Experimental Modelling of Hydrocarbon Migration Processes

E D Mukhina¹,², A Yu Kolesnikov¹, A Yu Serovauskii¹,² and V G Kutcherov¹,²
¹ Gubkin Russian State University of Oil and Gas, Moscow 119991, Russia
² KTH Royal Institute of Technology, Stockholm SE-100 44, Sweden

E-mail: mukhina.e@gubkin.ru

Abstract. One of the most important questions in the frame of the concept of deep abiogenic origin of hydrocarbons is how hydrocarbons generated under the upper mantle conditions could migrate upward to the Earth’s crust to form hydrocarbon deposits. Two different ways of fluid migration were proposed and simulated – slow migration during hundreds of years and fast migration – eruption. Influence of the fluid’s migration speed on the final hydrocarbon mixture composition was studied. The received results show that the relative chemical composition of the hydrocarbon mixtures probably does not depend on the cooling conditions (the speed of the fluid migration).

1. Introduction

Our knowledge about the behavior of hydrocarbons under extreme thermobaric conditions is very limited. This knowledge is important for a wide range of topics that include the Earth’s global carbon cycle, the origin of life and global size, location and distribution of hydrocarbon reserves.

According to the concept of deep abiogenic origin of hydrocarbons, complex hydrocarbon mixtures can be generated from inorganic substances under thermobaric conditions corresponding to the conditions of the deep Earth’s layers. Several experimental works were devoted to this process [1]–[7]. The experiments confirming the possibility of the formation of hydrocarbon mixtures with composition similar to natural gas was published in [8].

This work continues series of authors’ research devoted to the origin and phase behavior of hydrocarbons under extreme thermobaric conditions.

One of the most important questions in the frame of the above-mentioned research is how hydrocarbons generated under the upper mantle conditions could migrate upward to the Earth’s crust to form hydrocarbon deposits.

It is proposed, that the process of hydrocarbon fluid’s migration from the upper mantle may occur in two different ways. The way of slow ascent lasts for thousands of years; during eruption it may proceed in hours (figure 1). Different speed of the fluid depends on geological setting between the zone of hydrocarbon generation and reservoir rock in the crust – crystalline, volcanic, sedimentary – where hydrocarbons can be accumulated. We assume that rocks overlying generation zone occasionally can carry large deep faults. These deep faults can be caused by meteorite impact or seismic activity, such as shift of tectonic plates. In case of their presence upward migration should be fast, along with eruption processes. The author of [9] gives examples of magma ascent rates up to 0.04 m/s, that is relatively fast in geological timescale. Considering hydrocarbon fluid as more pervasive than melts, the speed should be even higher.
In some geological areas such as the middle of thick tectonic plates, it is possible to expect absence of the deep faults. In this case rocks surrounding the generation zone that bear fractures, fissures or pores will have to transmit the substances. Hydrocarbon fluid is presumably able to seep through any kind of rock defect. The fluid’s speed in this case will be low and much more time will be necessary to migrate through tight fractures compared to deep faults.

During the process of migration variety of factors are changing around the fluid. These factors are pressure, temperature, chemical composition of surroundings. All these factors can affect the final hydrocarbon mixture, causing its phase and chemical transformations.

We attempted to simulate the migration process by changing the most important parameters: the duration of thermobaric exposition and the cooling rate.

![Figure 1. Two possible ways of the of hydrocarbon fluid migration.](image)

2. Equipment and Methods

2.1. Method of high pressure and high temperature experiment with large volume

The large volume high pressure apparatus “URS-2” with “Toroid” type chamber and resistive heating was chosen to perform simulation of both generation of hydrocarbons and migration processes. The working volume of used metallic capsules (figure 2) is ~0.8 cm³. Such volume was enough to observe the difference in gas composition between experiments recognizable by means of gas chromatography. The other important advantage of large volume technique is control the amount of initial components.

![Figure 2. (a) Scheme of filled capsule inside Toroid chamber of “URS-2”: 1 - graphite heaters, 2 - foil, 3 - thick paper, 4 - standard substance, 5 - filled capsule, 6 - hard alloy base, 7 - matrices-anvils, (b) photo of the Toroid chamber with a capsule inside covered by a graphite heater.](image)

Initial inorganic substances – calcium carbonate, water and iron oxide (II) – were weighted and mixed using a mortar and placed into the metallic capsule in the exactly same relative amount for every
experiment. The closed capsule filled with initial mixture was placed inside the Toroid chamber and covered by graphite heaters from both sides.

In calibration experiments the reference substance (Bi, PbTe, PbSe for pressure; Ni, Al, Sn, Pb for temperature) was placed between one heater and the capsule, covered by aluminum foil. Reference substance changed its structure during increasing pressure or temperature and corresponded resistivity jump was detected by “URS-2” device control system.

After certain exposure at chosen pressure and temperature sample was cooled and hydrocarbon gases were analyzed by gas chromatography.

2.2. Gas chromatography analysis
The gas chromatograph injecting system was modified by adding the specially constructed device where an experimental capsule was opened in the helium atmosphere and gas products from the capsule were transferred directly to the gas chromatograph.

The gas extracting cell (figure 3) consists of the body (1) with a recess and connection to the gas chromatograph, and the cap with a screw-needle (2) inside, that can move up and down, penetrating the capsule (3). After the capsule was inside the cell, the cell was closed and the air from inside of the cell was blown away with the flow of carrier gas (He). Then, the needle penetrated into the capsule and the gas products were immediately released (4) from the capsule. The sealing rubber ring (5) between the body of the cell and the cap didn’t allow the gas to escape from the cell. After some time the gas spread throughout the cell and was taken to the gas chromatograph (7) with the flow of carrier gas (He).

![Figure 3. The gas-extracting cell outside (a) and inside (b) 1 – body of the cell, 2 – moving up and down screw-needle, 3 – capsule, 4 – hydrocarbon gas spread inside the cell, 5 – sealing rubber ring, 6 – solid product, 7 – contact with a chromatograph.](image)

The described way of gas extracting decreases the possibility of losing some of gas compounds, and gives an opportunity to make the most reliable analysis.

3. Experiments
The main idea of the experiments was to simulate the hydrocarbon formation process and to change the experimental conditions in the one of three ways. Quenching gave us information about a “fresh-generated” hydrocarbon system. A long exposure experiment ending with quenching simulated the slow migration processes where thermobaric parameters are almost not changing in the scale of hours. The experiments with the slow cooling to the ambient temperature after certain exposure at chosen PT-parameters fulfilled general picture and modelled eruption migration process. The large volume high pressure device “URS-2” with “Toroid” chambers can perform almost any duration of PT exposition and any rate of cooling.

Five experiments were conducted, each of them was repeated at least three times. In every experiment pressure was 60 kbar and temperature was 900°C, which corresponds to the depth of ~100-150 km according to the cold geotherm [10].

Initial inorganic substances were calcium carbonate as the donor of carbon, water as the donor of hydrogen and iron oxide (II) as the simulator of oxygen fugacity near the wustite-magnetite/FeO2 buffer. Assumed reaction is taken from [8]:

\[ n\text{CaCO}_3 + (9n+3)\text{FeO} + (2n+1)\text{H}_2\text{O} \rightarrow n\text{Ca(OH)}_2 + (3n+1)\text{Fe}_2\text{O}_4 + C_n\text{H}_{2n+2} \]  

(1)

Durations of exposure and cooling are presented in the table 1.
Table 1. Conditions of experiments.

| Initial substances | P, kbar | T, °C | Depth, km | Duration of exposure, s | Duration of cooling, s | Calculated migration rate, m/s |
|--------------------|---------|-------|-----------|------------------------|------------------------|--------------------------------|
| 1                  | 60      | 900   | 100-150   | 300                    | 21600                  | ~ 5.5                          |
| 2                  | 60      | 900   | 100-150   | 300                    | 14400                  | ~ 8.3                          |
| 3                  | CaCO₃ + H₂O + FeO | 60 | 900 | 100-150 | 300 | 2400 | ~ 50 |
| 4                  | 60      | 900   | 100-150   | 300                    | 1                      | -                              |
| 5                  | 60      | 900   | 100-150   | 2400                   | 1                      | -                              |

Experiments no.1 and 2 represent formation of hydrocarbon fluid during 5 minutes and slow migration from generation zone to the surface. Experiment no.3 represents fast fluid migration after 5 minutes formation. Experiments no.4 and 5 represent conditions of the formed fluid after 5 and 40 minutes of exposure respectively, or, in other words, very slow migration of the order of meter per years.

4. Results

Figure 4 shows chromatogram of the gas product from one of iteration of experiment no.2

![Figure 4. Chromatogram of gas product from the experiment no.5 (exposure 40 min, cooling 1 s)](image)

Figure 5. Standard deviation of methane in experiment no.5. Exposure = 40 min, cooling = 1 s

![Figure 5. Standard deviation of methane in experiment no.5](image)

Figure 6. Relative distribution of gas product components (average values) in comparison with experiment no.5 and its standard deviation. E – exposure, C – cooling.

![Figure 6. Relative distribution of gas product components](image)
Figure 6 shows relative distribution of methane in the gas component in the experiments no.1-5. For better perception only first seven members of gas products are presented – methane (CH\(_4\)), ethane (C\(_2\)H\(_6\)), propane (C\(_3\)H\(_8\)), n-butane and i-butane together (C\(_4\)H\(_{10}\)), n-pentane and i-pentane together (C\(_5\)H\(_{12}\)).

The bars on the figure 6 are the standard deviation of methane in five repeated experiments no.5 (figure 5).

5. Conclusions

Hydrocarbon-forming reactions from inorganic substances under the conditions corresponding to the conditions of the Earth’s asthenosphere were investigated. Composition of synthesized complex hydrocarbon mixture was similar to natural gas. To model different types of upward fluid migration we proposed several high pressure experimental procedures. Cooling during 40 minutes represented fast fluid migration, cooling during 4 and 6 hours represented slower migration and quenching represented no migration – fluid as it was formed.

The experimental results showed that the relative chemical composition of the generated hydrocarbon mixture did not depend on the cooling conditions. According to the suggested model these results mean that mantle generated natural gas does not change its composition during its upward migration to the Earth’s crust to form hydrocarbon deposits.

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