

The Role of CO₂ and H₂O in the Formation of Gas-Oil Hydrocarbons: Current Performance and Outlook

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Abstract: Scientists still are debating whether oil has a non-biological or a biological origin. The subject of scientific debates between the proponents of abiogenic and biogenic theories reduces to the question about the origin of the carbon, constituting the basis of the formation of gas-oil hydrocarbons. The results of many geological, geochemical and chemical studies indicate an intricate relationship between the mechanisms of the genesis and evolution of all global changes taking place in the interior and exterior domain of our planet. The formation of gas - oil hydrocarbons corresponds to a certain higher stage of evolution of the geochemical cycle of the primary elements of hydrogen, carbon, oxygen, nitrogen and sulfur, which have also played an important role in the emergence of the organic world. Nature selectively created two different mechanisms for activating molecules of water and carbon dioxide. Redox reactions are the basis of both global processes in which electrons are transferred from the donor-H₂O to the acceptor-CO₂ to form hydrocarbons and carbohydrates, respectively. The global cycle of carbon oxide and water may serve as a unifying thread between the presumed process of gas-oil formation in the deep layers of the Earth and the well-known phenomenon, aerobic photosynthesis, on an outer surface of our planet. This article discusses some of chemical peculiarities of the origin of oil and photosynthesis which are of considerable interest for the elucidation of formation mechanism of gas-oil hydrocarbons. Presumed pathway for the formation of petroleum hydrocarbons from carbon dioxide and water along with endogenic methane predicts that the resources of gas - oil hydrocarbons are practically inexhaustible. Moreover, the prospects for the synthesis of fuels and other valuable organic materials based on CO₂ and H₂O open the new possibilities for their efficient and environmentally friendly artificial production.

Keywords: Global changes in nature; CO₂ and H₂O as the renewable raw materials; Mechanism of catalytic activation of the molecules water and carbon oxide in the Earth's depths; Mechanism of activation of the molecules water and carbon oxide on the Earth; Artificial energy from CO₂ and H₂O.

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1. Introduction

The concepts concerning the origin of oil, whether from the flowing deep Earth fluid, or from the remains of organic matter buried in sedimentary rocks, are based on the huge number of experiments of long-term research of several generations of geologists, geochemists and chemists. This subject of scientific debates between the proponents of abiogenic and biogenic theories continuing for many years reduces to the question about the origin of the carbon, constituting the basis of the formation of gas - oil hydrocarbons.

Many studies in recent years have shown that all the existing physical, chemical and biological laws of nature facilitate self-organization and self-regulation of the global changes taking place in the interior and exterior domain of our planet [1-3]. The results of many geological, geochemical and chemical studies indicate an intricate relationship between the mechanisms of the genesis and evolution of these global phenomena. The formations of oil and photosynthesis process certainly belong to the category of such fundamental natural phenomena. Despite the huge number of studies, there are more uncertainties concerning the questions of the genesis of the underground oil fields than extremely complex mechanism of photosynthesis, continuously taking place on an exterior sphere of the planet. This article discusses some of chemical peculiarities of the origin of oil and photosynthesis, which are of considerable interest for the elucidation of formation mechanism of gas-oil hydrocarbons.

The formation of gas -oil hydrocarbons corresponds to a certain higher stage of evolution of the geochemical cycle of the primary elements of hydrogen, carbon, oxygen, nitrogen and sulfur, which have also played an important role in the emergence of the living world [4-7]. The elements at initial high temperatures were very active chemically and their interactions have led to the synthesis of a number of simple molecules like H₂, O₂, N₂, CH₄, CO₂, NH₃, H₂O, H₂S, also hydrides, oxides and carbides of different metals. The atmosphere of the early Earth also consisted mainly of carbon dioxide gas of endogenous origin, and the process of photosynthesis during several billion years cleared the atmosphere of CO₂ (up to ~ 0.03%) and saturated it with oxygen [8].

Automatic interplanetary stations have given abundant information proving that the most important elements for the formation of oil and the origin of life precursors - C, H, N, O, S and P are among the most common in the universe. It was revealed that the primary interstellar medium and all the planets contain different molecules of these elements. The various inorganic and organic molecules and radicals such as CH, CN, C₂, C₃, CH, CN, OH, NH, NH₂, CO, N₂, carbides, SiC, Fe₃C or even relatively complex organic compounds as acetic acid and urea were revealed in the gas-dust environment of interstellar space and in the spectra of comets. Atmosphere of Saturn, Jupiter, Uranus and Neptune contains a huge amount of CH₄. The

atmosphere of Venus contains a lot of CO₂, CH₄, C₂H₂, C₂H₄, Mars - CO₂, COS and so on. These data support the potential abiogenic origin of methane and other simple organic compounds in the mantle conditions from the initial elements. It should be also noted that namely the interaction of these compounds is considered in many schemes of prebiotic evolution of the Earth.

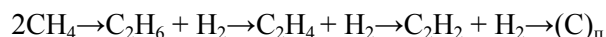
2. Chemical Peculiarities of Activation of CO₂ and H₂O in the Depths of Earth

Methane is the first member of the homologous series of alkanes, which are the basis of oil. As seen from the schemes presented below, methane could be formed from the elements and simple molecules in the mantle conditions by various ways:



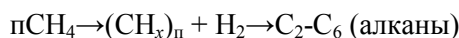
The chemists have devoted considerable time and efforts to activate the methane molecules [9]. The main purpose of these studies was to work out an effective technology for the synthesis of liquid hydrocarbons and other valuable petrochemical products directly from abundant raw material as methane. The results of these studies are also important to determine the possible role of methane in generation of oil under natural conditions.

Methane has a high thermal stability and begins to decompose above 1600-1700 K. The formation of higher hydrocarbons requires cleavage of C-H bond in the methane molecule, but its high dissociation energy (435 kJ/mole) makes this process highly endothermic. For this reason, only when the temperature exceeds 2000 K, methane is converted to acetylene by intermediate formation of ethane and ethylene, which are then converted into the graphitized carbon:



Conversion of methane to its homologs can occur at lower temperatures in the presence of catalysts. The process may be implemented by direct or indirect ways with or without oxygen. The various hydrocarbons could be formed depending on the selected types of catalysts with different structures and compositions. In the presence of oxygen at 900-1200 K, main product is ethylene [10]. Conversion of methane on metal catalysts in the absence of oxygen takes place under milder conditions to yield C₂-C₆ alkanes [11, 12]. Recently developed nanostructured bimetallic catalysts allow homogenization of methane at atmospheric pressure and 400-600 K [13, 14]. The catalysts containing Pt, Re, Ru, Co exhibit the highest activity. To circumvent the

thermodynamic limit, dissociative adsorption of methane may be carried out at 600 K, followed by hydrogenation of the adsorbed on the catalyst (CH_x)_n fragments at the same or at a lower temperature (about 450 K). Under optimum conditions, the methane coupling process reaches up to 40% [14].



Catalysts based on zeolites selectively convert methane to aromatics at 973 K [15]. The catalyst Mo / HZSM-5 is selectively formed benzene in a yield over 7%:

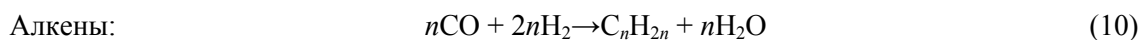
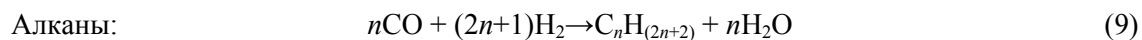


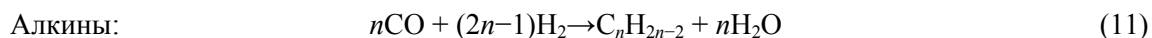
The combination of Mo with the Pt, Re, Zr and Co significantly improves the efficiency of the catalyst [14]. A mixture of methane and hydrogen can be converted also into cyclohexane and its derivatives at temperatures of 545-570K, and atmospheric pressure in the presence of catalysts Ni- and Ni-Cu fixed to the SiO₂ [16]. Despite the intensive efforts of many researchers it was failed to develop an effective method for the direct conversion of methane to higher hydrocarbons of petroleum range. However, according the analysis of research results of geological and geochemical parameters received in the South Caspian basin, a possibility of oil formation through the phased transformation of endogenous methane was offered [17]: **a)** the formation of CH₄ from hydrogen and carbon (core-lower mantle); **b)** condensation of CH₄ to ethane-hexane alkanes (middle-upper mantle); **c)** formation of paraffinic, cyclic and aromatic components of petroleum under thermobaric and catalytic conditions of the lithosphere.

Higher hydrocarbons can be synthesized under more favorable thermodynamic conditions on the basis of "synthesis gas", produced previously by the reforming of methane:



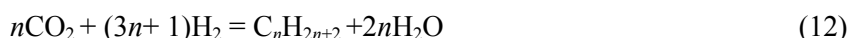
Manufacturing of "synthesis gas" is widely commercialized and series of high-performance technologies were developed for the production of hydrocarbons on an industrial scale. The most practical importance has got the Fischer-Tropsch (FT) process representing the wide range of chemical reactions that convert gaseous mixture of carbon monoxide and hydrogen into hydrocarbons [18 -20]:





FT process is carried out in the temperature range 450 – 600 K and pressures up to 10 MPa. The salts and transition metal oxides are used as catalysts - mainly iron, cobalt, nickel, including promoters - oxides of potassium and copper, fixed on the SiO₂, Al₂O₃ and zeolites. The mentioned above catalysts are also used to implement the process of Kelbelya-Engelhardt (12):

$(3n+1)\text{CO} + (n+1)\text{H}_2\text{O} = \text{C}_n\text{H}_{2n+2} + (2n+1)\text{CO}_2$ in combination with the reaction:



Researches from the Bath University (UK) have developed a catalyst representing the iron nanoparticles embedded in carbon nanotubes. The new iron-containing catalyst promotes the conversion of carbon monoxide and carbon dioxide in the presence of hydrogen. When carbon dioxide is bound to the nanoparticles of iron, a high content of hydrogen in the system facilitates the formation of hydrocarbons. In this process, 55% of carbon dioxide was reduced to hydrocarbons and the remaining 45% of carbon dioxide was converted to CO [21].

All the above-mentioned processes are exothermic and they are accompanied by a large release of heat. Thermal energy of Fischer-Tropsch and Sabatier reactions equals - 165 kJ/ mol, and the process of Kelbelya-Engelhardt - 244.5 kJ/mol. Therefore, in the presence of necessary components, hydrocarbons can be produced without energy supply, as it required in the case of direct methane homologation. In this series, the Sabatier process is representing the selective synthesis of methane in the presence of nickel catalysts by reduction of carbon dioxide with hydrogen at 550-700K (Scheme 2). Considering high selectivity of this process, NASA is planning to use it in the piloted exploration of Mars to produce a fuel (CH₄) by using the resources of this planet (CO₂).

It should be emphasized that these processes have been well studied in the laboratory and are used in industry on a large scale for the production of any molecular weight hydrocarbons, such as those found in the oil composition. Many salts and metal oxides used as catalysts are part of different sedimentary rocks. Moreover, some natural materials, such as clays, aluminasilicates and zeolites are widely used as active catalysts in these processes [19, 20]. A mixture of hydrocarbons of different compositions, from predominantly methane to liquid hydrocarbons such as *n*-alkanes, isoparaffins, olefins and aromatics are formed on these bi-functional catalysts. It seems that the synthesis of hydrocarbons in oil and gas origin from inorganic compounds at natural conditions can be readily modeled with a number of chemical processes described above. These reactions are assumed prototypes of widespread formation processes of oil

hydrocarbons in the mantle conditions from carbonates, carbon oxides and hydrogen. This conclusion is confirmed by the results of several studies.

A large number of experimental studies were dedicated to the molecular weight distribution (MWD) of the products of FT synthesis [22]. The main feature of FT process is that the product distribution by molecular weight under stationary conditions obeys the Anderson-Schulz-Flory rule (ASF) and is described by the formula:

$$W_n/n = n(1-\alpha)^2\alpha^{n-1} \quad (I)$$

where W_n/n - mass concentration of alkane of a carbon number n , $\alpha = k_1 / (k_1 + k_2)$, k_1, k_2 – the constants of growth rate and chain termination, respectively. The values of the parameter α dependent on catalyst type and process conditions. The yield of long-chain hydrocarbons increases by increasing α . Table 1 shows the values of the parameter α of FT products obtained on iron catalysts of various compositions [23]. It is clear from the received results that when the temperature changes from 432 to 558 K parameter α varies slightly in the presence of iron catalysts. A comparison of FT process products MWD and crude oils hydrocarbons founds them very similar. The study of the composition and structure of oils from different fields: Tengiz [24], West Siberia [25], Rift Guayama in the Gulf of California [26] and a number of other oils showed that the mechanism of formation of hydrocarbons that make up a significant part of oil, in particular n-alkanes, belong to the same type of polycondensation products as in the case of FT process and their MWD obeys model ASF.

Table 1
The values of the parameter α for the FT process

Catalyst	T, °C	Parameter, α	Average value, α
100 % Fe ₂ O ₃ + (2-3)% Al ₂ O ₃ (0.7-1.2)CaO (0.5-0.8)K ₂ O +0.4% SiO ₂	285	0.61	0.62 ± 0.01
	273	0.59	
	262	0.61	
	251	0.60	
	239	0.60	
	231	0.62	
	241	0.59	
	223	0.63	
	214	0.60	
	199	0.64	
100 % Fe ₂ O ₃	188	0.68	0.63 ± 0.04
	261	0.66	
	251	0.66	
	224	0.69	
100 % Fe ₂ O ₃ + +0.6% Al ₂ O ₃	211	0.68	0.67 ± 0.01

These similarities between MWD of FT products and hydrocarbons from different oil fields lead to a conclusion on the universality of the formation of *n*-alkanes in both cases. These facts clearly indicate the identity of the polycondensation type formation mechanism of hydrocarbons in the FT synthesis in the laboratory at 370-600K, and in crustal rocks [27]. In this respect, the fundamental importance has an analysis of the results of the joint experiment of US and Russian researchers on the synthesis of complex hydrocarbon systems under conditions corresponding to the conditions of the Earth mantle. The starting materials for the synthesis of hydrocarbons were chemically pure compounds - FeO, CaCO₃ and double distilled water [28]. The experiment yielded a hydrocarbon mixture containing 89.6% of methane at temperature and pressure conditions of 1200 K and 3000 MPa. A team of American researchers also used high-pressure equipment, which allows implementing a method of Romanov spectroscopy in diamond anvil cells by laser heating [29]. Upon heating the mixture of reactants like FeO, CaCO₃ and H₂O at 1700 K and a pressure of 7000 MPa *in situ* was also recorded mainly methane. The calculation shows that at temperature of 1000 K and pressures of 25-40 kb all hydrocarbon molecules are chemically and thermodynamically unstable with respect to methane [30]. Obviously, high oil hydrocarbons are unstable in the lower mantle conditions and quickly decay into methane and highly carbonized residue, up to graphite. As noted above, a molecule of methane formed in the mantle conditions could undergo chemical conversion itself via interactions with oxygen, water, and carbon dioxide. Thus, the transfer of the principal place of formation of petroleum hydrocarbons from the deep interior of the Earth (lower mantle) to the horizons of the crust gets sufficiently strong experimental basis. As noted above, the compounds of terrestrial rocks contain different metals, which may well serve as active catalysts for the conversion of carbon oxides and water to hydrocarbons (Table. 2) [31]:

Table 2

Composition	Ocean.kora	Rock bark	Kraton	Low temp. kraton	High temp. kraton
Basic element composition various rocks,%					
SiO ₂	44,66	44,98	44,47	44,18	44,51
TiO ₂	0,01	0,08	0,09	0,02	0,11
Al ₂ O ₃	0,98	2,72	2,50	1,04	0,84
FeO	8,28	8,02	8,19	6,72	8,08
MgO	45,13	41,15	41,63	46,12	44,76
CaO	0,65	2,53	2,44	0,54	1,08

Studies have shown that catalyst activation by hydrogen is necessary for starting the FT process. The growth of the hydrocarbon chain may be represented as a chain reaction (Fig.1) [18]. Probably, a content of the active catalyst and synthesis parameters (temperature, pressure) should also substantially influence the composition of hydrocarbons. The decisive role belongs to the stage of dissociative adsorption of hydrogen, which activates the catalyst, promotes the effective splitting of the C=O bonds and provides an exothermic process of the hydrocarbons formation. Thus, generation of atomic hydrogen may initiate a synthesis reaction of hydrocarbons from carbon oxides (CO, CO₂) and water at much lower temperatures and pressures.

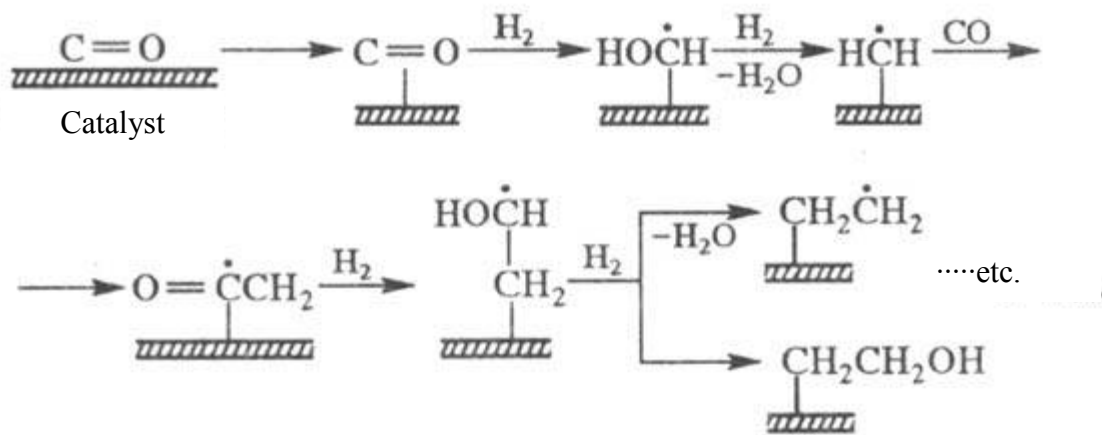
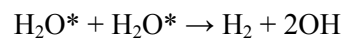
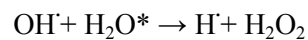
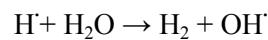
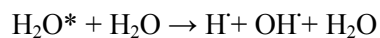


Fig.1 Growth of the hydrocarbon chain in the Fischer-Tropsch process.

Water is a very stable chemical compound. At 298 K the dissociation constant of water is equal to $1,8 \cdot 10^{-16}$ mol/l [32]. Gravitational decomposition constant of water with separation of free hydrogen and oxygen at 298K is characterized by a negligible value equal to 10^{-83} , making it one of the most resistant compounds in nature, substantially in capable of spontaneous decay in the crust. It is therefore believed that the decomposition of water into hydrogen and oxygen under ordinary temperature and pressure conditions is extremely unlikely without significant energy supply from the outside. Moving water from the free to the bound state is accompanied by a sharp increase of H⁺ and OH⁻ concentrations in the solution. This, in turn, should facilitate the involvement of the water in a variety of geochemical processes. In early 1960s it was found that hydrogen is generated during grinding of rock and passing through rock samples of seawater [33]. Such active hydrogen can be involved in the synthesis of hydrocarbons from the carbonaceous materials. According to Pourbaix diagram [34], if the reduction potential provides a displacement of the active hydrogen from water, the hydrocarbon synthesis based on carbon oxides (CO, CO₂) and water can be realized at much milder conditions. Mechanical activation of mineral particles can occur not only as a result of a special crushing and abrasion, but also because of the deformation of rocks under tectonic and seismic processes [35].

Seismic data "transmission" of the Earth showed that the active processes that form the structure of the Earth's crust are generated in the lower mantle at its boundary with the core [36]. According to geochemical data in this zone at a depth of 660 km there is a reservoir, where the endothermic phase transition of olivine to ringwoodite takes place at very high pressures and temperatures [37]. Recent studies of US scientists have shown that a composition of this zone is ringwoodite containing up to 3% of water, which is held in the molecular structure of the mineral in its activated form [38]. This means that the transition zone can potentially accommodate the same amount of water as all the oceans in the world. The water contained in ringwoodite is displaced when the mineral melts at the boundary of the lower mantle with the nucleus to form another mineral perovskite. Dissociated highly active particles of water, as they pass to the Earth's crust through carbonate rocks can initiate the polycondensation synthesis of hydrocarbons.

It is also experimentally established that in low elastic deformation under the influence of seismic waves rocks emit electrons [39]. In the aquatic environment, these electrons actively interact with water molecules, transforming them into an excited state H₂O*, which corresponds to the standard electrochemical potential E° = -2.77V. As a result, equilibrium system of water, in accordance with Pourbaix diagram, moves into the region where the active hydrogen H[·] is formed [40]:



It is believed that occurred dislocation in the inside surface of the grains at stresses exceeding the tensile strength of rock leads to splitting of chemical bonds between molecules to form free radicals, which causes a significant increase in the Gibbs free energy (ΔG). The free energy change ΔG of initial or final products of chemical reactions by the amount a few tens of kJ/mol, can change the direction and conditions of the reactions themselves. As a result, the reactions thermodynamically allowed at temperatures 800-1300 K and above, can proceed at lower temperatures (below 400 K) [35]. Due to the additional energy for activation of rocks, it becomes possible to synthesize a number of gas-oil hydrocarbons from CO₂ and H₂O on the surface of mineral grains species. The formed oxygen binds to the rock matrix and a rising H[·], H₂ and CO are adsorbed on the surface of the pores of the matrix, where interacting with each other they participate in the synthesis of hydrocarbons, similarly to the way it occurs in processes of the FT. These outlined views were verified experimentally and it was confirmed that in an aqueous medium, containing the free electrons (hydrogen atoms), reduction of carbon CO₃²⁻ and CO₂ takes place to produce a wide range of hydrocarbons

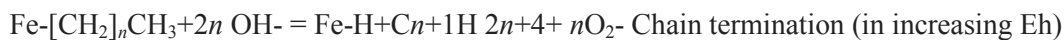
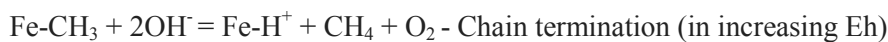
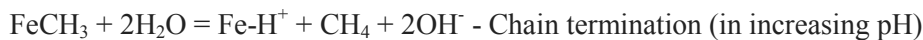
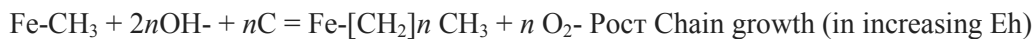
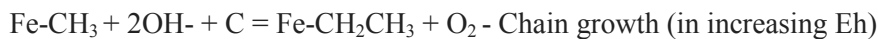
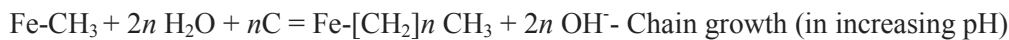
(saturated, unsaturated and aromatic). These processes are structurally similar to the Fischer-Tropsch and Kelbelya-Engelhardt type synthesis. Distinct from the known processes is that the formation of hydrogen from H₂O occurs at the beginning of these reactions, which reduces CO₃²⁻ and CO₂ to CO, then the hydrocarbon synthesis takes place according to the above shown scheme. The distribution of n-alkanes in the experiments carried out is described quite well by the model ASF with parameter $\alpha = 0.67$ [22]. An important specification of these processes is that the active metal (for example iron) in the synthesis of hydrocarbons is not only a catalyst but also as a reagent for binding of formed oxygen [41].

There are a large number of articles and patents describing the results of experiments on low-temperature synthesis of hydrocarbons from CO₂ and H₂O. The patent US5516742 [42] describes a method of producing a mixture of hydrogen, carbon monoxide, oxygen and hydrocarbons by reaction of carbon dioxide and water in the presence of a catalyst containing magnesium carbonate. The authors believe that in the synthesis of hydrocarbons from CO₂ and H₂O in nature the heat source can come not only from the bottom by geothermal flux, but also from the exothermic process of hydrocarbon formation. The thermal energy of the process can intensify the destruction and converting of carbonaceous matter of sedimentary rocks to hydrocarbons.

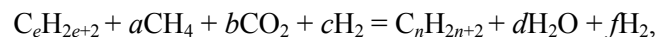
The patent RF 2495080 [43] applies a method for producing hydrocarbons, hydrogen and oxygen by bubbling carbon dioxide saturated water through a reactor containing iron oxides or iron swarf as catalyst. The experiments were performed at room temperature. In dynamic mode, the pressure in the reactor usually did not exceed 10 atm., in the steady state growth of reactor pressure was limited to 25 bar. The authors believe that other metals such as Co, Cu, Ag, Mn, metal oxides: MgO, CaO, SrO, BaO, BeO, Al₂O₃, La₂O₃, CeO₂, ThO₂, UO₂, U₃O₈, SnO₂, Bi₂O₃, CdO, ZnO, as well as natural minerals, in particular clay and zeolites may also be used in this process as effective catalysts. The distribution of *n*-alkanes in the carried out experiments is described quite satisfactorily by the model ASF with parameter $\alpha = 0.7$. The difference between the developed and the Fischer-Tropsch and Kelbelya-Engelhardt processes consists in the fact that the value of the Gibbs energy for the reagents of developed reaction is higher than that of its products. This circumstance makes this reaction thermodynamically unfavorable that excludes its spontaneous flow without supplying additional energy. It is possible that in this case decisive role in the destruction of the water molecules and hydrocarbon formation belongs to the electrochemical processes involving free electrons produced at contact of rock minerals with water, as earlier it was experimentally determined [33, 35]. The experiments using iron filings revealed that arising O₂ in contrast to H₂ is almost completely absorbed by swarfs. Therefore, the iron filings played the part, not only of catalyst but also actively have interacted with oxygen to form iron oxides removing O₂ from the system.

Some sediment usually contains small amounts of alkanes, alkenes, cycloalkanes, and aromatic hydrocarbons. Traditionally, they are interpreted as migrated thermogenic oil. In order to study mechanism of this process, carbon dioxide was passed through salt water containing Ca-montmorillonite and FeO during 300 days at 288-298 K [44]. It was found that the hydrocarbons were formed by reacting of the allocated CO₂ from the rocks and water. It was shown that the presence of NaCl, Fe-montmorillonite, CaCO₃, Ca(OH)₂, MgSO₄, (NH₄)₂SO₄, K₂SO₄ in the reaction mixture acts as promotor.

The following possible mechanism is proposed for the formation of hydrocarbons [44]:



Thermodynamic calculations show that upon addition of alkane (e.g. C₃H₈) to the reaction mixture of CO₂, CH₄ in water in the presence of a catalyst (e.g., FeO or Fe_xO_y), exothermic growing of hydrocarbon chain will occur at ambient temperature and pressure, according to the following reaction equation: C₃H₈ + bCO₂ + aCH₄ + bH₂ = C_nH_{2n+2} + cH₂O + dH₂ (n=3+a+b). Formation of a number of gas-oil hydrocarbons in general can be represented by the reaction equation:



where $n=e+a+b$; H₂ = 2H₃O⁺ or 2H⁺ or 2Fe-H⁺ or Me-H⁺

An analysis of the above data shows that the formation of hydrocarbons that form the basis of oil and gas deposits, can occur at depths of the upper mantle and crust. Thermobaric parameters of this earth area are fully suitable for implementation of processes for formation of oil components based on methane, carbon dioxide and hydrogen or water. Erupting deep fluid contains all primary components: CH₄, CO₂, H₂, H₂O and potential catalysts. A high content of NaCl in rocks causes intense inclusion of CH₄ and CO₂ into the growing chain to allow the formation of hydrocarbons of higher molecular weight. A well-known way of converting a mixture of carbon dioxide with hydrogen to CH₄ by methanogenic bacteria in the bowels of the earth depths of 8-10

km may also point to the probability of hydrocarbon formation by the reaction of CO₂, H₂, and H₂O at geochemical conditions through the underground rocks [45].

Carried out intensive search has created real preconditions for the practical development. Recently the Audi Company (Germany) has produced the first batch of diesel fuel made from water and carbon dioxide [46]. For the production of high-temperature fuel, water is electrolyzed at 800°C. The obtained hydrogen reacts with carbon dioxide in the reactor for synthesis of fuel-fluid compositions of long chain hydrocarbons. All the necessary carbon dioxide was drawn from the surrounding atmosphere. Further expansion of production of such fuel would lead to a reduction in the greenhouse effect. In essence, a closed cycle of the production process was developed. Unlike conventional diesel fuels containing impurities of sulfur and oil-fractions, the new fuel does not poison the environment. It is also characterized by high efficiency (70%) during operation. At present a pilot plant in Dresden produces only 160 liters of such fuel a day. There are plans to construct a full-scale industrial complex. It is expected that the market price of the environmentally friendly fuel will be around one euro per liter.

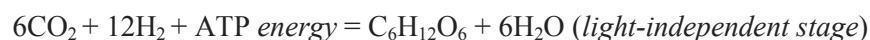
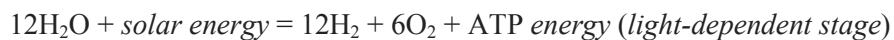
3. Chemical Peculiarities of CO₂ and H₂O Activation of in the Aerobic Photosynthesis Cycle

Recently, the German researchers reported that plants are capable of producing methane in normal aerobic conditions [47]. Their suggestion has drawn much attention [48-51]. Despite much uncertainty and skepticism, the most of further studies concluded that the phenomenon is true. Some factors such as UV radiation, rising temperatures and reactive oxygen species stimulate methane emissions from plants. All these facts show that living plants synthesize methane themselves, without the involvement of microbes. By measuring the intensity of methanogenesis in many species of plants from different climatic zones, the researchers tried to calculate the total amount of methane emitted by all green plants of the planet. According to the first rough estimate it turned out that living plants emit about 10% of the total amount of methane emissions in the atmosphere [47].

These extremely important facts in the global cycle of carbon and water may serve as a unifying thread between the presumed process of gas-oil formation in the deep layers of the Earth and the well-known phenomenon, aerobic photosynthesis, on the surface of our planet. Nature selectively created two different

mechanisms for activating molecules of water and carbon dioxide. Redox reactions are the basis of both global processes in which electrons are transferred from the donor- H₂O to the acceptor- CO₂ to form hydrocarbons and carbohydrates, respectively. If the supposed activation of water and carbon dioxide with the subsequent formation of hydrocarbons in the Earth's mantle takes place at termobaric, mechanochemical, tektono-seismic and catalyst impact on carbon-containing minerals, then a similar process of activation of water and carbon dioxide followed by a synthesis of carbohydrates on the surface of the planet occurs by transforming the solar energy into chemical energy by entering carbon into biochemical cycle.

Aerobic photosynthesis is the most important type of photosynthesis for the modern conditions of life on the Earth. This is, like the catalytic synthesis of hydrocarbons from CO₂ and H₂O, a complex multi-step redox process [52]. Presented in Fig. 2 diagram illustrates the processes occurring during aerobic photosynthesis. Decomposition of water into hydrogen and oxygen atoms represents the primordial light-dependent stage of photosynthesis process: where in the produced oxygen is carried away to the atmosphere, while the hydrogen reduces CO₂, converting solar energy into chemical energy. Two stages of aerobic photosynthesis can be expressed by separate equations:



The global cycle of oxygen, carbon and other elements involved in photosynthesis, supports the current atmospheric composition necessary for the existence of modern forms of life on Earth. As a result of photosynthesis, the vegetation of the globe forms more than 150 billion tons of organic substances annually, converting about 200 billion tons of CO₂ and releasing about 200 billion tons of free oxygen into the environment. Photosynthesis is the only process in the biosphere, leading to increase its energy due to an external source. The stored energy in the products of photosynthesis satisfies the need for food of all living creatures on our planet. Recent observations have shown that green plants are able not only to use the carbon dioxide and water to form a carbohydrate, but also possibly to convert CO₂ and H₂O to hydrocarbon [47].

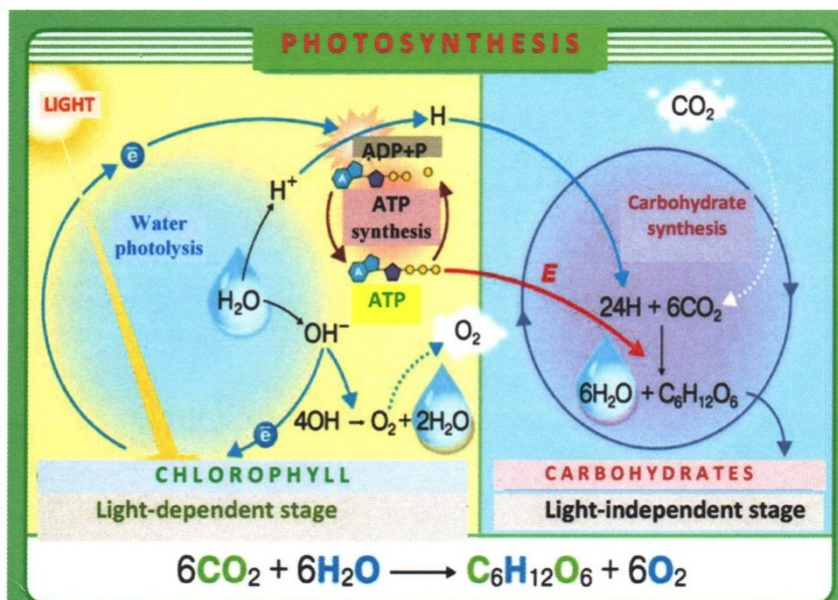


Fig. 2 Diagram of the process of photosynthesis

Thus, it is presumed that the mechanism of formation of hydrocarbons in the Earth's depths also includes a series of chemical reactions between the water and carbon dioxide molecules similar to a process of photosynthesis. In both cases, the process consists of two extremely important stages: oxidation of water and of carbon dioxide molecules. As noted above, in the Earth's depths estimated oxidation of water molecules and reduction of carbon dioxide molecules take place under the influence of mechanical, seismic, tectonic and catalytic factors to form hydrocarbons, while in the process of photosynthesis, water seeping through the root system of the plant is oxidized by the energy of sunlight absorbed by the chlorophyll, followed by transfer of electrons to CO₂ molecules to form glucose [52]. At the same time methane perhaps is formed as a by product of photosynthetic catalytic cycle [47]. The possible formation of methane in green leaves helps the identification of common aspects of the mechanism of the genesis of oil and energy foundations of life on Earth, indicating that both potential fuels-carbohydrates and fossil hydrocarbons – can be obtained from the same renewable raw materials CO₂ and H₂O originating from both non-biogenic and biogenic sources.

4. Creation of Artificial Energy on the Base of CO₂ and H₂O

90% of modern energy sources come from the fossil fuels: coal, oil and natural gas. Intensive growth of the development of raw materials and fuel production significantly pollutes the soil and atmosphere. Current levels of carbon dioxide in the atmosphere exceed the conditionally permissible percentage. It is believed that the achievement of a threshold of CO₂ concentration of 450 ppm will cause an uncontrolled heating of

the earth's surface. Therefore, scientists and engineers need to find not only a more efficient ways of production, processing and use of fossil fuels to reduce emissions, but also to find alternative renewable clean energy sources. The researchers in many countries associate the solution to this problem with the possible implementation of a natural phenomenon-the photosynthesis in the laboratory. It is known that the sun provides more energy to the earth for one hour than all kinds of energy sources used throughout the year. Creating an industrial technology based on sunlight may help solve two problems at once: provide a clean, renewable alternative to fossil fuels and stop global warming.

Artificial photosynthesis is not exactly the same process that occurs in plants. But it strives to create similar beneficial compounds rich in energy reserves from water, carbon dioxide and sunlight rays. In normal photosynthesis, the light rays act as a catalyst with chlorophyll. However, the light reaction center is equipped with such an amazing structure formed by plants for nearly 3 billion years of evolution that chemists cannot yet accurately replicate it in a laboratory. Development of catalysts that mimic the properties of chlorophyll for effective oxidation of water molecules and reduction of CO₂ is the basic concept of artificial photosynthesis. It is important that catalysts being developed should be able to use not only ultraviolet rays, which comprise not more than 2% of the solar light, but also a "visible light", which accounts for 40%. At present time there are many examples of synthetic molecules that are able to absorb solar energy and use it for efficient charge separation [53-55]. There is a significant progress in the production of two very important types of fuel by means of artificial photosynthesis: 1) hydrogen, which may be used as a transportation fuel and raw material for industry; 2) methane, carbon monoxide and methanol - raw materials for the manufacture of a wide range of synthetic liquid fuels, fertilizers, pharmaceuticals, plastics, and others.

In September 2011, a research team from Japan presented a report on the world's first successful synthesis of organic matter using only water, carbon dioxide, and solar energy [56]. They used visible light for reduction of CO₂; however, for the oxidation reaction of H₂O ultraviolet rays were applied. The energy conversion rate was about 0.04%. Later, Toshiba has announced the development of technology that allows the production of the carbon compounds from carbon dioxide and water using the solar energy, suitable for industrial application as a chemical feed stock or fuel [57]. They used gold nano-catalyst and a semiconductor element that absorbs light of the visible part of the spectrum with high efficiency. The proposed technology is characterized by efficiency of 1.5%, which is the highest figure to date. The long-term goal of the project is to create technology that is compatible with existing systems capturing carbon dioxide, established in thermal power plants and industrial enterprises.

The researchers in the Australian National University first reproduced photosynthetic reaction in the

laboratory by applying natural protein ferritin, modified with manganese, in combination with the photosensitive pigment - zinc chlorine as catalyst [58]. Clear indication of electric charge transfer, the same that occurs in plants, has been fixed when the catalyst was exposed to sunlight. Another group of researchers from Monash University (Australia) were able to create a nanocomposite photo-catalyst based on copper oxide, which can directly convert carbon dioxide dissolved in water to methanol using sunlight as an energy source [59].

Berkeley Lab (US) has managed to master the decomposition of water using solar energy on a silicon oxide and titanium oxide [60]. Nanowires used as catalyst resemble a wood technology: their tree structure improves the efficiency of catalyst. Such nano structures are able to receive the rays on the large areas. There researchers from the Rochester University (UK) presented a new hydrogen-generating system, which allows using sunlight, nano crystals and a nickel catalyst to obtain hydrogen fuel [61]. According to the authors, they use the most workable to date scheme that provides conversion of water into hydrogen and oxygen by solar energy.

Many research centers and companies continue intensive search. It is believed that the achievements of high efficient artificial photosynthesis technology, based on carbon dioxide, water and sunlight, will provide a large part of the clean fuel requirements from the "solar fuel" factories in the near future.

5. Conclusions

In recent years, an increasing number of researchers come in agreement with the concept that the formation of oil and gas deposits took place by transformation of products of both mineral and organic nature. The concept of polygenic origin of gas-oil hydrocarbons corresponds to the approach that all the natural processes on the Earth are in deep relationship. The results of long term geological, geochemical and chemical studies lead to the conclusion that nature has the mysterious levers of regulating the mechanisms of global changes occurring in the depths and on the outside domain of our planet. In this aspect the nature used the whole arsenal of needed means and routes for implementation of the processes to form the oil, plants and living world, by creating the most favorable conditions.

Analysis of many articles and patents shows that the raw materials CO₂ and H₂O utilized in the photosynthesis using sunlight energy could also play a decisive role in the formation of oil deposits along with endogenic methane, with the participation and the catalytic action of various mineral compounds in the deep layers of the Earth. Understanding of the mechanism methane formation in green leaves is extremely important in detecting the common aspects of origin of oil and photosynthesis on Earth, as well as their close relationship in the geochemical cycle of carbon and water.

It is assumed that the formation of hydrocarbons inside the Earth also consists of a series of chemical reactions between the water molecules and carbon dioxide (or carbonates). If in the process of photosynthesis, water seeping through the root system of the plant is oxidized by the energy of sunlight absorbed by the chlorophyll, followed by reduction of the CO₂ molecules to form glucose (and may be methane), presumed oxidation and reduction processes yielding hydrocarbons in the depths of the Earth takes place under the influence of mechanical, seismic, thermobaric and catalytic factors. As in the case of photosynthesis, the process can be imagined in accordance with the scheme of non-equilibrium flow reactor. Apparently, the nature also created the conditions necessary for the smooth circulation of the reaction products (e.g. fluid flowing by "degassing pipes"). Within the framework of such mechanism, the most of the strictly abiogenic or biogenic explanation of formation of gas-oil hydrocarbons loses its categoriality.

Despite the fact that oil and gas is currently classified as renewable natural fossils, predictions are periodically appearing regarding fast exhaustion of their reserves. Presumed pathway for the formation of petroleum hydrocarbons from carbon dioxide and water predicts that the resources of oil and methane are practically inexhaustible. Moreover, the prospects for the synthesis of fuels and other valuable organic materials based on CO₂ and H₂O open the new possibilities for their efficient and environmentally friendly production. Possibility of catalytic synthesis of hydrocarbons from CO₂ and H₂O is described in the numerous patents and first developed the technology of production of diesel fuel by AUDI Company (Germany).

Understanding the mechanisms of methane formation in green leaves gives a unique opportunity to modify the process of photosynthesis and aid in the production of fuel and other valuable organic materials from CO₂ and H₂O using solar energy. The main obstacle to overcome is the development of efficient catalysts, allowing the replication of photosynthesis in the laboratory. It is important that catalysts being developed should be able to use a "visible light" accounting for 40%, in addition to ultraviolet rays, which comprise not more than 2% of the solar light. By creating an industrial technology based on CO₂, H₂O and sunlight we can solve two problems at once: provide a clean, renewable alternative to fossil fuels and stop global warming. The United States, Netherlands, China, Japan and South Korea have organized special research centers for this purpose. Currently, there has been significant progress in the production of two very important types of solar fuels: 1) hydrogen-which can be used as a transportation fuel and raw material in the industry; 2) methane, carbon monoxide and methanol-raw materials for the manufacture of synthetic liquid fuels, fertilizers, pharmaceuticals, plastics, and others.

Along with photosynthesis there are reverse processes continuously taking place in nature producing carbon dioxide and water – the oxidation end-products of organic matter. Many industrial emissions also

increase the level of greenhouse gases (CO₂, CH₄, N₂O and fluorinated gases) in the atmosphere, among which carbon dioxide is the largest component. These emissions are associated with the human activities. The concentration of carbon dioxide and methane in the atmosphere continue to rise, which, according to climatologists, is the main cause of global warming. Based on the prediction of the Intergovernmental Panel on Climate Change (IPCC), by 2100, the atmosphere level of CO₂ may rise to 570 pp. In this regard, a number of UN conventions [the Kyoto Protocol (www.un.org/ru/documents/decl/kyoto.pdf), the Durban Platform (www.dw.de/p/13Qei)] obliges countries to reduce greenhouse gas in the atmosphere. New and improved energy technologies will be one of the ways in which countries would be able to fulfill the commitments made. The use of atmospheric CO₂ and CH₄ in the production of solar fuels will undoubtedly allow to significantly reducing the greenhouse effect.

Currently there are a number of projects around the world performing for the capture, transport and storage of emitted carbon dioxide in industrial enterprises with the purpose to use in the petrochemical synthesis. Successfully implemented program of Energy "Energy City" Fund (CIUDEN) (Spain), whose aim was to create systems that allow capturing carbon dioxide emitted during manufacturing operations [62]. These units are intended for use by thermal power plants, oil refineries, steel plants and cement plants, as industries with the most "dirty" production. Center for CO₂ capture in El Bierzo has already announced its readiness to sell the technology to domestic and foreign markets.

Recently the methanol production plant was built in Japan with a capacity of 100 tons yearly, where hydrogen, obtained by decomposition of water by means of solar energy, and CO₂, recovered from the waste gases of ethylene units of Mitsui Chemical Complex (Osaka) are used as raw materials [63]. SABIC (Saudi Arabia) is planning with the help of Linde Group (Germany) to build the largest plant in the world with a daily capacity of 1,500 tons for the extraction and use of carbon dioxide from the waste gases of ethylene units in Jubail [64]. Mitsubishi Heavy Industries, Ltd. (Japan) signed a license with the company Gulf Petrochemical Industries (Bahrain) on the construction of installations for separation of CO₂ from the waste gases of petrochemical enterprises with daily capacity of 450 tons [65].

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