1915

The relation of the composition of petroleum to its origin and occurrence

John Warder Shotwell

Department: Mining and Nuclear Engineering

THE RELATION OF THE COMPOSITION OF PETROLEUM TO ITS ORIGIN AND OCCURRENCE.

BY

JOHN WARDEN SHOTWELL

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

BACHELOR OF SCIENCE IN MINE ENGINEERING

Rolla, Mo.

1915.

Approved by C. H. Cox
Professor of Geology and Mineralogy.

THE RELATION OF THE COMPOSITION OF PETROLEUM TO ITS ORIGIN AND OCCURRENCE.

TABLE OF CONTENTS.

THE RELATION OF THE COMPOSITION OF PETROLEUM TO ITS ORIGIN AND OCCURRENCE.

CHEMICAL AND PHYSICAL NATURE.

Petroleum is a mixture of hydrocarbons. It is a liquid varying from colorless, through yellow and brown to black. It varies from 1.00 to 0.80 in specific gravity, which corresponds to 10° to 45° Beaume. It varies widely in physical properties, such as viscosity, ignition point, polarization of light, etc.

Chemically, it is composed essentially of carbon and hydrogen, but usually contains impurities such as sulphur and nitrogen. The carbon and hydrogen combine with each other to form certain series, or "chains." Those which are important in the study of petroleum, are:

a. The Methane Series - C_nH_{2n+2}

b. The Ethylene series - C_nH_{2n}

c. The Acetylene series - C_nH_{n-2}

d. The Polymethylene series = C_nH_{2n}

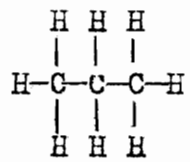
e. The Aromatic series - C_nH_{2n-6}

Of these, the first three are so-called "straight-chain" series, and the others are the "ring-chain", or "cyclic" series.

a. The Methane Series.

The Methane, or paraffine, series is made up of hydrocarbons having the composition of C_nH_{2n+2}. Members from CH_4 to $C_{60}H_{122}$ have been identified. Of these, CH_4 to C_5H_{12} inclusive, are liquids; and all above $C_{15}H_{32}$ are solids.

The general structural formula for the members of the methane series is illustrated by the following, which is the formula for propane:



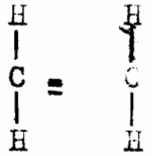
Carbon has a valence of four, and it will be noticed that, in the methane series this valence is satisfied; i.e.,there are no loose bonds. For this reason these compounds are more stable; i.e.,less liable to explosion, combination, and solution than the unsaturated series.

The methane series is of first importance in the composition of American petroleums. The high-grade, light oils consist almost entirely of paraffines; and the value of an oil varies in almost direct ratio to its parafinne content.

b. The Ethylene Series.

This series has the general composition

C_nH_{2n}, but we meet with only one of its members in the study of petroleum. This is C_2H_4. Its structural formula is written thus:



It has the so-called double bond, which indicates that it is less stable than the members of the methane series. It is said to be "unsaturated". It has comparatively small importance in petroleum.

c. The Acetylene Series.

This series has the general composition C_nH_{2n-2} but only one of its members, C_2H_2, acetylene, is of interest in the study of petroleum. It has a triple bond, and is even less stable than ethylene. Its structural formula is

Its importance in the study of petroleum is comparatively small.

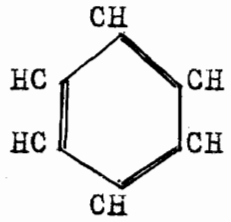
d. The Polymethylene Series.

The Polymethylene, or naptha, series seems to consist of CH_2 molecules combined with each other in varying numbers. They are thought to be "unsaturated". They are important in Russian petroleum, but

not in American. A grear deal of research work has been done on them recently, but no very reliable records of the results have been made public.

. The Aromatic Series.

The aromatic, or benzene, series is next in importance to the methane. It has the general Composition C_nH_{2n-6}, and is the principal member of the so-called "cyclic" series. The structural formula of benzene is written thus:



It will be noticed that it has the double bond, showing it to be "unsaturated" and more or less unstable. It is heavy and dark, and has a sweet odor when not polluted with sulphur. The members of this group make up the bulk of the so-called asphaltic oils.

ORIGIN.

There are two general theories for the origin of petroleum:

a. Organic.

b. Inorganic.

Of these the organic theory is the one most generally accepted among geologists, and is the only one which

will be considered in this discussion.

a. Organic theory.

1. Animal.

2. Vegetable.

It is an observed fact that paraffine hydrocarbons can be formed from the fatty tissue of animals and plants by the natural process of distillation. According to the organic theory, organic matter, plant or animal, is laid down in the sea and covered with sediments, particularly mud, before becoming decomposed. As time goes on the oil is distilled out of the organic matter, and collects in the porous strata.

There is a great deal of evidence of all kinds in support of this theory, but the simple statement of it is judged to be sufficient for the purpose of this paper. In the following discussion it will be assumed that the oil was originally formed in this way.

OCCURRENCE.

Certain conditions are known to influence the occurrence of petroleum. The most important of these are as follows:

a. Adequate Source.

1. Thickness of sediments below.

2. Amount of organic matter below.

3. Area drained.

b. Structure and Stratigraphy.

1. A pervious bed to form a reservoir in which the oil can accumulate.
2. Anticlines and synclines.
3. Depth of water table.

   The oil lies on top of the water. When the water table is high, the oil will tend to be in the anticlines; when it is low, in the synclines.

4. Terraces.

   A terrace, being usually a superimposed fold, is likely to collect all the oil in its immediate vicinity, and prevent it from going to the crest of the major fold.

5. Faults.

   A fault, by fracturing the rocks, generally provides a way for the escape of the oil; and hence is regarded as a bad sign. But in certain districts, by forming impervious gouge across a pervious member, faults have halted the upward progress of oil along that member.

6. Lensing of sand.

Sand is a shallow-water formation, and for that reason it is subject to very considerable changes in thickness. At times it even dies out altogether. This is known to oil men as "lensing".

As the oil follows the sand, it is obvious that where there is no sand there can be no oil, no matter how favorable all other conditions may be.

From the above it will be seen that the occurrence of oil is not a thing which can always be determined by mechanically following a pre-determined procedure; but that each case must be studied carefully as a separate problem, to the solution of which must be applied both geologic knowledge and common sense.

POSSIBLE CAUSES AFFECTING COMPOSITION.

It is a fact which has long been known that petroleums from different districts vary widely in composition. For a time it was thought that the petroleum of Pennsylvania was an entirely different substance from that of Russia, for instance, etc. The main question is- Were our petroleums formed as they now exist, or were they originally the same substance, which has been changed by peculiarities of occurrence to the present forms? This question has been in the mind of probably every investigator who has taken up the study of petroleum in a broad way, but unfortunately the men who have done the field work in petroleum geology have generally been too much interested in the more purely economic side of the work to give this phase much attention. Such evidence as has been collected is scattered through a large number of publications; and, when gathered together and boiled down, it is not in every sense, satisfactory. However, it does throw some light on the subject; at the least it will serve to give a fairly definite idea concerning the present state of our knowledge along this line.

The most important economic difference in the composition of petroleum, is the fact that certain oils are predominantly paraffine or aromatic; i.e.,they are

either of paraffine or asphaltic base. The oils having a paraffine base are, as a rule, lighter in color and gravity than those having an asphaltic base. The paraffine oils are suitable for the manufacture of gasoline and kerosin by refining, while the asphaltic oils are suitable only for fuel and lubricating purposes.

There are certain things to which differences in the composition of petroleum may be ascribed. They are as follows;

1. Difference in origin.
2. Difference in character of oil-bearing formation.
3. Difference in depth at which oil occurs.
4. Difference in amount of migration of oil.
5. Difference in degree of metamorphism, i.e., heat and pressure, which the oil has undergone.
6. Difference in geologic age of oil.

These points will be taken up in the order given above. An effort will be made to show what evidence we have for and against each of these assumptions, and the cause and extent of their influence on the composition of petroleum.

Difference in Origin.

A number of the foremost students of petroleum hold that the major difference in the composition of the various petroleums are due to a difference in origin. They claim that the oil produced from the decomposition of

of animal matter, such as fish, would be quite different in nature from one produced by the decomposition of vegetable matter. They hold that the decomposition of fish and other fleshy animals produced our light paraffine oils, while the vegetable and low forms of animal organizations produced our heavy, asphaltic oils. This theory seems reasonable from a theoretical point of view. When the evidence has been searched out and examined it is found to be somewhat conflicting.

Evidence - in favor.

a. The decomposition of fish in the laboratory produces an oil greatly resembling the paraffine oils of nature.

b. The decomposition of fish, as said to have been observed in the Red and Caspian Seas, produces a scum of light oil on the surface of the water, and a gas which is said to be methane.

c. Remains of fish - scales, teeth, etc., found in the strata adjoining the Wall Creek and Shannon sandstones, which carry light paraffine oil, 24°-40° Beaumé, in the Salt Creek Field of Wyoming!* Below this paraffine oil, in the Dakota sandstone where no such fish remains have been found, occurs a heavy, asphaltic oil, 23° Beaumé.

* Bull. 452, U. S. Geol. Survey.

It is said that such fish remains also occur near some of the Pennsylvania oil sands, which carry oil high in paraffines.

d. The heavy, asphaltic oils of California are apparently derived from the great beds of diatomaceous earth of which underlie the oil sands. Diatoms are a low form of life, which are placed by some authorities in the animal. kingdon, and by others in the vegetable.

e. Sulphur is taken by chemists to point to vegetable rather than animal origin. The paraffine oils of Pennsylvania and Wyoming* are notably low in sulphur. The asphaltic oils of the Gulf Coasr and other districts are high in sulphur.

Evidence - against.

a. The decomposition of vegetable matter produces methane, as in swamps. This would indicate that the paraffine oils can be produced from vegetable growths.

b. Paraffine oil is often found far removed from any fossils or other animal remains. Also a great deal of paraffine oil is found closely associated with coal beds, as in Pennsylvania.

c. The oil from the Trenton limestone of Ohio, which runs fairly high in paraffines in notably

* Bull.452, U. S. Geol. Survey.

high in sulphur, 0.5 to 2.5%. The same is true of some of the Oklahoma oils.

From the above it will be seen that nothing is definitely proven, except in the case of the California oils. No doubt seems to exist but that in this case the oils was derived from diatomaceous earth. But even in this case there are a number of other things beside origin that could easily have influenced the composition, as will be seen later.

Character of Oil-bearing Formation.-

A reason that has often been advanced, especially by U.S.Geol.Survey men, to account for variations in the nature of the oil of the same field, has been the character of the "oil sand". For instance, Washburn makes the statement* that the lightest oil occurs in the shale. Eldredge' states "The oil from the shales is lighter than that from the sandstones." Schrader and Haworth,** in writing of the oil of the Independence Quadrangle, Kansas, state "The oil from the shale is generally lighter than that from the sandstone and conglomerate." Ralph Arnold says "Other things being equal, it is generally the case that the lighter oil comes from the finer sediments." On the other hand, Eldredge and Arnold in reporting on the petroleum of Pico Canyon*' state:

* Bull. 381, U. S. Geol.Survey.

' Bull. 213, U.S. Geol.Survey.

** Bull. 296, U. S. Geol.Survey.

'' Bull. 321, U. S. Geol.Survey.

*' Bull. 309, U. S. Geol.Survey.

"Apparently the texture of the bed is without influence on the oil" However, in most cases where anything is reported on this subject the texture of the bed seems to be regarded as influenceing the nature of the oil.

There seems to be no entirely satisfactory reason why lighter oil should occur in the shale than in the sand of the same district. To account for such a phenomenon it would be necessary to assume that there has been movement of oil through the beds. That light oil should remain in the shale, while heavier oil goes through, does not appeal to the reason; and it is not borne out by experiments on the subject. Altogether, one is inclined to think that the cases which been observed are either coincidences, or else due to the well-known tendency of the U. S. Geol. Survey geologists to support each other's theories.

Depth at which Oil Occurs.

It has sometimes been observed that the oil of the same field varies considerably with the depth of the oil sand. In most cases the gravity of the oil decreases with the depth of the oil sand.

For instance Eldredge*, in writing on the oil fields of California, mentions several cases where the oil from the deeper sand is lighter than that from the shallower; and apparently considers the fact significant. In reporting on the Gulf Coast Field, Fenneman' makes a similar observation.

Attention is called by Eldredge and Arnold** to several places in California where the lower sand yields the lighter oil. On the other hand several cases have been noted where the oil from the upper sand was lighter. For example, Arnold and Anderson*' state, in reporting on the Coalinga (Cal.) District, that the lightest oil comes from the uppermost sand. Also there are cases where, of three oil sands, the middle contains the lightest oil.

It will be seen that the evidence on this point is highly contradictory. The geologists working in the California districts noted that in many cases the oil from the upper sand was heavier than that from the lower ones. This fact, which is

* Bull. 213,U.S.Geol.Survey.

' Bull.282, U.S.Geol.Survey.

** Bull.309, U.S.Geol.Survey.

*' Bull.357, U.S.Geol.Survey.

contrary to what would naturally be expected, as the tendency of oil is to move up, made an impression on them and caused them to think it significant. But investigation shows that the upper oil sand, being nearer the surface, it is easier for the lighter constituents of the oil to escape, leaving a heavy residuum. The fact that most of the recorded cases of heavier oil in the upper sand were observed in California, where the strata have been highly crushed, fractured and faulted, leaving a good opportunity for escape of light oil, tends to strengthen this hypothesis.

Amount of Migration.

It has frequently been noticed that the oil from the crest of the anticlines is lighter than that on the limbs.*

This can be explained in two ways: (1) by arrangement of oil according to specific gravity, and (2) by supposing that the difference is due to the effect of greater migration of the oil in the crest. Of the two the first seems the more natural and reasonable explanation.

Bull. 452, Bull. 296, U.S.Geol.Survey.

Another point to be considered in this connection is the actual diffusion of oil through different strata of rock. Certain experiments have been made in the laboratories of the U.S.Geological Survey by Gilpin and Bransky , under the supervision of Dr.David T.Day, on the upward diffusion of crude oil. It was found that when crude oil is introduced under pressure into the bottom of tube packed with fuller's earth, the lighter portion of the oil will diffuse upward and finally come out at the top, while the heavier constituents are left behind in the fuller's earth. The theory, having these experiments for its base, has been advanced that the light paraffine oils have actually been separated from a heavier residue by diffusing up through beds of shale which at present underlie them. This theory would certainly account for many of the differences in the composition of petroleum. There are, however, certain difficulties in the way of adopting such a solution which are hard to overcome. In the first place the shale beds of nature are quite different from fuller's earth, and it has not been shown that petroleum could penetrate them under natural conditions. It seems signigicant that the shale beds which at present overlie oil sands form

very efficient barriers to upward progress of the oil.

Subjection to Metamorphic Processes.

It is well known that the heating of oil causes what is known as "cracking", or breaking up of complex compounds into simpler ones, very materially changing the nature of the petroleum. This is noted in the Engler distillation, where a temperature of only a few hundred degrees is attained. What the effect would be if subjected to a high heat under pressure can be seen from the process for making synthetic crude oil, a description of which has recently appeared in the technical journals. The statement is made that heavy gas oil and other low-grade, high-gravity mixtures when subjected to a high temperature under pressure can be transformed into a crude oil resembling that of Oklahoma. In nature, there is a case on record of a well in a crystalline schist at Placerita Canyon, Cal.* which produced petroleum having a gravity of 50° Beaumé, whereas other California oil varies from 10° - 28° Beaumé. The only explanation of this fact is that the metamorphism which formed the schist transformed the oil at the same time. On the

* Bull. 309, U. S. Geol.Survey.

other hand it has been noted that where the bedding has been much disturbed by dynamic action the oil is heavy.* This is explained by the fact that fractures give an opportunity for the light oil to escape. As dynamic action usually accompanies conditions of heat and pressure, whatever light oil is formed under such conditions would generally have a chance to escape. It may be, however, that the heat and pressure which accompanied the folding in such districts as the Oklahoma and Pennsylvania may have had a considerable effect upon the character of the petroleum. In the California field the dynamic action was so severe as to provide fractures for the escape of the lighter constituents of the oil while, in the Gulf Coast field there has been no folding.

Geologic Age.

Age of oil sands in various districts:

1. Appalachian - Mississippian, Pennsylvanian, Devonian.
2. Ohio - Ordovician.
3. Illihois - Devonian, Pennsylvanian, Mississippian.
4. Mid-Continent - Pennsylvanian.

* Bull. 357, U. S. Geol. Survey.

5. Wyoming - Cretaceous, Permian, Carboniferous.

6. California - Tertiary.

7. Gulf Coast - Tertiary, Cretaceous.

There are two ways in which it would seem possible for the age of the formation of the oil to affect its composition. They are:-

1. Difference in form and amount of animal and vegetable life of the different geologic periods.

2. Difference in age of the oil, during which it has had an opportunity to change its form.

The occurrence of much of our oil in the Pennsylvania" presents a strong argument in favor of its vegetable origin. The presence of petroleum high in paraffine in the Ordovician- Trenton limestone - is also evidence against the theory of animal origin, as it is probable that the shell fish were the most highly developed organisms at that time. The fact that our lowest gravity (Beaumé) asphaltic oils occur in the Tertiary (California and Gulf Coast fields) seems significant, but just what this indicates is not easy to state.

SUMMARY.

In summing up the influence of the various factors of origin and occurrence, it becomes evident that no truly definite conclusions are warranted.

It appears evident that origin has been the main factor in determining the composition in at least some cases. The oil in the upper sands seems to be, in the majority of cases, of lower gravity (Beaume') than that in the sands which are deeper, although having the same base. This may be explained by the greater evaporation of the more volatile constituents of the oil in the upper sands, due to easier access to the surface.

That the lithologic character and structure of the oil-bearing formation has any influence on the nature of the oil seems doubtful. It is the opinion of some very eminent petroleum experts that the amount of migration of the oil, especially through shales, very materially influences its composition by causing a fractionation into its components. As no good evidence has been given to show that petroleum does migrate through shales under natural conditions, and as considerable evidence to the contrary is known, this must be looked upon as an hypothesis.

It seems possible, and even probable, that in certain cases where the oil was subjected to conditions of heat and pressure, a considerable change has been effected in both its chemical

and its phycical nature. Such conditions could, however, have applied in only a comparatively small proportion of our petroleum fields.

The geologic age of the oil may have been important in determining the kind of life from which it was derived, and also the length of time during which it has been subjected to metamorphic processes.

On the whole, however, it would seem that our present state of knowledge of the subject is not sufficient to warrant a definite statement as to what influences have been effective in determining the composition of petroleum; and the relative importance of each. At the present time, a great deal of field and research work is being done on the subject of petroleum; which it is to be hoped will result, within a few years, in the solution of this problem.