

Article

Stability of a Petroleum-Like Hydrocarbon Mixture at Thermobaric Conditions That Correspond to Depths of 50 km

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Abstract: The commercial discovery of giant crude oil deposits at depths deeper than 10 km in various petroleum basins worldwide casts doubt on the validity of the theoretical calculations that have determined that the main zone of petroleum formation is at depths of 6–8 km (the ‘oil window’). However, the behavior of complex hydrocarbon systems at thermobaric conditions, which correspond to depths below 6–8 km, is poorly known. We experimentally investigated the thermal stability of a complex hydrocarbon system at the pressure-temperature conditions of Earth’s lower crust by means of Raman and Mössbauer spectroscopies. Our results demonstrated the chemical stability of the complex hydrocarbon system at thermobaric conditions corresponding to depths of 50 km, including the redox stability of the hydrocarbon system in a highly oxidative environment. The results of these experiments allowed us to revise the depth range in which petroleum deposits could occur.

Keywords: petroleum; the Earth’s crust; ultra-deep deposits; hydrocarbons; high pressure; high temperature; diamond anvil cells

1. Introduction

During the last several decades, giant ultra-deep petroleum deposits were discovered at depths deeper than 10 km in various petroleum basins worldwide [1–3]. These deposits are located below the main zone of the petroleum formation, which is traditionally called the ‘oil window’ and generally occurred at a depth of 6–8 km [4–6]. Numerous efforts have been devoted to study the thermal evolution of organic compounds and petroleum, particularly in Earth’s crust. Until the early 1990s, most studies concluded that only the deposits of natural gas could be found at depths with temperatures higher than 170–180 °C. These conclusions were based on the theoretical approach developed by Tissot and Espitalié [7]. Commercial discovery of gas condensate deposits with temperatures about 200 °C (for example, the Elgin and Franklin fields, located in the Central Graben area of the North Sea Basin) [8,9] casts doubt on the validity of the above-mentioned theoretical calculations.

In theoretical modeling [10], a high-pressure factor is taken into consideration, and it has been shown that crude oil could be stable at temperature up to 240–260 °C, and the thermal cracking of crude oil into gas is not possible under reasonable basin conditions.

The results of an experimental study of the thermal stability and decomposition of individual hydrocarbons at temperatures up to 450 °C are presented in the literature [11–13]. In another study, experiments have been conducted under a pressure of 70 MPa at temperatures up to 330 °C [14]. One of the main conclusions from the above-mentioned experimental results could be summarized as follows:

the thermal stability of individual hydrocarbons differs greatly from that of the same hydrocarbons in a mixture.

In our study, we investigated the thermal stability of a model petroleum system under pressures of 0.7–1.4 GPa and temperatures of 320–450 °C. These thermobaric conditions corresponded to a depth of 20–50 km. Moreover, we investigated the possible influence of oxidized surroundings of the low crust on the stability of hydrocarbons. It seemed to be relevant in modeling deep conditions [15]. This work provided a detailed description of the experimental procedure and results that confirmed the thermal stability of complex hydrocarbon systems to depths of 50 km.

2. Materials and Methods

2.1. Experimental Setup

Symmetric BX90-type DACs (diamond anvil cells) with culets of diameter 250 µm were used in all experiments. As the sample chamber, a pre-indented steel gasket (thickness of 250 µm) with a hole (diameter of 125 µm), drilled in it, was prepared. The hole was filled with the synthetic hydrocarbon mixture, and the Sm:YAG and ruby chips were placed inside the cell. The liquid hydrocarbon mixture also served as a pressure medium. Pressure and temperature were measured by the Sm:YAG and ruby wavelength shifts [16,17] using Raman spectroscopy (He–Ne laser wavelength of 514.5 nm and power from 0.001–0.6 W). For additional temperature control, a Pt/Pt–Rh (10%) thermocouple was used in the DAC (the thermocouple touched the side of the diamond and the gasket for efficient heat exchange (Supplemental Materials, Figure S1)).

A Pt heater was mounted inside the cell with a thermostable glue that also served as isolation for the Pt wire and the thermocouple. The temperature was increased at the speed of 50–60 °C/h, according to the thermocouple data. Several times, per hour, the temperature and pressure inside the sample were measured by the Raman wavelength shift. The pressure was kept constant inside the sample by using the DAC screws to correct it. When the required temperature was reached, it was held during the exposure time (the pressure and temperature inside the sample were checked 2–3 times per hour during the exposure). The exposure time was varied from 3 to 12 h. Then, the heating stopped, and the sample was quenched (the pressure inside the cell was controlled and kept constant). The sample in the DAC was analyzed under pressure using Raman spectroscopy before the sample was heated and after the sample was cooled.

In the second set of experiments, a powder of Fe₂O₃ was added to the sample chamber. The DAC design was the same as the earlier experiments, except a rhenium gasket (thickness of 250 µm) was used in this experiment for Mössbauer spectroscopy. A conventional Mössbauer spectroscope with a ⁵⁷Co point source was employed at the Bayerisches Geoinstitut, University of Bayreuth (BGI), as a diagnostic method for detecting new iron compounds after heating. Mössbauer spectra of the sample were collected before heating and after cooling, at the same pressure. Raman spectroscopy was not used for hydrocarbon analysis in these series of experiments because Fe₂O₃ significantly absorbed the Raman laser radiation, and the hydrocarbon peaks were not visible.

A flow chart presenting the complete sample handling is described in Supplemental Materials, Figure S3.

2.2. Materials

A sample of natural Astrakhan petroleum from the Korchaginskoe deposit (see Supplementary Materials, Table S1 for more details) and an artificially synthesized hydrocarbon mixture (Supplemental Materials, Figure S2, Table S2) were used in the experiments. The composition of the hydrocarbon mixture was obtained by treating the gas chromatogram of the hydrocarbon system. The volume concentration of each individual component was calculated by the proportion of an area under the corresponded peak to the total area under all peaks of the chromatogram.

In the second set of experiments, powdered ⁵⁷Fe-enriched Fe₂O₃ was loaded in the sample chamber.

3. Results

3.1. Thermal Stability of the Hydrocarbon System

Experiments were conducted in diamond anvil cells (DAC) with resistive heating and in-situ Raman spectroscopy analysis (see Methods section for more details). The use of natural petroleum as the main source of the experimental sample was an issue due to the high luminescence in the Raman spectra (Figure 1a), which was caused by the presence of resinous-asphaltenic compounds in natural crude oil. Therefore, the artificially synthesized hydrocarbon mixture, similar to natural gas-condensate, with a known quantitative and qualitative composition, was used in the experiments. This synthetic hydrocarbon system had clear Raman spectra without luminescence (Figure 1b).

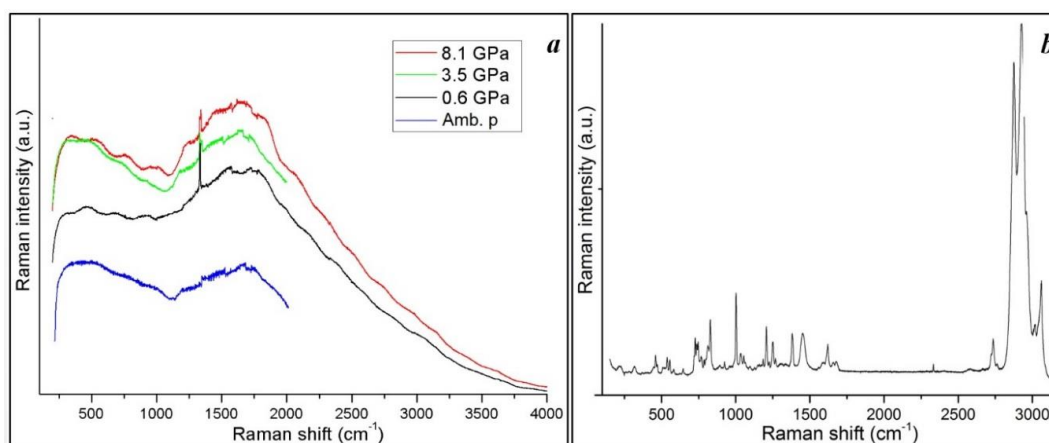


Figure 1. Raman spectra of the Astrakhan crude oil at ambient temperature and a pressure range of 0–8.1 GPa (a), and the synthetic hydrocarbon mixture at ambient temperature and pressure (b).

To investigate the thermal stability of the model hydrocarbon system, three series of experiments were carried out at temperatures of 320–450 °C and pressures of 0.7–1.4 GPa at various exposure times (Table 1).

Table 1. Conditions of the experiments with the synthetic hydrocarbon mixture.

Experiment	Sample	Pressure (GPa)	Temperature (°C)	Corresponding Depth (km)	Exposure Time (h)
1	Synthetic hydrocarbon mixture	0.7	320	20–30	3
2	Synthetic hydrocarbon mixture	1.2	420	30–40	3
3	Synthetic hydrocarbon mixture	1.4	450	40–50	12
4	Synthetic hydrocarbon mixture + Fe ₂ O ₃	1.4	450	40–50	12

The results of the experiments showed that the hydrocarbon mixture was thermally stable at these thermobaric conditions. The Raman spectra of synthetic petroleum, before and after heating, are presented in Figure 2. The composition of the hydrocarbon mixture did not change in all three series of experiments. All representative peaks of the hydrocarbons on the spectra kept their shape, Raman shift, and intensity; no new peaks appeared after heating. Increasing the exposure time of the heating four times (from 3 to 12 h) in the third series did not influence the composition of synthetic petroleum.

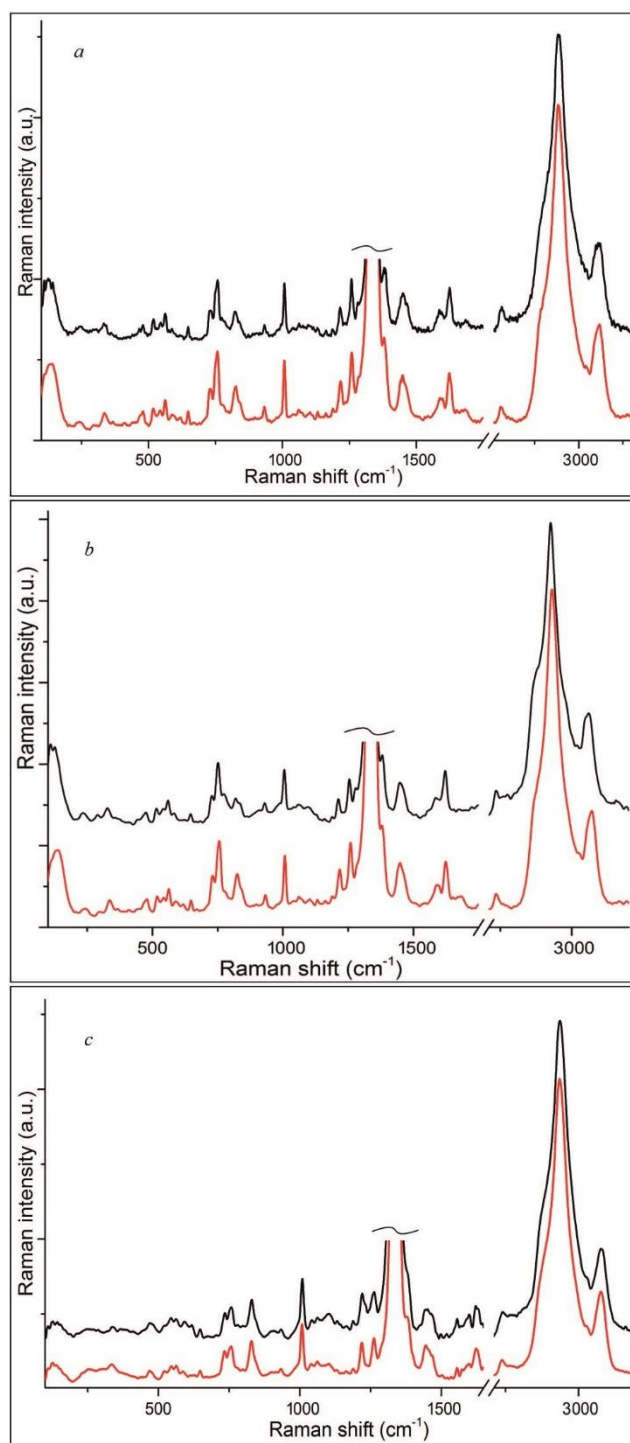


Figure 2. Raman spectra of the synthetic hydrocarbon mixture before heating (the red curve) and after heating (the black curve): (a) at a pressure of 0.7 GPa and heating at 320 °C for 3 h, (b) at a pressure of 1.2 GPa and heating at 420 °C for 3 h, (c) at a pressure of 1.4 GPa and heating at 450 °C for 12 h.

3.2. The Oxidation Resistance of the Hydrocarbon System at the Thermobaric Conditions of Earth's Crust

The next step of the research was to investigate the oxidation resistance of petroleum at the thermobaric conditions of Earth's crust and its possibility to react with the solid oxidative environment. Iron is the abundant element in Earth's crust with variable valence states, and its compounds are considered to control the oxygen fugacity in Earth's interior [15]. In this study, Fe_2O_3 was used as a potential component of the crust with the strongest oxidizing properties [18]. In this compound,

iron has the maximum oxidation degree and could behave as an oxidizer at high temperatures in the presence of a reducing agent (such as hydrocarbons, graphite, and molecular hydrogen).

A finely ground powder of Fe_2O_3 (99% reached ^{57}Fe) was loaded into the DAC with the synthetic petroleum. The sample was pressurized to 1.4 GPa, and the Mössbauer spectra of the sample were registered at ambient temperature, both before and after the 12 hours of heating at 450 °C (Figure 3). There was no change in the Mössbauer parameters for the sample before and after the heating experiments. No new iron compounds appeared in the sample; therefore, the iron oxide did not take part in any chemical reaction with the hydrocarbons during the 12 h of heating.

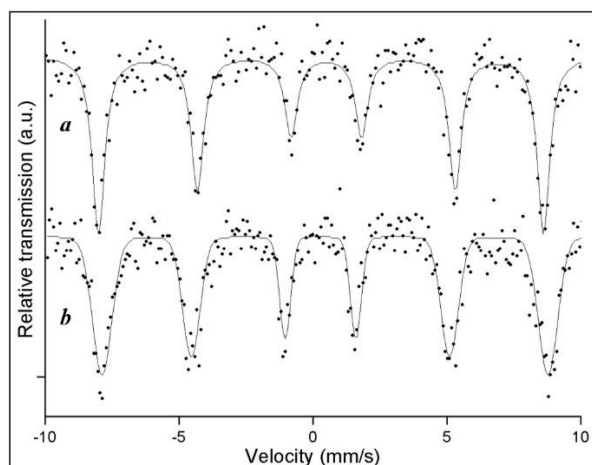


Figure 3. The Mössbauer spectra of the Fe_2O_3 and synthetic hydrocarbon mixture at 1.4 GPa and ambient temperature before (a) and after 12 h of heating at 450 °C (b).

4. Discussion

The experimental results demonstrated that the synthesized hydrocarbon mixture remained its qualitative and quantitative composition at temperatures of 320–450 °C and pressures 0.7–1.4 GPa, similar to the thermobaric conditions of Earth’s crust to depths of 50 km. The hydrocarbon mixture composition was similar to gas condensate (Figure 4) and was not transformed into natural gas, as it was declared by Tissot and Welte [4] and Barker [19]. Given that the minerals of Earth’s crust are in solid form, the oxidizing resistance of hydrocarbons was tested in the modeled solid environment of Earth’s crust. Fe_2O_3 was chosen as the hypothetical Earth’s crust component with the highest possible oxidizing properties [20]. The hydrocarbon stability in the presence of Fe_2O_3 at the thermobaric conditions of the low crust was demonstrated in our experiments (during the experimental exposure time). We did not assert the equilibrium in our sample after the 12 h of heating; however, it is expected that in natural conditions of Earth’s crust, where the oxygen fugacity is lower, the petroleum will be oxidation-resistant to stay in the stable or metastable condition during even much longer period of time.

The experiments carried out by Dominé et al. [10] demonstrate that significant changes in the composition of the hydrocarbon system during thermal cracking occur in the first 20 h of experiments that last for 1000 h. In the first series of experiments in this study, the hydrocarbon mixture did not change in composition at 320 °C and 0.7 GPa over the 3 h of heating. In the next series of experiments, the exposure time was four times longer, 12 h; however, the composition of the sample did not change at the even more intense thermobaric conditions. Therefore, our experimental results could be extrapolated for a much longer period of heating (months or even years).

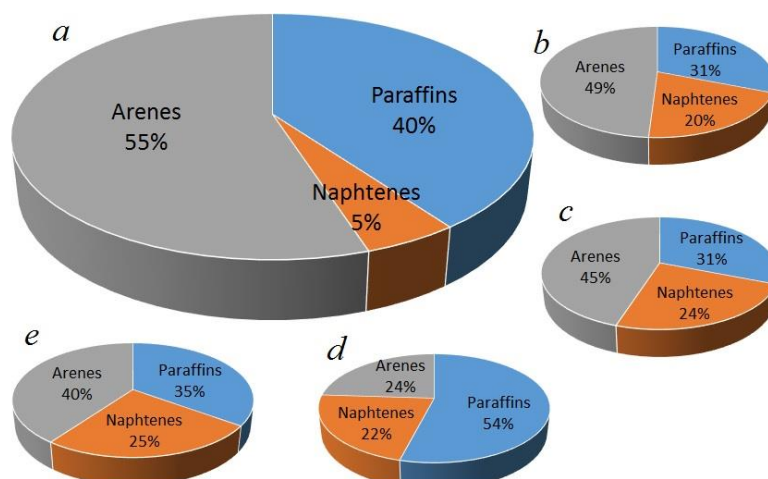


Figure 4. Fraction composition of model petroleum, compared to natural gas-condensates: (a) model petroleum ($\rho_{20}^4 = 794.7 \text{ kg/m}^3$), (b) Ust-Labinsk gas-condensate ($\rho_{20}^4 = 826.1 \text{ kg/m}^3$) [21], (c) Berezansk deposit ($\rho_{20}^4 = 764.8 \text{ kg/m}^3$) [21], (d) Krasnodar deposit ($\rho_{20}^4 = 774.0 \text{ kg/m}^3$) [22], (e) Yamburg deposit ($\rho_{20}^4 = 792.8 \text{ kg/m}^3$) [22].

Modeling real natural pressure of the depth seems to be crucial for the stability of hydrocarbons at extreme thermobaric conditions. The investigations of the water-petroleum fluid interaction behavior at high thermobaric conditions, carried out by Balitsky et al. [23] and Balitsky et al. [24], demonstrate the starting point of the hydrocarbon cracking process at 600 K and at pressures of 30–150 MPa, which (pressure) is significantly lower than corresponding to the experimental temperatures, according to geotherms [25,26]. Moreover, the local geothermal gradient of 15 to 40 degrees over 1 km [23] seems to be an overestimation, and the temperature range of 350–400 °C should correspond to much deeper depths than the range of 10–12 km.

The data obtained not only experimentally modeled the natural deep hydrocarbon deposits at depths of 11–12 km but also presumed the possible occurrence of petroleum as deep as the crust-mantle boundary. The evidence of the existence of petroleum in such deep zones of Earth's crust may be further proof of the abiogenic abyssal petroleum generation theory [1], in which there is no organic source material for the biogenic petroleum formation at these depths, and the only source for these deep petroleum deposits is the hydrocarbon fluid from mantle [27].

In addition, the results of this investigation might have practical applications. The data obtained would broaden the knowledge of the existing range of depths for petroleum fields in Earth's crust. Deep hydrocarbon deposits seemed to be more commercially attractive due to higher reservoir pressure. Therefore, proof of deep petroleum deposits might become a strong rationale for the prospecting of petroleum accumulations in deeper zones and developing drilling and exploration technologies for deep petroleum production.

Future experiments at higher thermobaric conditions, corresponding to deeper depths (down to the upper mantle), will allow to investigate the thermobaric limit for the hydrocarbons stability and mechanisms of possible hydrocarbons transformations. Such investigations seem to be prospective in light of the results of this paper and experiments of hydrocarbons formation from inorganic sources at upper mantle thermobaric conditions [28,29]. Moreover, the investigation of the mechanical stability of hydrocarbon systems inside the reservoir rock with taking into consideration geomechanics effects at extreme thermobaric conditions will provide a better understanding of hydrocarbon systems behavior in natural conditions [30].

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/4/355/s1>, Figure S1: Pt-Pt/Rh thermocouple, touching the surface of the diamond, Figure S2: Chromatogram of the synthetic hydrocarbon system, Figure S3: Summary of the completed experimental procedure, Table S1: Characteristics

of the crude oil from the Korchaginskoe deposit (Astrakhan region), Table S2: Composition of the synthetic hydrocarbon system.

Author Contributions: V.K. designed the study. L.D. and A.S. designed the experiments. A.S. carried out the experiments and analyzed the data. A.S. and V.K. wrote the manuscript, with substantial contributions made by L.D. All authors discussed the results and implications and commented on the manuscript. All authors have read and agreed to the published version of the manuscript.

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