

THE OHIO JOURNAL OF SCIENCE

VOL. XLVIII

JULY, 1948

No. 4

THE ORIGIN OF PETROLEUM IN THE LIGHT OF RECENT RESEARCH

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The story of the formation of crude petroleums and natural gas is not only an intriguing, scientific puzzle, or rather a series of scientific puzzles of general chemical and geological interest, but it is of the greatest practical importance to petroleum geologists. If we knew the entire story it would enable us to understand why large continental areas are entirely without accumulations of petroleum of commercial importance and why, in certain areas, perfectly good geological structures favorable to the accumulation of petroleum have been drilled and no petroleum or natural gas whatever has been found. A great deal of geological and chemical knowledge has been accumulated, particularly in recent years, and some of the questions in regard to the origin of petroleum and natural gas can now be definitely answered; other facts still await definite or plausible answers. Our knowledge of the subject to date represents a vast amount of investigation by a great many able chemists, geologists and others, and the general overall problem still includes many unsolved questions, the answer to which will require much more work and the best thought of the best minds.

I believe that our present knowledge enables us to draw certain conclusions which should be helpful to petroleum geologists and should be helpful to chemists and refiners in understanding the nature of crude petroleums with which they have to work. It is not too much to say that study of this problem now enables us to predict with fair assurance the nature of a crude petroleum which might be expected when drilling to various depths into oil-producing strata of different geological ages. If it is known beforehand at about what depth a particular producing sand is to be expected, we may be reasonably sure of the kind of crude we will find. There are some exceptions to this and the reasons for these exceptions are also significant and are part of the story.

The following diagram indicates approximately what the distribution of carbon is in the lithosphere (Fig. 1), which is as far as our knowledge goes. The relative proportions of carbon locked up in carbonate rocks, particularly limestones and dolomites, coal and petroleum, is roughly indicated. The carbon in oil shale was overlooked but should be a figure somewhat greater than that for oil. The source of the carbon dioxide before it was locked up in these carbonate rocks and, through animal and plant organisms, in oil shale, coal and petroleum is another story involving the source and nature of the earth's primitive atmosphere.

It is apparent that no figures for these quantities of carbon can be really accurate but their *relative* magnitude approximately, is as follows:

Carbon in carbonate rocks.....	2,310,000
Carbon as CO ₂ and CO ₂ in sea water.....	2,180
Carbon in coal.....	1,200
Carbon as CO ₂ in air.....	68.
Carbon in petroleum.....	4.2

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The latter figure is based upon an estimate of the world's *known* recoverable reserves made for the Government during the last war. The actual figure may be twice or three times this figure (or about 150 billion barrels).

FUNDAMENTAL GEOLOGICAL CONDITIONS

Although the aspects of the origin of petroleum and natural gas which we are discussing here are mainly chemical, we must first consider a little geological history and the fundamental conditions which geology imposes upon us in considering the problem. Thus geology gives us the framework as to time, temperatures and pressures, the original environment and present environment, and probable nature of the original source material of petroleum, within which set of conditions we must work out the story of petroleum formation.

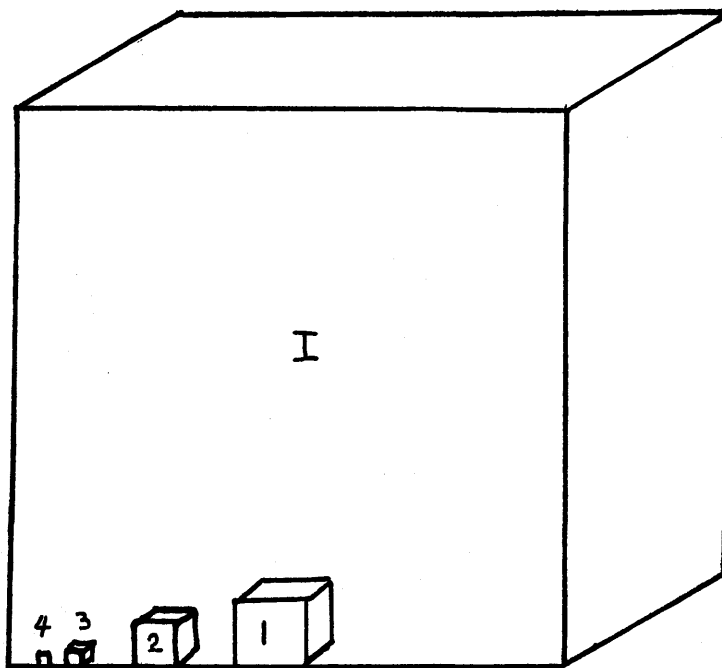


FIG. 1. Distribution of carbon, according to J. G. Bennett.

I. Carbonate rocks.

1. CO₂ in Sea water. 2. Coal. 3. CO₂ in atmosphere. 4. Petroleum.

Most of the theories proposed by chemists for the origin of petroleum and natural gas have neglected to take into account these fundamental conditions which have been by now firmly established by petroleum geologists, and most of them must be rejected because they do violence to and cannot be reconciled with these fundamental conditions. As stated by Beeby Thompson (2), "In seeking the origin of petroleum one must not introduce extraordinary theories for its occasional occurrence amongst unusual surroundings, but consider only such views as will account for its extensive production and wide distribution by common processes of nature."

At this point we may refer to a simplified geological column, Fig. 2, which shows the order in which the sedimentary rocks of the different periods were laid down. By the study of radioactive minerals in intrusive rocks, such as pegmatites,

	GEOLOGICAL SCALE	AGE IN MILLIONS OF YEARS	OIL FIELDS
Quaternary			
Tertiary	Pleistocene	13 ± 1	{ Caucasus, Iran, Irak California Gulf Coast Salt Domes
	Pliocene		
	Miocene		
	Oligocene	18 ± 1.5	{ Venezuela, Colombia Trinidad
	Eocene	34 ± 2	
	Poleocene	57 ± 1.5	
Mesozoic	Cretaceous	85	{ Texas, East Texas Rodessa field
	Jurassic		
	Triassic	165	{ Woodbine sand Mexico
	Permian	Palisades Uplift 180 Watchung Mts.	
	Carboniferous	230 ± 15	
Paleozoic	Devonian	300	{ West Texas and Eastern New Mexico
	Silurian	Adirondacks 370 ± 30	
Eozoic	Ordovician	400	{ Ohio-Indiana Wilcox Sands of Midcontinent
	Cambrian		
		535 ± 25	
	Kewenowan		

FIG. 2. Time or geologic age based upon a study by W. D. Urry and others from the study of radioactive minerals in pegmatite intrusions.

we now know fairly accurately the age of these sedimentaries in terms of millions of years. Beginning with the top of the Cambrian series with an age of about four hundred million years, we come down to the most recent periods containing petroleum, to the Pliocene, geologically very recent with an age of about ten to twelve million years. This simplified geological column is drawn to a scale proportional to time and bears no relation to the thickness of the strata in the various series. Approximately two-thirds of our current oil production and known reserves occur in the Cretaceous and above. The reason for this is that by this time the continental areas had become much more extensive and the erosion from these continental areas resulted in the deposition of thick marine sediments, and where this erosion and deposition took place relatively rapidly in lagoons or large basin areas or, in some cases, along shore lines, we then have the first basic requirement for the ultimate production of petroleum and natural gas.

There are three general types of organic matter found in large quantities practically throughout this geological column; they are, coal, the so-called kerogen in oil shales, and petroleum and natural gas. Coals are generally believed to have been derived from quite different source material than kerogen, petroleum and gas, and evidently were fresh water or marsh deposits derived from lush vegetation, and cellulose, lignins and resins constitute the principal source material. The original organic source material of kerogen, petroleum and natural gas, was laid down in *marine* and in fresh water sediments.

The original organic source material which resulted in the formation of kerogen and of petroleum and natural gas is still uncertain and may have varied somewhat. Shales, in general, are deep water deposits whereas sandstones and limestones are laid down at relatively shallow depths. It is a striking fact that the so-called kerogen of oil shales has persisted, apparently unchanged, from geologic times as remote in certain cases as the upper part of the Cambrian series, or about four hundred million years. In other words, there is no evidence that the temperatures and other conditions normally prevailing in any of these old strata has ever decomposed kerogen or converted it to oil. Most oil shales contain no petroleum whatever, and others only very minor proportions. Oil shales containing kerogen may be as much as four hundred million years old, as the New Brunswick oil shale, (9) or the extensive black shales of New York, Ohio and Michigan, which are Devonian. Yet petroleum may be as recent as the Pliocene as, for example, those from the Midway fields of California. The original organic source material of both oil shale and petroleum was at least associated with, and probably derived from, at least in part, green algae, since Treibs (28) has found chlorophyll porphyrine in all oil shales examined by him and in all petroleum containing asphalt or, in other words, in all petroleum not purified by selective adsorption during migration. This discovery of chlorophyll porphyrins is undoubtedly the most important single discovery bearing upon the question of petroleum origin. It definitely connects up both oil shales and petroleum with green algae and proves that both have never been at any time in their history subjected to high temperatures and, in agreement with other evidence, shows that the original organic source material was deposited sufficiently rapidly to seal in the organic debris under anaerobic conditions. Certain oil shales studied by Treibs contain half as much chlorophyll porphyrin material as can be derived from dried green leaves. All sorts of marine animal and vegetable life probably contributed to the organic debris deposited in the original ocean sediments. Several years ago, the American Petroleum Institute conducted extensive investigations under the direction of Parker D. Trask into contemporary sediments currently being deposited in various parts of the oceans. These investigations found no petroleum in these sediments and do not throw much light on the nature of the organic material contained in them. The kerogen of oil shale is a highly complex material, evidently in a highly polymerized condition as indicated by its insolubility in all organic solvents at ordinary temperatures.

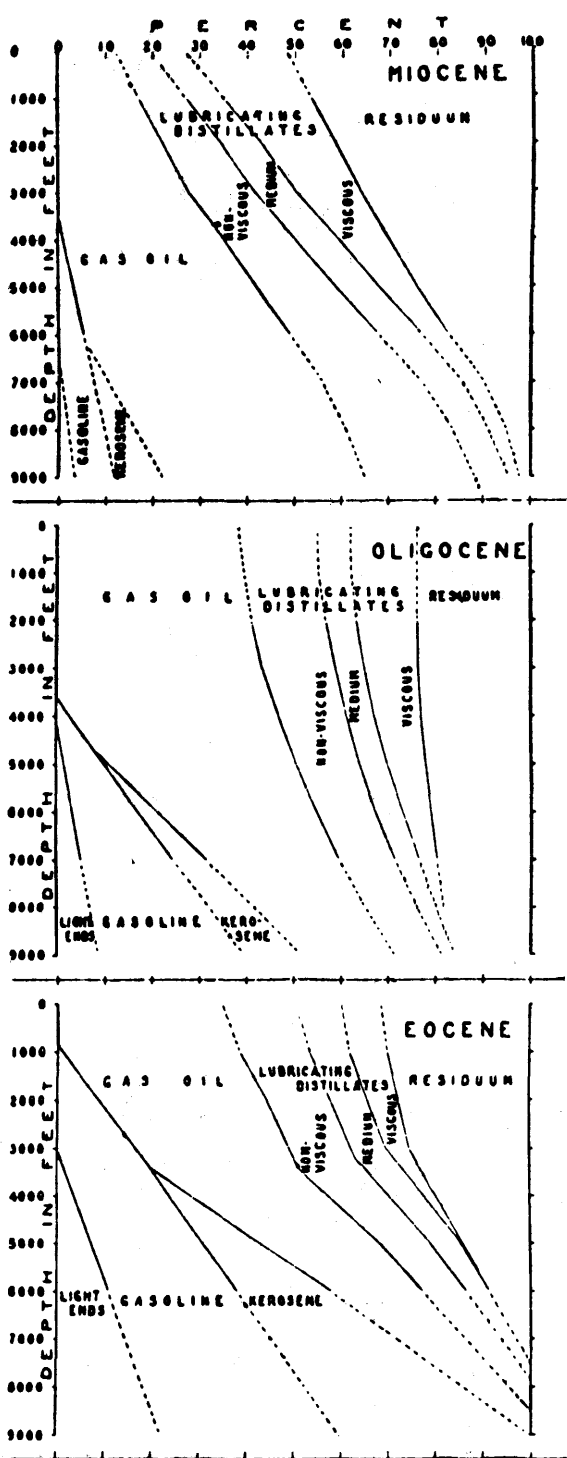
It can be extracted by solvents only at temperatures at which it begins to be decomposed. Fatty oils found in very recent deposits of decaying algae have been found to be already in a partly polymerized condition.

As might be expected from considerations of the original environment and original organic source material of kerogen, oil and gas, and coal, there are deposits of fossil organic material which are difficult to classify and fall in between the three typical major materials just named. Thus there are oil shales which are very rich in organic material yielding upwards of a hundred gallons of oil per ton and include the type of shales known as torbanites. Closely related to these are the cannel coals which contain a high percentage of organic material yielding oils and paraffins by destructive distillation. In fact, the low temperature destructive distillation of coals, particularly those of the cannel coal type, yield distillates rich in paraffins and unsaturated hydrocarbons and, in general, such distillates are not very different from shale oil. Typical oil shale yields oil consisting mainly of paraffins, naphthenic hydrocarbons, and unsaturated hydrocarbons, but also relatively large proportions of phenols, nitrogen bases, ammonia and sulfur derivatives. Typical petroleum also contains complex substances which are decomposed on heating to give phenols and sulfur derivatives such as the mercaptans, thio-ethers and thiophenes which are not present in the original crude but are decomposition products of thermo-labile complex substances in the crude. Similarly, crude petroleum contains complex nitrogenous material which is decomposed at moderate temperatures to give nitrogen bases found, for example, in the kerosene distillates in small proportions of all petroleum. Also, the naphthenic acids found in the distillates are almost wholly formed by the decomposition of more complex material in the original crude oil. Cracked gasolines contain small proportions of phenols and these have sometimes been industrially recovered from cracked gasolines. The proportions of these so-called impurities, phenols, naphthenic acids, nitrogen bases and sulfur derivatives, are much smaller in cracked gasoline than in shale oils and distillates made by the low temperature carbonization of coal, but their presence is indicative of the same or similar substances in the crude materials.

The existence in crude petroleum of these thermo-labile complex substances which yield mercaptans and other sulfur derivatives, naphthenic acids, nitrogen bases, together with the presence of chlorophyll porphyrins show that petroleum has never been subjected to very high temperatures at any time during its history. (6) This chemical evidence of low temperature history is consistent with the evidence of low temperatures derived from the actual measurement of bottom-hole temperatures in oil fields, the consideration of temperature gradients in oil fields and general geological considerations.

LACK OF KNOWLEDGE OF PETROLEUM IN TRANSITION STAGES

Referring again to the simplified geological column, no petroleum or other bituminous material has been investigated chemically which is more recent than the Midway-California oils from Pliocene sands in California. In other words, there is at present a complete gap as regards the transformation of organic matter in contemporary sediments into petroleum, between the Pliocene of about ten million years ago and the sediments now being deposited. It should be expected that a satisfactory chemical history of this transformation could be found by the examination of organic material in intermediate states. Such material certainly exists and awaits study. The organic matter in the sediments is solid, or semi-solid, and has to be in order to be retained in the sediments as they are laid down. Such material in intermediate stages, before it has become fluid enough to flow, migrate and collect in so-called pools, would be disseminated through the geologically recent sands or shale, and would have to be recovered by extraction. A few years ago, Donald C. Barton, (1) Petroleum Geologist of the Humble Oil Com-



pany, as a result of a study of Gulf Coast petroleum and the relations between their composition and geological age and depth, arrived at this conclusion merely by extrapolation when the data was plotted geographically.

The heavy, black, tarry oils in geologically recent tar sands should repay investigation as possibly being petroleum in very early transition stages of formation. At some early stages geologically recent natural bitumens might be expected to show a much higher content in organic acids than typical petroleum. The observation of Pyhala (18) that in the case of two Russian oils, the distillates showed 11 to 12 times as much naphthenic acids as the original crudes suggests that determination of saponification numbers on crude petroleum, particularly heavy naphthenic, geologically recent oils and tars would probably show much higher saponification numbers in the recent material. The organic nitrogen content would also be of interest. There are reasons, mentioned later, for expecting that such transition material would show substantial olefinic unsaturation, perhaps unsaturated fatty acids or their polymers.

Barton's studies are shown in the accompanying graphs, Figures 3, 4 and 5. It has long been recognized that, in general, the light crudes containing much

FIGS. 3-5. Composition of Gulf Coast oils, plotted graphically according to D. C. Barton.

gasoline and generally paraffinic in type, are geologically much older than the heavy, asphaltic crudes containing little or no gasoline. Barton's study of the Gulf Coast oil was the first systematic investigation bearing on this point. Subsequent investigations in the Gulf Coast area have shown that the relations are not so simple as indicated by these graphs, but the general results or the average of the results are as shown by Barton. In other areas, notably in Wyoming and California, the relations found by Barton do not hold very well, but many of the apparent exceptions are due to changes in the crude oil by selective adsorption in migration.

TEMPERATURE IN OIL FORMATION

The subject of temperature as a factor in petroleum formation has been very frequently discussed since it was first suggested by Warren and Storer in 1863 and later in 1888 by Engler, (10) that petroleums resulted from a destructive distillation of fatty oils derived from fish or other marine life, but it has become increasingly difficult to reconcile such a process with the chemical and geological evidences of low temperature history.

We now know a good deal concerning the individual hydrocarbons present in petroleums, particularly in the gasoline and lighter kerosene fractions. This information, which has largely been a result of about twenty years of investigation by the U. S. Bureau of Standards (19) as a research project financed by the American Petroleum Institute, is summarized in the following tables. (22) Consideration of the composition of these gasolines permits the conclusion to be drawn that they are not equilibrium mixtures corresponding in composition to any particular thermal condition.

TABLE III
HYDROCARBON TYPES IN STRAIGHT-RUN GASOLINES

CRUDE OIL	END POINT (° C.)	PER CENT BY WEIGHT OF		
		Aromatics	Naphthenes	Paraffins
Oklahoma City, Okla.....	177	10	29	61
Tonkawa, Okla.....	150	9	35	56
“ “	210	12	37	49
Davenport, Okla.....	150	8	28	64
“ “	210	11	28	61
East Texas.....	159	6	42	52
Mexia, Texas.....	150	22	21	57
“ “	210	18	21	61
Rodessa, La.....	160	10	20	70
Santa Fe Spr., Cal.....	151	10	50	40
Kettleman Hills, Cal.....	151	8	45	47
Signal Hill, Cal.....	153	6	52	42
Huntington Beach, Cal.....	155	7	49	44
“ “ “	210	11	54	35
Turner Valley, Canada.....	150	11	38	31
“ “ “	200	15	35	50

TABLE IV
CHEMICAL COMPOSITION OF LIGHT PARAFFIN-NAPHTHENE FRACTION,
40° TO 102° C. OF U. S. STRAIGHT-RUN GASOLINES

GASOLINE	PERCENTAGE BY VOL.			
	Normal Paraffins	Isoparaffins	Cyclopentanes	Cyclohexanes
Ponca, Okla.....	35.7	20.5	23.4	20.4
East Texas.....	24.7	27.3	26.0	22.0
Bradford, Pa.....	34.4	32.2	13.4	20.0
Greendale-Kawkawlin, Mich.....	63.1	13.2	8.0	15.7
Winkler, Texas.....	9.5	61.6	8.4	20.5
Midway, Cal.....	10.0	21.5	41.0	27.5
Conroe, Texas.....	18.2	20.3	17.3	44.2

The aromatic content of the gasoline, distilled up to 180° C. from the same crudes is as follows:

TABLE V
CONTENT OF AROMATICS IN U. S. STRAIGHT-RUN GASOLINES (E. P. 180° C)*

Gasoline	Aromatic Content (% by weight)
Ponca, Okla.....	9.8
East Texas.....	10.4
Bradford, Pa.....	8.3
Greendale-Kawkawlin, Mich.....	7.2
Winkler, Texas.....	4.9
Midway, Cal.....	8.0
Conroe, Texas.....	27.6

Dr. Frederick Rossini, under whose direction much of this analytical study was made, and in my opinion the analytical results are beyond question, has recently pointed out that the relative proportions of certain *selected* groups of constituents correspond approximately to the proportions required by thermal equilibrium at about 400° C. or 752° F. (20). Dr. Rossini stated that this would have to be taken into account in any theory of the formation of petroleum. However, the geological history and other chemical evidence must be taken into account. Also, it should be pointed out that all of the analyses are taken into account, it is apparent that these gasolines do not represent thermal equilibrium mixtures. At temperatures below about 200° C. thermo dynamic considerations teach that the iso-paraffins are more stable than the normal paraffins. Yet the gasoline fraction from Michigan crude contains 63.1 per cent of normal paraffins and 13.2 per cent of iso-paraffins. In contrast to this, the gasoline from Winkler crude contains 95. per cent normal paraffins and 61.6 per cent of iso-paraffins. The gasoline from Yates, Texas, crude is reported to contain no normal paraffins. The Michigan crude is geologically much older than the Winkler crude and both are obtained from wells whose bottom-hole temperatures are below 100° F.

The above tables also show the greatest variation in the relative proportions of cyclopentanes and cyclohexanes and there is no simple relation between the proportions of cyclohexanes and aromatic hydrocarbons. There is no indication that the aromatic hydrocarbons have been derived from cyclohexanes by catalytic dehydrogenation. It will be noted that the gasoline from Conroe crude, containing 27.6 per cent of aromatics is entirely out of line with all the others studied and

* Possible deviations from the above figures = 0.2 to 0.5.

is quite unlike gasolines from other crudes of similar geologic age, depth of producing strata, and observed bottom-hole temperatures.

If petroleum was produced from the original organic source material by thermal action *alone*, then oils of similar age and similar temperature history should have the same composition, but this is not even approximately true. The following table gives the approximate age, observed bottom-hole temperatures and depth of the producing formation for the seven crudes investigated by the Bureau of Standards. The highest bottom-hole temperature is that of the Conroe field where the temperature at 4,900 foot depth is 172° F. In the Permian basin of West Texas, the temperature is only 126°F. at 5,900 feet below sea level. In the East Texas field, the producing formation is the Woodbine sand of the Cretaceous producing from a depth of 3,300 feet below sea level and a bottom-hole temperature of about 146° F. Oils of the Permian basin of West Texas are much older than either the Conroe or East Texas oils.

The temperature history of petroleum begins with the temperature at which the original source sediments are laid down in the ocean, probably an average of 60-70° F. As the deposits build up in thickness they serve as an insulating blanket and in the course of time the temperature slowly rises as the thickness of the strata or depth increases. The temperature gradients in the various oil fields varies from about 50 feet to 100 feet for each increase in temperature of one degree Fahrenheit. (13) The present observed bottom-hole temperatures probably represent the maximum temperature for the entire geologic history of a particular producing formation, except in old regions which have been highly eroded and where the producing sands are now near the surface. McCoy and Keyte (16) state that "most of the known oil fields surely were formed at temperatures lower than 140° F." Some of our most prolific fields yield oil from formations whose bottom-hole temperatures do not exceed 100° F. At Oklahoma City, a temperature of 100° F. is found at 4,100 feet.

Barton states: "The geologic history of the Gulf Coast is relatively simple. It is quite impossible that the Gulf Coast crude oils which are now being produced have been subjected to temperature as (high as) 100° C. Some of the crude oil from the deeper sands may have been subjected to temperatures as high, but not much higher than 70° C. Much of the crude oil cannot have been subjected to temperatures much higher than 50° C.—the normal average crude oil is indigenous to the formation in which it is found and has not migrated up from greater depth."

Since the straight run gasolines that have been most carefully analyzed are those noted in the above tables, the following data are given for these crudes:

TABLE VI
GEOLOGICAL AND FIELD DATA FOR SELECTED CRUDES

Field, Source of Crude	Producing Sand	Series	Depth, Average Feet	Bottom Hole Temp. °F.	Estimated Age in Million Years*
Ponca, Okla.....	Wilcox.....	Middle Ordovician.....	3,872	139°	360-380
East Texas.....	Woodbine.....	Cretaceous.....	3,300	146°	60-80
Bradford, Pa.....	Bradford.....	Devonian (Chemung)...	2,000	72°	300
Greendale, Mich..	?	Middle Devonian.....	5,300	96°	300
Winkler, Texas....	Big Lime.....	Permian.....	3,000	85°	200-230
Midway, Cal.....	Pliocene.....	2,050	115°	10-13
Conroe, Texas.....	Cockfield.....	Eocene.....	4,900	172°	40-50

* Based upon estimates by W. D. Urry and others from the study of radioactive minerals pegmatite intrusions.

CATALYTIC ACTION OF ACTIVE SURFACE MINERALS

The low temperature history of petroleum must be considered as firmly established by the field observations and the geological and chemical evidence.

However, we must consider the evidence that petroleum do change. Heavy, asphaltic, naphthenic oils change to lighter, more paraffinic oils and contain more light constituents, such as gasoline, as these changes proceed. We must also consider the great complexity of petroleum and the very large number of hydrocarbons present, beginning with the gases, methane, ethane and propane, et cetera, up to and including mixtures of high boiling hydrocarbons which are beyond our power of analysis and identification. It has been calculated, (23) by employing the velocity constants for cracking, that at 212° F. the higher paraffins have a stability greater than the element potassium, and according to these calculations, the paraffins would remain substantially unchanged if maintained at 300° F. throughout geologic time from the middle Ordovician to the present. These facts can be reconciled, however, if we suppose that *clays and possibly other minerals common in the strata in contact with petroleum have a catalytic action, at the observed relatively low temperatures, on the crude oil and on the heavy bituminous material formed in the early stages of oil formation.* That clays and certain other minerals may have such a catalytic effect is indicated not only by the evidence just noted, but also by the fact that certain natural clays and special silica-alumina catalysts and silica-magnesia catalysts are industrially employed in catalytic processes at relatively high temperatures, 850–950° F. and that at low temperatures many of these clays and minerals show very high catalytic activity with respect to the polymerization of unsaturated hydrocarbons. Clays such as Fuller's earth are capable of polymerizing iso-butene at temperatures as low as –100° C. and, in general, the lower the temperature the higher the molecular weight of the polymers formed. 2-Butene is 85 per cent polymerized by Fuller's earth on standing four months at room temperature. This property of polymerizing unsaturated hydrocarbons is not limited to Fuller's earth but, as pointed out in an earlier paper by the writer, is a general property common to all clays and rocks containing clay. Very reactive hydrocarbons such as trimethyl ethylene, isobutene and pinene are polymerized at room temperature with evolution of heat by clays, not of the Fuller's earth type, bentonite, bauxite, sandstones and green-sand, although the activity of silica gel and pure kaolin is very slow.

The specimens of sedimentary rocks from Oklahoma which were tested for polymerizing activity are shown in the following table: (6)

POLYMERIZING EFFECT OF OKLAHOMA SEDIMENTARY ROCKS AND SOME MINERALS ON TURPENTINE

<i>Mineral</i>	<i>Per Cent Polymer</i>
Fuller's earth of Georgia.....	75
Sylvan shale.....	76
Red-bed clay.....	65
Tertiary clays.....	68
Greensand, New Jersey.....	72
Greensand, Texas.....	70
Serpentine, Easton, Pa.....	60
Gray Persian sandstone.....	56
Stanley shale.....	57
Regan sandstone.....	50
Calvin sandstone.....	46
Simpson sandstone.....	34
Permian sandstone.....	30
Bentonite.....	34
Bauxite, Georgia.....	58
Silica gel.....	23
Kaolin.....	12
"Glaucosil" (acid leached greensand).....	45

<i>Mineral</i>	<i>Per Cent Polymer</i>
Prehnite (zeolite).....	None
Stilbite (zeolite).....	None
Talc.....	None
Infusorial earth.....	None
Powdered pumice.....	None
Ferric oxide, pure.....	None
Aluminum oxide, pure.....	None

It will be noted in the above table that the six typical sandstones tested show a catalytic activity as indicated by polymerization averaging better than half the catalytic activity of typical Fuller's earth and that three Oklahoma clays showed activity very nearly as high as typical Fuller's earth. Even bauxite, which can have only a very small percentage of clay as an impurity, shows about two-thirds the polymerizing activity of Fuller's earth. It is indicated by these results that catalytic activity is not limited to acid clays, but is due to active surfaces which strongly adsorb the hydrocarbons.

At elevated temperatures different active surface materials show different results in catalytic cracking and other reactions. Thus, in catalytic cracking, the character of the gasoline obtained using a silica-alumina catalyst is different from the gasoline produced by a silica-magnesia catalyst, both at the same operating temperature. The silica-alumina catalyst yields more butenes and low boiling material and has a somewhat higher octane number. In a study of the catalytic action of Fuller's earth and other catalysts on propylene it was found (12a) that at 350° C., or well below ordinary cracking temperatures, the product consisted of both isoparaffins and olefins, including many isomeric C₆, C₆, C₇, C₈ and C₉ hydrocarbons (29a). The gasoline thus produced had an octane number of 91. Synthetic aluminum silicate had approximately the same catalytic activity as the best activated Fuller's earth, and a catalyst made up of one per cent alumina on silica was twenty times as active as the best activated Fuller's earth.

These results show that paraffins are formed from olefins, that isomerization and splitting of the hydrocarbon molecules takes place very rapidly at temperatures substantially below cracking temperatures, in fact, high temperatures alone do not produce the same results noted in this catalytic conversion of propylene. Here we note much the same so-called "hydrocarbon dispersion" that is found in the composition of typical petroleum. This action of Fuller's earth and other active surface catalysts *proves* that many of the changes with which we are concerned in accounting for the complexity of petroleum do take place rapidly in the presence of such catalysts at temperatures at which the hydrocarbons are relatively stable, and that the reactions are in some respects different in kind from those resulting from the action of heat alone. The formation of some of the products in the resulting mixture can only be explained in the same way that the numerous products of the alkylation of isoparaffins by olefins are explained.

It is true that the complicated reactions which take place in low temperature alkylation processes occur through the action of reagents such as concentrated sulfuric acid, hydrofluoric acid, and aluminium chloride. Such processes include isomerization, the splitting of hydrocarbons and the synthesis of new ones, molecular rearrangements and so-called hydro polymerization. The mixture of hydrocarbons which results contains no olefins at all and when using isobutane and butenes the mixture contains not only the expected C₈ hydrocarbons, but also pentanes, hexanes, heptanes, nonanes and small proportions of heavier hydrocarbons. These reactions take place at low temperatures, refrigeration being required.

It is now generally accepted that all of these results are best explained by the formation of carbonium ions. The low temperature formation of the great number of hydrocarbons found in petroleum through the action of active surface minerals must have a similar mechanism.

Further evidence that the catalytic active-surface minerals play an important role in the formation of petroleum is found in the nature of the hydrocarbon constituents of typical petroleum. The fact that straight-run gasolines and kerosene contain no unsaturated or olefinic hydrocarbons is a strong indication of this and also the complexity of such oils or, in other words, the very large number of hydrocarbons, isomeric paraffins, naphthenes and aromatic hydrocarbons, has no other plausible explanation. The great number of hydrocarbons present in petroleum was one of the primary considerations of the old destruction distillation theory of Warren and Storer and of Engler, but the relatively high temperatures postulated by Engler, and recently by Rossini, are clearly beyond consideration.

The extremely great differences in the composition of petroleum and the wide variations in the composition of gasoline fractions have been noted and are shown by the above tables. Some differences in petroleum could be expected as a result in differences in composition or types of organic material which constitute the original source material, but such differences in source material could still not possibly account for the great number of hydrocarbons which are evidently present in all petroleum. Some recent investigators have called attention to the fact that paraffins are found in nature in many plants, being formed by bio-chemical processes in the living plants. Some unsaponifiable hydrocarbon oil has been found in material extracted from decaying algae. However, it should be pointed out that when paraffins occur in nature, only one or two paraffins are formed and at most, not more than four in any one occurrence, and practically all of them are normal paraffins having an odd number of carbon atoms. They were apparently formed by loss of CO_2 from fatty acids which are found associated with these paraffins. Isomeric paraffins, naphthenes, or aromatic hydrocarbons, have never been found in such cases. In the decay of organic matter containing fatty oils, the hydrolysis to free fatty acids, the formation of insoluble soaps, loss of CO_2 , and polymerization has been observed and probably takes place very early in the sequence of changes which form petroleum. But the formation of anything other than a very small number of normal paraffins by any biochemical process, including bacterial fermentation, has never been observed.

Consideration of all the above mentioned facts, and particularly the complexity of petroleum composition, leads directly to the conclusion that petroleum origin involves two general processes, (1) conversion of the organic source material into heavy, bituminous material approaching a hydrocarbon mixture in overall composition and, (2) what might be termed the "chemical dispersion" of this essential hydrocarbon material into the great series of paraffins and isomeric paraffins from methane to the solid waxes and also naphthenes and aromatic hydrocarbons. The very heavy viscous oils, often quite free from the lighter hydrocarbons such as gasoline, probably represent petroleum in a very early transition stage. There are many such tarry oils in the so-called tar sands as, for example, the very heavy asphaltic oil found in the upper sands of the Maracaibo basin.

Barton arrived at a similar conclusion in his study of Gulf Coast oils and their geology. "Evolution of crude oil from an original oil, perhaps something like the heaviest end of the residuum of the present Miocene Gulf Coast crude oils,—. The tentative deduction follows that the ancestral crude oil of the Gulf Coast crude oils was a heavy oil which, under the U. S. Bureau of Mines' method of analysis, would consist of residuum. Oils of that type should be too thick and viscous to move except through open channels. They may never be found in appreciable accumulations and may have to be sought as droplets scattered through the source formation."

In considering this suggestion of the role of the catalytic action of active surface minerals, we may summarize the limitations which appear to be imposed by the geologic history, physical conditions, and possible differences in environment which

have to be considered in any attempt to account for the differences in type and composition of petroleum:

1. Maximum temperatures varying from about 100° F. to 250° F.
2. Maximum pressures varying from possibly as low as about 1,500 pounds per square inch to about 6,000 pounds per square inch.
3. Time since deposition of original source sediments varying from about 10 to 350 million years (to middle Ordovician).
4. Contact with clays and sands of varying catalytic effects.
5. Unknown differences in type and chemical composition of original source material.
6. Selective adsorption during migration.

Some of the above named factors have already been commented upon. High pressures have often been assumed to have been a factor in the formation of petroleum. It is very doubtful, however, if pressures have been a factor of any importance. As indicated by observed bottom-hole pressures, these pressures vary from about 1,500 pounds, or even less, per square inch to the higher pressures found in deep wells in the range from about 3,000 to 6,000 pounds per square inch. The observed pressures are seldom as great as the calculated hydrostatic head corresponding to the depth. Theoretically, the effect of high pressures, if any changes are effected by such pressure, should be to produce heavy oils with increasing depth and increasing pressure, which is just contrary to the facts generally observed. Such pressures as those just mentioned are hardly enough to influence chemical changes in the oil mixture. Thus it is frequently assumed that pressures would bring about polymerization of any unsaturated hydrocarbons originally present. As against this it may be pointed out that Conant (7) and Peterson found that high pressures up to 15,000 atmospheres did not cause the polymerization of such very reactive, unsaturated hydrocarbons as isoprene and butadiene unless such material had previously been subjected to oxidation with the formation of peroxides which in themselves are well known polymerizing catalysts. They concluded that such high pressures, which are many times greater than those encountered in oil fields, cannot cause polymerization of even such very reactive dienes.

Changes in petroleum by selective adsorption during migration are well known and need not be reviewed here.

If the catalytic action of active surface minerals, such as clays, has been a factor in producing the chemical changes noted by Barton in the Gulf Coast fields as mentioned above, then it might be expected that oils found in reservoir rocks, such as limestones, which have no catalytic action on hydrocarbons might be found to be out of line or inconsistent with the regularities noted by Barton. Once petroleum has migrated into a limestone reservoir rock it should undergo little or no further chemical change. An oil might even have been subjected to such catalytic action and have been converted into a relatively light crude before migrating into a limestone reservoir. Actually we do find many examples of very heavy oils containing little or no light constituents, such as gasoline, occurring in limestone reservoirs even though we would expect from their geologic age and depth that they would be much lighter and more paraffinic. Such oils are the very heavy, asphaltic crudes in Mexico, for example, the Panuco crude which is found in a Cretaceous limestone. A research committee of the Tulsa Geological Society, including H. M. Smith of the United States Bureau of Mines, in a study of Mid-Continent oils (25) has shown that the Arbuckle limestone in southeastern Kansas contains a heavy, asphaltic oil containing none of the lighter fractions, and this is in great contrast to the lighter typical Mid-Continent crudes from much younger formations. The crude oil from the Trenton limestone of the Lima-Indiana field is much heavier, more naphthenic and contains much less gasoline than the geologically more recent oil of the Bradford sand of Pennsylvania.

Differences in the catalytic activity of different formations of minerals in contact with crude oil may also account for the very puzzling fact that crude oils considerably different in composition are sometimes found separated vertically by only one or two hundred feet without any unconformity between the two producing formations. In such cases, the two oils must be of substantially the same geologic age and must have been subjected to substantially the same temperatures and pressures throughout their history. Smith and his associates suggested that such differences in crude composition may have been due to differences in the original environment of the source material or differences in the chemical composition of the original source material. There seems to be no tangible evidence for such assumed original differences but the observed facts may very plausibly be due to differences in the catalytic activity of the strata with which the oil has been in contact.

In the much folded, faulted and metamorphosed Rocky Mountain area the regularities in oil composition shown in the Gulf Coast fields is not shown. Dobbin (8) states that the quality of the oils in the Rocky Mountain area bear no demonstrable relation to the dynamic metamorphism which the region has undergone and notes, "It is evident, therefore, that in addition to metamorphism, there are other factors responsible for the quality of the oil, such as differences in origin—and *natural processes of refining or filtration.*"

FORMATION OF AROMATIC HYDROCARBONS

The apparently universal occurrence of aromatic hydrocarbons in petroleum, isolated and identified in straight-run gasolines, presents special difficulties. The proportions of aromatic hydrocarbons in various gasolines is given in the foregoing tables. In a few gasolines, such as that from Conroe, Texas, and certain of the Borneo crudes, the per cent of aromatics is very large. No type of abundant and widely-occurring possible source material contains aromatic groups sufficient to account for the presence of the aromatic hydrocarbons by any processes of simple degradation. Lignin and humic acids are the only natural materials occurring in abundance in nature which contain the benzene nucleus in its complex structure but they are almost certainly absent from the organic matter in marine deposits. They probably contribute to the formation of coal but not petroleum. The formation of aromatic hydrocarbons from paraffins has been treated from the thermodynamic standpoint by A. W. Francis (11) who states that temperatures in the range 550–900° C. are required, assuming the splitting off of hydrogen. According to Francis, the reactions possible below 550° C. are different in kind, so that at the lower temperatures the formation of aromatics from paraffins could not be expected even during geologic time. Experimental work bears out Francis' conclusions very well, so far as paraffins are concerned, although his temperature of 550° C. may be about 50° C. too high. The conclusions of Francis are very well confirmed by Taylor and Turkevich. (27)

There is a very extensive literature on catalytic dehydrogenation and the dehydrogenation of cyclohexane and its derivatives to benzene and its derivatives is a reversible process. The lower temperatures, in the presence of hydrogen, favor the conversion of benzenes to cyclohexanes, this reaction proceeding well experimentally at temperatures as low as 80°–100° C. with active catalysts. The dehydrogenation of cyclohexene to benzene in the presence of catalysts becomes noticeable experimentally at 170° C. Perhaps more significant is the fact that cyclohexene in the presence of certain catalysts undergoes hydrogen disproportionation being rapidly converted to benzene and cyclohexane, and pinenes are converted by Fuller's earth to cymene and para menthane, probably through the intermediate formation of terpinene, with evolution of considerable heat. The action of clays in causing such disproportionation reactions has also been mentioned by A. V. Frost, (12) in Russia, who also has suggested recently that clays have a role in

petroleum formation. According to Herington and Rideal, (14) the formation of aromatics from paraffins in the presence of a chromium oxide on alumina catalyst at 475° C., proceeds through the formation of a mono-olefin. Nenitzescu, (17) who also urges the study of geologically recent bituminous deposits as possible intermediates in petroleum formation, concludes that aromatic hydrocarbons are formed "at some low temperature" by an unknown process.

OTHER RECENT THEORIES

Brief mention should be made of recent researches seeking to explain petroleum origin by bacterial action and by the effect of alpha radiation from radioactive minerals upon methane or upon the original organic source material of petroleum.

With respect to bacterial action, it is well known that methane is formed by bacterial action on cellulose. However, the formation of hydrocarbons, other than methane, in this way has never been observed and this appears to be a specific bacterial degradation of cellulose. Methane in relatively small amounts is frequently observed in coal deposits, but in such cases is not accompanied by the series of methane homologs found together with methane in natural gas. These two occurrences of methane appear to be entirely unrelated.

Loss of CO₂ from fatty acids has been observed in anaerobic fermentations and the destruction of petroleum oils by bacterial action (30) under *aerobic* conditions, probably by oxidation, has been reported by several observers.

NATURAL GAS AND THE RADIOACTIVITY THEORY OF PETROLEUM ORIGIN

S. C. Lind (15) has shown that the action of alpha radiation from radioactive material on gaseous hydrocarbons results in the splitting off of hydrogen and the formation of a complex mixture of liquid hydrocarbons. He mentions that rocks of the earth's crust are universally radioactive, although in very low intensity. The oily products formed under such circumstances are highly unsaturated. Lind considered this an objection to such a theory of petroleum origin. The unsaturated hydrocarbons could be polymerized, but the disappearance of hydrogen would be more difficult to account for. In any case, the non-reactive by-product helium should persist. Helium rarely occurs in natural gas and its occurrence, from about 0.5 to 2.0 per cent in some of the natural gases in northern Texas, western Kansas and Oklahoma, is to be explained by the proximity of old buried granite ridges and the Shinerump conglomerate of Colorado, which contains carnotite. (4) The gases richest in helium contain no hydrogen. In a private communication Lind states that he is unable to see any solution of the hydrogen and helium difficulty.

To assume that hydrocarbon gases, or methane, is the parent substance of petroleum would still leave unanswered the origin of the methane. Sheppard and Whitehead, (24) on the other hand, query the action of alpha radiation on the buried organic matter in the sediments. Their very painstaking and careful work shows that CO₂ is split out of fatty acids.

There can be no doubt, of course, of the experimental results. However, the principal objections to the theory that petroleum has been formed from either methane or buried organic matter in the sediments by radioactivity are probably as follows: (a) the composition of natural gas, the complete absence of hydrogen and only the occasional presence of helium; (b) there is no relation between the abundance of petroleum and natural gas and the proximity of radio-active minerals (intensity of alpha radiation); (c) the absence of olefinic unsaturated hydrocarbons in gases of petroleum. If the process is as stated to be, dependent upon the widespread radioactivity of low intensity, then the process must be a continuing one and unsaturated hydrocarbons and hydrogen would be expected. The most serious discrepancy between the observed facts and the alphasradiation theory is

that the outstanding experimental result of the action of alpha radiation on hydrocarbons is that it knocks off hydrogen atoms. Such continued action would produce progressively heavier oils poorer in hydrogen. This is quite contrary to the observed facts with respect to the geologically old, light paraffinic crudes (d) Optically active hydrocarbons in petroleum could not be expected, but petroleum do contain slightly optically active hydrocarbons. (e) Substance found in petroleum and derived from organic matter buried in the sediments, such as chlorophyll porphyrins, naphthenic acid complexes, nitrogen bases and labile sulfur complexes, must either escape destruction by alpha radiation or these substances must be picked up subsequently by the oil, possibly during migration. In 1944 Sheppard concluded, "In this survey of the origin of petroleum from the physicist's point of view, no conclusions can be drawn as to whether or not radioactive processes are significant in petroleum genesis."

In this connection it should be noted that marine shales, rich in kerogen, show exceptionally high radioactivity, but as already noted, such shales may be geologically very old, rich in organic material and contain little or no oil as such.

Finally, when oil (or gas) does come into contact with radioactive minerals extensive decomposition with carbon formation occurs as is shown by the mineral thucolite. In Canadian pegmatites, near Parry Sound, Ontario, and near Buckingham, Quebec, the mineral thucolite occurs, sometimes as a pseudomorph after uraninite. Analyses showed the mineral to contain 50.8 to 61.5 per cent carbon, about 2 per cent moisture, 20 per cent volatile hydrocarbons (gases) and 16.6 to 26.8 per cent ash consisting largely of uranium and thorium oxides. (26) Crevices and cracks in the adjacent pegmatite rock contained an oil substance which apparently had seeped into the pegmatite from the country rock subsequent to the intrusion of the pegmatite. Thus the action of the radioactive material on the oil was apparently extremely local and resulted in the formation of carbon and gases, a result to be expected from the experimental results showing splitting off of hydrogen.

SUMMARY

(1) A relatively low temperature history, through geologic time to the present, is indicated by the presence in petroleum of thermo-labile types of substances and by geological considerations. Temperatures within the range of 100° to about 250° F. have probably been the rule for most petroleum-bearing strata and source beds.

(2) The presence of chlorophyll porphyrins is also evidence of low temperature history, but this fact also shows that the material containing chlorophyll, probably marine algae or kelps, was deposited and preserved from aerobic bacterial action by rapid sedimentation. Petroleum containing porphyrins were probably derived from deposited organic material associated with green algae or kelps. Rapid sedimentation in relatively shallow, subsiding basins is also indicated by geological evidence.

(3) The chemical complexity of petroleum, together with the evidences of low temperature history, are best accounted for by *catalytic activity of active surface minerals*, particularly clays, with which oil has been in contact for long periods of time. Petroleum are not equilibrium mixtures produced by thermal action alone. The time element and evident geological history precludes oil or its source material ever having been heated to temperatures as high as 400° C.

(4) There is much evidence that low intensity radioactivity has had nothing to do with the origin of petroleum.

(5) Formation of hydrocarbons, other than methane by bacterial action, has not been demonstrated. Bacterial action undoubtedly occurred in the fresh sediments, as laid down, but later action to form hydrocarbons, is highly specu-

lative. Bacterial action cannot reasonably explain the complexity of petroleum as to number and types of hydrocarbons found in petroleum.

(6) Differences in original organic source material may explain the formation of coal, kerogen of shales and petroleum, including natural gas, as final end products. Such possible differences may account for some of the differences in petroleum, but cannot possibly account for the number and types of hydrocarbons found in typical petroleum.

(7) Fatty oils appear to be the most likely source material of petroleum, with proteins and cellulose probably also contributing.

(8) We lack chemical knowledge of the organic matter deposited in contemporary and recent sediments. Chemical investigation of organic matter in geologically recent strata should provide a chemical history of petroleum formation in intermediate transition stages.

(9) The formation of petroleum appears to have taken place in two general stages; first, an early stage, in which organic matter buried in marine sediments is chemically changed to material consisting largely of carbon and hydrogen but containing few hydrocarbons; second, a later stage in which a very large number of paraffins, isoparaffins, naphthenes and aromatics were formed by catalytic action of active surface minerals, including clays, at relatively low temperatures.

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