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THE SYNTHESIS OF HYDROCARBONS IN THE EARTH'S CRUST

by

N. E. Vanderborgh

ABSTRACT

This report suggests an alternative theory for the generation and migration of petroleum. Considerable evidence supports the conclusion that life processes persist deep within terrestrial and marine environments. Such *in vivo* processes may survive in photon-free ecologies using mechanisms that both reduce carbon dioxide and oxidize sulfides. These *in vivo* conversions create petroleum.

Past studies have proved that large quantities of hydrocarbons are concentrated within discrete sections of the earth's crust. Even though petroleum genesis-migration has had careful study, considerable speculation remains about both the origin of these organic compounds and the mechanisms for accumulation that concentrate large quantities from diverse generation strata into particular porous zones.¹ Initially, generation theories assumed that the origin of hydrocarbons was nonbiogenetic, and that they issued from the polymerization of intermediates from thermally produced carbides.² More recently, generation theories state that observed hydrocarbons result from thermal degradation of biologically produced molecules that are caused primarily by thermal cracking of Type I kerogens^{3,4} and perhaps Type II kerogens. These biotic theories of petroleum generation hold that source rocks are converted to hydrocarbons at modest temperatures over extended time periods. Careful examination of laboratory results shows that hydrocarbons can be generated thermally from source rocks although laboratory simulation of the slow reactions at modest temperatures thought to occur naturally is not feasible. However, explanations of total quantities of petroleum found in localized zones and the mechanisms of accumulation generally remain unconvincing.⁵ This study suggests an alternative generation-accumulation scheme.

Microorganisms and especially aerobic species had been thought to be unable to survive in the earth's crust except within the first few meters. Continued monitoring, however, demonstrates that deep microbiological activity does indeed exist. Suitably executed sampling techniques show that, even as deep as hundreds of meters, self-contained, synergistic colonies of aerobic-anaerobic bacteria coexist in appreciable populations.*⁶ Similar colonies are now being observed in deep marine environments.^{7,8} Significant populations of microorganisms are found along deep venting zones near the ocean floor. Like deep terrestrial zones, these marine environments have low oxygen concentrations, no sunlight, and similar conditions of temperature and pressure. Thus, we conclude that reasonably dense populations of microorganisms do exist in localized zones deep in terrestrial and marine environments. Although we have no clear information, we need not assume that microorganisms in marine brines are different from those in terrestrial brines. Of course, larger species may exist in marine environments than in porous rock. For example, the ten-foot long tube worms, observed in deep marine environments may not find sufficient volume in terrestrial systems.

*R. Pellet, French Institute of Petroleum, Paris, France, verbal communications to N. E. Vanderborgh, 1979.

Ecological observations of these life systems are just beginning. Removing segments of populations from warm, high-pressure, deep environments to oxygenated surface conditions may kill unique fractions of the total population. Thus, until new sampling techniques are developed, complete bacterial typing is unreliable. Likewise, metabolic pathways can only be inferred.

Life-supporting energy for these deep life systems must be gained by consumption of energy produced during chemical reactions. At the earth's surface, life exists through participation in cycles involving photon-assisted energy transport; that is, energy is contributed, in part, by solar photons. Organisms grow by cycles that include the photosynthetic reduction of atmospheric CO_2 . Other types of life, those that exist beyond regions penetrated by solar-assisted chemical processes, require different life-support strategies. Known systems derive energy from the oxidation or reduction of sulfur compounds. Other biosynthetic routes convert sulfides to pyrites, sulfur, or sulfates. Thus, either chemical oxidation or reduction can occur, depending on ambient conditions and the type of organism.

The predominant form of carbon within the earth's crust is carbon in the plus-four oxidation state, CO_2 , or carbonates.⁹ Carbon dioxide seems ubiquitous even in the porosity of basement rocks. This carbon gas is derived either from thermal processes, such as the degradation of mineral carbonates or cellulose, or as a by-product of biological activity. Within the pores surrounding source rocks, carbon gases are admixed with liquids, particularly water, and traces of liquid hydrocarbons. The gases (carbon dioxide and methane) are three orders of magnitude lower in viscosity than the pore-filling liquids.

Although liquid hydrocarbon compounds indeed result from simulated thermal degradation of kerogens, these thermal reactions generate carbon dioxide as the predominant product. Results now show that the generation of carbon dioxide overwhelms the generation of liquid products by at least a factor of 10^3 (Ref. 10). Of course, the plethora of hydrocarbons found in petroleum is generated concurrently but only in small yield.

Migration processes transport liquid hydrocarbons through distances between suspected source beds and observed petroleum reservoirs. Perhaps migration is assisted by carbon dioxide.¹⁰ In slow transport processes, fluid dynamics states that mobile species move at rates

inversely proportional to component viscosity. The difference between gaseous viscosity and liquid viscosity is again a factor of 10^3 . In a steady-state migration process, by far the largest flux of carbon between a source bed and reservoir is carbon dioxide or perhaps methane.

Both generation of viscous hydrocarbons in relatively low yield and their migration at much slower rates indicate primary transport favoring lighter components. To an observer stationed along the migration pathway, the visible carbon flux (moles carbon/time-area) is carbon dioxide. This significant carbon flux must be an important factor in petroleum concentration.

This migration concept is central to these arguments. A plausible explanation of localized hydrocarbon concentration must include:

- (1) reasonably efficient generation mechanism from source beds,
- (2) directed transport from source zones into reservoir formations,
- (3) an efficient process for carbon transport from source beds to reservoirs, and
- (4) efficient long-term storage of carbon within a reservoir.

Data show that carbon dioxide is the only carbon compound generated in high yield (99.9%) during diagenesis; moreover, carbon dioxide migrates at higher rates than do viscous liquids. Therefore, carbon dioxide formation and transport appear to be the principal means for moving the carbon in source rocks to the carbon found in petroleum reservoirs. Carbon is then fixed in that location.

Other gaseous fluxes are also observed within the earth. Ample evidence suggests that quantities of hydrogen sulfide exist deeper within the earth's crust. Sampling experience shows that below 30,000 ft, increasing fractions of the total available porosity are filled with H_2S . Reducing gases, H_2 , H_2S , and perhaps CH_4 , may result from outgassing of deep interior zones.¹¹

We suspect that *in vivo* processes immobilize H_2S by the formation of low-mobility carbon compounds where a flux of H_2S mixes with a flux of CO_2 . We postulate the existence of biological processes supported by the chemical reactions of CO_2 and H_2S . The model is shown schematically as

Sufficient energy is available through this mechanism; the condition becomes even more favorable as pressures are increased. For instance, the conversion

is energetically favorable even at atmospheric pressure. At elevated pressures, conditions permit a wide variety of hydrocarbon formation reactions. In fact, at elevated pressure there is very little thermodynamic difference among many hydrocarbon types, and the process should produce many hydrocarbon compounds.

Because of these reactions, the localized sulfur chemistry should show an oxidation-reduction inversion to the carbon chemistry. The oxidized (hydrogen *deficient*) carbon species coexist with reduced-sulfur compounds and with few carbonate species (pyrites in coal). Conversely, the reduced (hydrogen-*rich*) petroleum types occur in formations that include excess sulfates and, in places, precipitated carbonates (marlstones). If general zones of oxidation-reduction occurred within the crust, they would generate parallel sulfur and carbon redox chemistry. However, quite the opposite is observed. Instead, we see a general inversion of the carbon couple with the sulfur one.¹² This inversion is one direct consequence of the above reaction scheme.

This concept of *in situ* hydrocarbon generation, where applicable, simplifies the mechanisms of petroleum migration. First, it does not demand migration of highly viscous materials through long distances with high yields. Second, it allows the major carbon compounds generated during diagenesis, mostly carbon dioxide, to participate in petroleum formation. A generalized scheme can be shown as follows.

Carbon-containing debris enters either terrestrial or aquatic zones. Such debris, mainly cellulose, lignin, and lipids, is converted to molecules of lower energy content by the action of aerobic bacteria. Additional polymerization of the degraded debris leads into a coalification cycle. Similar processes occur in marine environments.

Degradation proceeds through a series of biological processes. The initial degradation processes increase the oxygen content of the debris. Through time, the debris compacts and is buried. Thermal degradation produces carbon dioxide and low yields of more viscous hydrocarbons as previously described.

The carbon dioxide moves readily through permeable formations until the gas flux intercepts another flux of a reducing gas, perhaps H_2S . (This confluence can be represented as a plane that is the intersection of the two fluxes). At that plane, biological processes operate to yield liquid hydrocarbons. These compounds fill open porosity or invade polymeric structures into which they are firmly adsorbed.

These *in vivo* conversions may be limited either by the flux of carbon dioxide or by hydrogen sulfide. Light petroleum results during those conversions where CO_2 is in excess. With this excess, sulfides will probably oxidize through pyrites to sulfur or sulfates. Soluble sulfates migrate from the generating zone. Such processes may also result in Type I kerogens, although eventual compaction and mineral precipitation form a low-permeability deposit. When the two gaseous fluxes enter the reacting plane with H_2S at the higher rate, reactions lead to the production of different hydrocarbon types, viscous species that incorporate partially oxidized sulfides. In either case, the trapping mechanisms preclude H_2S from invading the atmosphere.

Tar sands represent one limiting case—synthesis of hydrocarbons within a carbonate formation. We know that tar sands frequently occur either within or adjacent to corroded limestone formations or within sandstones infiltrated with calciferous cements.¹³ With high enough pressures of H_2S , carbonates produce CO_2 . The process dissolves mineral carbonates. In this case, the H_2S flux always will be in excess because carbon dioxide is not available from carbonate rocks for the biological conversions in the absence of H_2S . Consequently, the stoichiometry is always CO_2 -deficient, and viscous, sulfur-rich organic deposits, or oil sands, result. For example, the Alberta, Canada, tar sands are located close to commercial gas wells that produce up to 75% hydrogen sulfide. Moreover, this hydrogen sulfide contains no carbon dioxide. Rather, it is diluted with methane.* Such large hydrogen sulfide production is expected in regions where significant tar sands and heavy crudes are located.

*H. Roy Krouse, Department of Physics, University of Calgary, Alberta, Canada, personal communication to N. E. Vanderborgh, July 1981.

Petroleum generation from Type I and II kerogens through thermal degradation may play a role in petroleum genesis, and sufficient quantities of such materials may be produced so that chemical analyses can detect specific compounds. (Of course, in slow-moving, diffusive transport, we may question the direction of migration.) Likewise, the biological-marker compounds, such as porphyrins, will invade a particular porous region. And, since marker compounds are found in low concentrations dispersed through a wide region,¹⁴ we also expect to find them dispersed within petroleum. This hypothesis is confirmed by data.

Perhaps the active reducing flux is hydrogen sulfide. Then too, H_2S may not be the primary agent. Equally likely, hydrogen is produced deep within the crust, possibly by the reaction between water and molten iron, and then that gaseous material moves outward. By the time the gas reaches shallow sediments, hydrogen may have reacted to form either methane or hydrogen sulfide. Such a reducing flux does not reach the atmosphere in concentrated form except in unusual cases. Such gas transport may account for other natural phenomena.^{15,16}

These mechanisms suggest that chemical evidence should exist to show reductive fluxes adjacent to oil reservoirs; in fact, limited data suggest this is the case.¹ Analyses of pore fluids show both reduced mineral species and reduced gases. For instance, data taken from the periphery of an oil reservoir show that subsurface waters contain, Cu^{++} , SO_4^- , and Fe^{++} , whereas over the petroleum deposit, pore fluids contain reduced species, such as CuS , H_2S , etc. Some results show a reducing halo around a petroleum deposit. Moreover, the halo (reduced species in pore fluids) is seldom symmetric. Rather it appears as a segment marking one verge of the petroleum. Such results probably mark the top of the petroleum generating zone.

If this process is operational, we expect to see altered heat flows around petroleum deposits. This expectation, too, is confirmed by data. Generally, petroleum occurs in zones of high heat flow.¹ Although the data are not conclusive, one explanation for existing results is increased heat transfer caused by the transport of gaseous components from deeper within the earth.

Petroleum may be generated mostly within the earth's crust by *in vivo* processes. To state that we understand the nature of such processes or the nature of the organisms involved is premature. Indeed, some of the changes may be entirely chemical. Such processes use carbon dioxide and hydrogen sulfide to synthesize liquid petroleum. We envision that petroleum production

involves migration of the *in vivo* process through the pores of a particular zone, continually moving away from the petroleum to the direction of the appropriate gaseous flux. Because the reductant flux is generally outward and the oxidant flux is generally inward (away from photon-assisted processes) the generating zone may be horizontal. These movements result both in liquid petroleum and Type I (and perhaps Type II) kerogens. Varying stoichiometry between CO_2 and H_2S results in different product types.

Through this model, we extend possibilities for inorganic to organic carbon conversion well beyond the zone of photon-assisted processes. For instance, such synthesis may occur deep within the earth's crust or deep within the oceans. Consequently, all carbon species, both organic and mineral, serve as sources for hydrocarbon production. Also, these considerations confuse the interpretation of carbon isotope data; likewise, abiogenetic-biogenetic distinctions become elusive. This model suggests that the origin of petroleum need not be ancient. Techniques for dating petroleum concentrate on carbon isotopes (difficult data to interpret) and on the source rocks or the reservoir formation. Previous correlations between source-rock age and the petroleum genesis timetable are confused. Therefore, we conclude that petroleum generation may be a dynamic process. Generation rates should be proportional to the number of active microorganisms. Such species grow geometrically, limited by nutrient supply rates. And, generation is essentially continuous, assuming constant nutrient fluxes, although rates of petroleum removal may exceed rates of generation.

Clearly, sulfur fluxes and general fluxes that mark reducing conditions are indicators of hydrocarbon potential. Furthermore, naturally occurring systems can be simulated by altering gaseous fluxes to increase the rates of petroleum synthesis, or flow introduction may alter the naturally occurring fluxes to more desired products.

This concept explains the synthesis of petroleum types, kerogen, and coals. Yet, questions remain. Additional study will require careful field measurements of mass balances (input and output quantities) in a dynamic system because such data do not exist. Certainly, sufficient quantities of sulfur exist in localized zones as elemental sulfur, pyrites, or sulfates to account readily for current petroleum deposits. Yet, sulfur deposits also result from a variety of geological and biological processes that may not involve the carbon cycle. Consequently, detailed volumetric arguments based on sulfur, or carbon for that matter, may not be definitive. Verification using

controlled injection of isotopically labelled compounds, followed by detailed sampling, so that the chemical dynamics of these *in vivo* systems become defined, is more likely. Work on marine systems may be as definitive as on terrestrial systems, and working in deep oceanic environments may be simpler. Results from such studies should lead to improved understanding of those mechanisms that synthesize hydrocarbons within the earth's crust.

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