispersed in a mixture of waxes, tars, and unchanged fatty acids in the form of a homogeneous semi-liquid mass.

Of interest is the scheme of the formation of petroleum hypothesized by Dobryanskiy, who established changes, in conformity to principle, of caustobiolites in two directions: (1) from vegetable remains: shale → asphalt → petroleum and (2) from sapropel: shale → sapropelite → asphalt → petroleum. However, each of the assumed stages of formation petroleum is already an end substance, for various reasons undergoing no further modification. It is thermodynamically impossible to assume that the polymers and tars composing these substances could be transformed, without the action of any agents and only through the process of time, into petroleum at low temperatures.

Berl's theory of the origin of petroleum from cellulose received rather widespread dissemination. Berl and his associates demonstrated that with treatment of cellulose at 310 to 400 degrees Centigrade with alkalis and carbonates (dolomite and chalk) it turns into plastic (at times a greasy or liquid) mass enriched with hydrogen and oxygen, which contains about 78-85 percent carbon, 12-13 percent hydrogen, 2-9 percent oxygen instead of the 44.2 percent carbon, 6.4 percent hydrogen, and 49.4 percent oxygen in the original cellulose. With hydration of this mass with hydrogen under pressure in the presence of iron and iodine as catalysts, Berl obtained petroleum-like substances. Berl suggested that proto-petroleum could be formed as a result of basic hydrolysis of cellulose, and that petroleum was then formed from proto-petroleum as a result of reduction by the hydrogen given off in the action of water on ferrous oxide, siderite, or iron sulphides. Berl demonstrated that the action of water on these substances leads to the formation of hydrogen. However, Berl did not succeed in proving that reduction takes place in the action of water on the mixture of hydrogen-generating iron compound with proto-petroleum and water. Still, Berl held that under natural conditions the reduction of proto-petroleum can occur under the influence of the catalytic action of rocks and salts contained in the water (in particular, iodine salts).

Berl's theory also requires high temperatures for conversion of vegetable material into proto-petroleum, and that is its most vulnerable point. However, if it were possible to reduce the temperature of Berl's reaction to 200 degrees Centigrade or lower through application of a catalyst, this theory would then acquire rights of citizenship.

Thus, although there still remain problems which have not been completely solved as to the nature of material (sea-weed, diatoms, marine grass, or other plants) deposited and then subjected to transformation into petroleum, the mineral deposits which accompany it, the degree of salinity of the water in the basin, and also the depth at which the transformation of organic remains takes place under the influence of bacteria in conditions of anaerobic fermentation, the primary stage of the formation of petroleum in salt-water basins does not call for serious doubts at the present time.

The second stage of the formation of petroleum -- the transformation of proto-petroleum into petroleum -- is imagined differently by different investigators. Part of them assume that further formation of petroleum from primary petroleum occurs as the result of distillation at high temperature, developed due to the near-by passage of magmatic masses or the deep depression of the deposits. However, as already pointed out above, high temperatures should be excluded from the conditions of the formation of petroleum.

In the opinion of others, the formation of petroleum occurs as the result of the forcing of the petroleum out of the mother rock into the porous rock of the collector. However, high pressure cannot in itself play a serious role in petroleum formation. At this point mention should be made of the theory of petroleum-producing strata. Certain geologists, on the basis of consideration of the conditions of occurrence of petroleum, reach the conclusion that petroleum was formed from clay-containing silts. Thus I. M. Gubkin writes that in the Maykop deposit, below the basic petroleum deposits, among a series

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of foraminiferous layers there occur beds of highly bituminous clay with droplets of petroleum scattered through the entire bed. If these were overlapped or underlain by a porous stratum, there would then in his opinion be a petroleum-bearing horizon there, and not just strata with diffusely scattered petroleum. Analogous thoughts have been expressed by Kreychi-Graf and Arkhangel'skiy. The latter, investigating a petroleum deposit in the northern Caucasus, arrived at the conclusion that the petroleum had been formed due to the organic substance of the argillaceous rocks and that the sandy layers were only collectors on the strength of their porosity, and that the petroleum had migrated to them. Meanwhile, in cases where the mother rock is at the same time also porous, or cut by cracks, the petroleum should from this standpoint remain in the strata were it formed.

The theory of petroleum-producing layers has been exposed to basic criticism on the part of a number of scholars. For example, Porfir'yev holds that, while answering all demands on the part of geology, this theory has a weak place -- the movement of the bituminous substance found in clays in a scattered state and at the same time in the form of kerogen into the sands where this substance is observed in the form of petroleum. Kerogen is a form of polymerizer of fatty acids with humus acids, tars, and a number of other components scattered in them, and extremely remote in its physical and chemical properties from petroleum. However, at the present time, as we shall see below, there are no bases for considering impossible the transition of kerogen into petroleum in the presence of suitable catalyzers.

Since far-off times the assumptions have been expressed that in the process of formation of petroleum catalysis could play a role (Kreychi-Graf, Poton'ye, Nametkin). However, only N. D. Zelinskiy, in the period from 1927 to 1931 succeeded in a number of brilliant works in proving that from a whole series of the products encountered in vegetable and animal residues at temperatures close to 200 degrees Centigrade substances which are found in petroleums and petroleum-like materials are formed as the result of the catalytic action of aluminum chloride. These works showed clearly the path which must be followed in searching for a solution of the problem of the formation of petroleum.

In 1927 Kobayashi and Yamamoto also approached the problem of the catalytic nature of the formation of petroleum. They set up experiments for the recovery of petroleum-like substances from fish fat under the action of Japanese acid clays, but the experiments were performed at 500 degrees Centigrade and the petroleum-like liquid that they obtained was the usual product of the thermal breakdown of fish fat.

The work of the Russian scientists Gurvich (1912) and Lebedev (1925-1935) showed that clays, floridine, acid Japanese earths and other substances also act like aluminum chloride and bromide, boron fluoride, and other catalyzers known in chemistry, which break down rapidly in contact with rocks and moisture. Through the work of the Russian scientist A. V. Frost (1936-1940) the low-temperature catalytic action of aluminum silicates and aluminum chloride on hydrocarbons was confirmed. At the same time: (1) at low temperatures polymerization of olefines takes place, (2) at increased temperature the process of polymerization is accompanied by isomerization and disproportioning of hydrogen, (3) at higher temperature breakdown of the saturated hydrocarbons takes place. Through subsequent experiments the author demonstrated that a number of clays, in contact with organic substances, even at low temperatures have a catalytic effect on the reactions of dehydration of alcohols, elimination of water from ketones, polymerization, disproportioning of hydrogen which leads to hydration of light olefines due to loss of hydrogen by part of the substance with the formation of heavy, poor-in-hydrogen substances which undergo the sorbating action of the clays. All this, in A. V. Frost's opinion, shows that in the temperature range 100 to 200 degrees Centigrade, in the presence of active clays in sufficient measure, the conversion of a number of products of the biochemical or basic change vegetable residues can produce petroleum-like products. The fact that in certain deposits (for example, the second Baku deposit) petroleum is not associated with clays cannot serve as refutation of the hypothesis expressed, since in such places other substances may be catalysts.

Taking the work done earlier in this field together with the data which he obtained, A. V. Frost draws two diagrams of the formation of petroleum in the bosom of the earth. According to the first, in the author's opinion the less probable, hydrolysis of vegetable (rich in cellulose) and animal residues by alkali water takes place at a temperature of about 200 degrees Centigrade under pressure, in agreement with Berl, and products poor in hydrogen are formed which are not soluble in water and which rise above the water layer and in contact with the clay, losing hydrogen in the form of water. These products, also under the influence of clays, are exposed to processes of disproportioning of hydrogen, being transformed into petroleum. The second diagram is represented by the author in the following manner. Considerable quantitites of dead marine plants and animals, mixed with clay and sand and the flinty and calcified skeletons of organisms, accumulate in a salt-water basin isolated from the open sea. The residues are subjected to anaerobic destruction by bacteria. The process of bacterial action is intensified due to the overlapping of the deposit by coverings of argillaceous sediments. Deep under the earth, the deposits are heated in consequence to 100 or 150 degrees Centigrade, increasing the speed of ensuing reactions of a catalytic nature, as a result of which the products of the breakdown of organic residues, consisting of tars, acids, alcohols, and ketones, are converted into petroleum.

From the attached review of literature it is obvious that the problem of the origin of petroleum, which has long engaged the minds of geologists, chemists, and microbiologists, is at present close to complete solution. The paths to solution of the basic problems, which 20 years ago were unclarified, have in any case been planned.

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Institute of Microbiology
of AN of the USSR
Moscow