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Influence of Biodegradation Processes on the Relative Distribution of Normal and Isoalkanes in Oil

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Abstract. The article presents research and describes the mechanism of aerobic biodegradation of oils of various origins. The influence of degradation processes on the relative distribution of normal alkanes and isoprenoids is considered. When drawing conclusions about the type of source substance, sedimentation conditions, and maturity parameters based on biomarker correlations, it is essential to exclude the presence of biodegradation, or take into account its influence in relation to the objects under study. The practical significance of the research lies in the fact that the selectivity of oil biodegradation in terms of various effects on the ratio of isobutane/n-butane can be used to clarify the remaining reserves of oil fields.

1. Introduction

Biodegradation of oil is the destruction of its components due to the impact of living organisms. This process negatively affects oil properties, thereby increasing the cost of its extraction and refining [1-3]. In this regard, the study of biodegradation processes, namely, the establishment of the mechanism of its behavior and the assessment of the influence of microorganisms on the oil composition is an urgent task at present.

The influence of oil biodegradation processes on its physical properties and composition has been known for a long time. Aerobic bacteria use molecular oxygen; hence the presence of infiltrated groundwater is indispensable for the aerobic biodegradation processes. Usually, biodegradation of oil is also accompanied by water leaching of light methane-naphthenic and aromatic hydrocarbons. However, this leaching does not significantly affect the chemical and physical properties of the oil. Biodegradation processes primarily affect hydrocarbons, so biodegraded oil is usually enriched with nitrogen-, sulfur-, and oxygen-containing components (NSO compounds) [4-6]. In addition, biodegraded oil has higher values of density, viscosity, increased content of resins, asphaltenes, metals (Nickel, vanadium, etc.), compared to non-biodegraded oils.

However, biodegradation is a quasi-sequential process. This means that the individual components of the oil are decomposed only after the removal of the other. There are various types of biodegradation scales for oils, but in this paper, we consider the influence of the degree of branching of molecules on the bacteria activity rate.

2. Experimental

The object of research is the samples of oils with various degrees of transformation. Chromatography and mass spectrometry studies were performed on a gas chromatograph "Chromatech-Crystal 5000"

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with a mass-selective ISQ detector. The Xcalibur software have been used for processing the results. The chromatograph is fitted with a capillary column, 30 m long, with a diameter of 0.25 mm. The speed of the flow of carrier gas (helium) — 1 ml/min. The injection temperature is 310 °C. The temperature program of the thermostat is a rise from 100 to 150 °C at a speed of 3 °C/min, from 150 to 300 °C at a speed of 12 °C/min followed by its isotherm to the end of the analysis. Electron energy — 70 eV, temperature of ion source — 250 °C.

3. Results and discussion

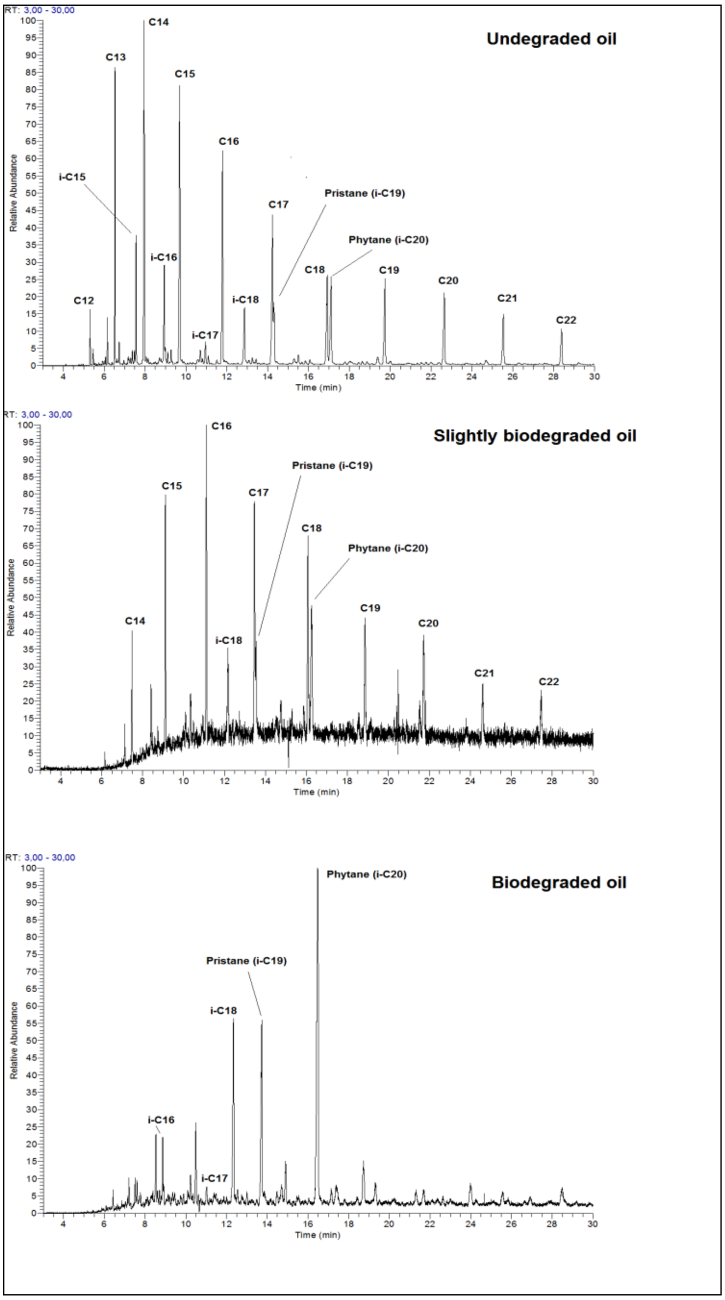

Figure 1. GCMS chromatograms for alkanes and isoalkanes (m/z = 57+71+85) of Romashkino field, Russia (top), Boca de Jaruco, Cuba (middle) and Nizhne-Karmalsky field (bottom), Russia.

The chromatograms formed by the selective ion monitoring (SIM) for untransformed oil of Romashkino field (Russia), extra-viscous oil of Nizhne-Karmalsky field (Russia) and oil field of Boca de Jaruco (Cuba) are shown at Figure 1. As can be seen from the chromatograms, untransformed oil contains a large number of normal alkanes that predominate over isoprenoids. Cuban oil probably underwent partial biodegradation, which resulted in a decrease in the concentration of n-alkanes compared to isoprenoid structures. The ultra-viscous oil of the Nizhne-Karmalsky field methane generation, which lies at a depth of 150-200 meters, was further affected by biodegradation processes, which led to the almost complete removal of n-alkanes. At the same time, isoprenoid compounds such as pristane and phytane were preserved in the converted Nizhne-Karmalsky field oil.

The above-described selectivity of biodegradation processes is due to the mechanisms of destruction of molecules. As it is well-known, there are two fundamentally different ways of biodegradation – aerobic and anaerobic [7-10]. Aerobic biodegradation is distinctive in oil fields, since water, which is always present in oil deposits, contains dissolved oxygen which is the main oxidizer. Aerobic biodegradation proceeds in several stages (Figure 2) [11].

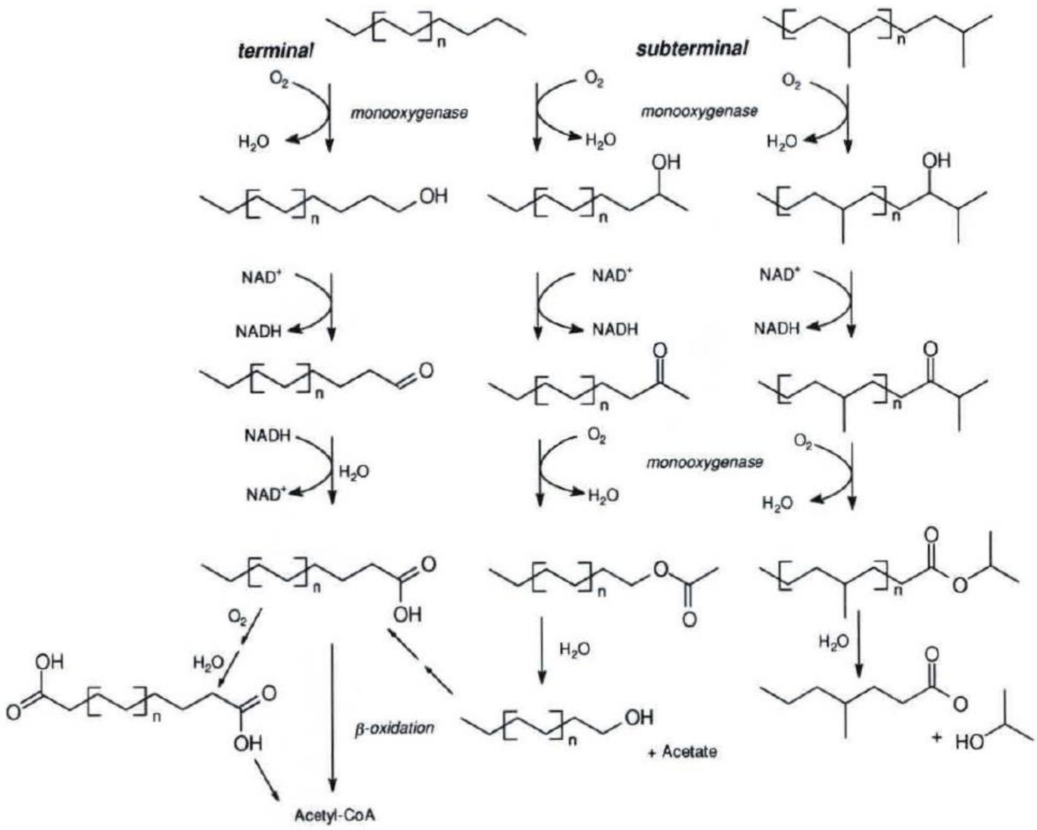

Figure 2. Aerobic degradation mechanism of normal and branched alkanes. Acetyl-CoA – acetyl co-enzyme A, NAD – nicotinamide adenine dinucleotide.

At first stage, molecular oxygen forms a hydroxyl group at the last next-to-last carbon atom, and the catalyst for this process is monooxygenase. When a hydroxyl group is formed at the last carbon atom, this mechanism is called terminal, while for the or next-to-last one it is called subterminal. The derived alcohol, under the influence of the coenzyme nicotinamide adenine dinucleotide, is further converted into aldehydes or ketones, depending on the mechanism. Then the formed carbonyl groups, in turn, are oxidized to carboxyl and ester groups. As can be seen from the presented scheme, normal alkanes can be oxidized both by terminal and subterminal processes, while isoprenoid ones can only be oxidized subterminaly. Thus, the greater the degree of branching in the hydrocarbon molecule, the lower the rate of its biological destruction. This is the main reason for the selectivity of biodegradation processes occurring in oil reservoirs.

The selectivity of biodegradation significantly affects the geological and geochemical interpretation of the conditions for the formation of oils and the rock organic matter. When making conclusions about the source type, sedimentation conditions, and maturity parameters based on biomarker correlations, it is necessary to exclude the presence of biodegradation, or take into account its influence in relation to the studied objects.

At the same time, the selectivity of oil biodegradation may also have practical importance. For instance, it can be used to locate residual oil reserves in fields that have entered the late stage of development. The essence of this method is to monitor changes in the ratio "isobutane/butane". In the primary oil, prior to the development, this ratio is generally less than 0.2, but during the development process, as a rule, it is increased. For example, at the Romashkino field, the average ratio has increased from 0.3 in 1980 to 0.5 by 2000 [12]. This trend is conditioned by intensive biodegradation of hydrocarbons.

However, it is worth noting that in the unrecovered part of the field, this ratio remains at the initial level, forming an inhomogeneous distribution of this parameter. Light components can periodically emit from the bypassed oil area under the influence of seismic activity, causing negative anomalies at the nearest producing wells. By registering these anomalies, it is possible to evaluate both the presence of the bypassed oil area and its estimated size. This method allows not only to identify residual reserves, but also to monitor the completeness of their production by the same parameters of the isobutane/butane ratio.

4. Conclusion

Studies have shown that the ratio of normal and isoprenoid alkanes in different oils may differ significantly. This process can be explained by the selectivity of aerobic biodegradation processes occurring in oil reservoirs. This effect of biodegradation selectivity on the composition of oil can be used to increase the efficiency of oil field development.

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