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Hydrocarbon composition and structural parameters of resins and asphaltenes of naphthenic oils of northern West Siberia

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Abstract

The composition of saturated and aromatic hydrocarbons and the structural-group characteristics of resins and asphaltenes in four oils of northern West Siberia have been studied. As follows from the distribution of hydrocarbons, the Cenomanian oils (pools in the beds PK and K_2c) of the Russkoe, Barsukovskoe, and Pangodinskoe fields are naphthenic and the Pangodinskoe oil sample from the Lower Cretaceous pool (bed BN_9) is methanoic. The hydrocarbon composition pattern of the saturated fraction and the characteristics of the heterocyclic components of these oils point to their formation from dispersed organic matter of mixed genesis in the oil window. Hence, the oil source rocks are localized at depths much greater than the present-day level of the oil pools. Secondary (cryptohypergene) alterations (oxidation and biodegradation) in the shallow-depth oils determined their current predominantly naphthenic composition and considerably hamper reconstruction of the types of initial dispersed organic matter. We assume that the mixed genetic type of the studied oils is not only due to their heterogeneous source but also due to the reorganization of primary oil pools at the Cenozoic stage of tectogenesis. The Cenomanian Russkoe and Pangodinskoe naphthenic oils are saturated with adamantoids, which can be selectively accumulated during biodegradation.
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Introduction

In northern West Siberia, there are Aptian–Albian–Cenomanian rich fields of heavy highly viscous oils (Russkoe, Barsukovskoe, Komsomol'skoe, Severo-Komsomol'skoe, Van-Eganskoe, Pangodinskoe, Srednemessoyakhskoe, etc.) (Kontorovich et al., 1975, 1994), the extraction and refining of which are steadily gaining interest.

Genesis of heavy highly viscous oils causes debates. Dobryanskii (1948), referring to Höfer's scientific works on the predominantly naphthenic composition of Eocene and younger oils, believed that the generation of oil started with maltha, or, more exactly, with aromatic and naphthenic hydrocarbons (HCs) grading into methane oil with depth. The current state of the theory of petroleum genesis in sedimentary basins as open self-organizing systems is described by Kontorovich (2004). As for the genesis of the Aptian–Albian–Cenomanian oils of northern West Siberia, their specific composition was earlier explained by the influence of migration processes (Galishev et al., 1984; Gurko and Galishev, 1981; Stasova, 1977) or by their formation at the early stages of oil generation process (Kontorovich and Rastegin, 1976; Kontorovich et al., 1975). Later research based on analysis of the distribution of typical HC biomarker groups (low contents or absence of *n*-alkanes, isoalkanes, and acyclic isoprenanes, demethylation of hopanes, etc.) showed that naphthenic oils are usually genetically different HC fluids of "normal" maturity modified during microbial oxidation (Fursenko and Borisova, 2006; Goncharov, 1987; Kashirtsev et al., 2013; Petrov, 1984).

There is no doubt that a comprehensive analysis of the composition and properties of oils, including the information about the distribution of HCs of different classes: saturated (aliphatic and cyclic), naphthene-aromatic, and alkyl-substi-

tuted aromatic, and the structural characteristics of high-molecular resin-asphaltene components, is the basis for reconstruction of the conditions of formation of HC pools. Genesis of oils is elucidated from their various HC composition characteristics. The diversity of saturated polycyclic and naphthene-aromatic oil HCs is due to the conversion of biologic steroid and terpenoid structures of the initial organic matter (OM) during diagenesis and catagenesis through decarboxylation, disproportionation, dealkylation, and aromatization (Peters et al., 2007; Petrov, 1984; Pevneva et al., 2010). Aromatic HCs are indicators of not only the initial oil source OM but also (and mostly) of thermodynamic and chemical processes of its transformation (Golovko et al., 2014; Radke et al., 1986; Shimoyama et al., 2000; Sivan et al., 2008). In contrast to aliphatic HCs, saturated polycyclic and naphthene-aromatic HCs are more resistant to biodegradation and other transformations of oils in the pool, i.e., preserve genetic features inherited from the initial OM and products of its transformation for a much longer time (Peters et al., 2007; Petrov, 1984; Tissot and Welte, 1978). Special attention should be focused on resins and asphaltenes: These are heteroorganic compounds of extremely complex composition and structure, worst studied among all oil components. Borisova (2009), Borisova and Kontorovich (2010), and Golovko et al. (2012) showed that the structural-group characteristics of resins and asphaltenes, like HC biomarkers, inherit the genetic nature of the initial OM and depend on the conditions of its fossilization.

The goal of this work was to enucleate the features of the HC composition and structural-group characteristics of resin-asphaltene components of naphthenic oils and elucidate the oil genesis on their basis.

Objects of study

The objects of our study were oils of the Russkoe oil and gas (Pur–Taz petroliferous area), Barsukovskoe oil and gas condensate, and Pangodinskoe gas condensate (both are in the Nadym–Pur petroliferous area) fields in northern West Siberia. The fields occur in local like-named structures. They are of complex geologic structure and consist of several oil pools; their HC fluids are accumulated in terrigenous reservoirs (Barsukovskoe..., 2008; Pangodinskoe..., 2006; Russkoe..., 2005). The formation temperatures of shallow-depth oil pools in Cenomanian deposits (Russkoe (871–898 m), Barsukovskoe (1821–1829 m), and Pangodinskoe (1275–1277 m) fields) are not higher than 60 ℃; a considerable area of these pools makes contact with formation waters. The deeper-seated oil pool of the Pangodinskoe field (2786–2789 m, bed BN_9, Megion Formation) has a temperature of 91 ℃.

Analysis of the oils implied elucidation of their physicochemical parameters and group and HC compositions. The density, viscosity, and fraction composition of the oils were determined by the All-Union State Standard (GOST) techniques.

The structural-group composition of oils and the corresponding fractions (saturated, aromatic, and resins) were determined by elution solid-liquid chromatography with preliminary precipitation of asphaltenes (Bogomolov et al., 1984). The procedure of separation and quantitative determination of asphaltenes included treatment of oil with excess *n*-hexane (1:40 by volume). Chromatographic separation of deasphaltized residue (malthenes) was made using glass columns filled with silica gel and, in the tip, Al_2O_3. As desorbents, we used petroleum ether (for HC fractions) and benzene and alcohol–benzene mixture (1:1) (for resins). The eluate flow rate was 2 ml/s. The accuracy of separation of saturated and aromatic fractions was estimated from the refraction index ($n_D^{20} \leq 1.48$ and $n_D^{20} > 1.48$, respectively).

The group composition of aromatic HCs was also determined by liquid-adsorption column chromatography (Pevneva et al., 2010): The oils were separated into saturated and mono-, di-, and triaromatic HCs. Neutral Al_2O_3 of Brockman activity II was used as an adsorbent. The adsorbent to oil sample ratio was 80:1 by weight. Hexane was used for HC desorption.

Chromatography–mass spectrometry analysis of the composition of the saturated fraction (*n*-alkanes, acyclic isoprenanes, steranes, and terpanes) was performed on a Hewlett Packard 5890 chromatograph combined with an MSD 5972A mass spectrometer with a ChemStation computer system for signal recording and processing. Operation conditions: HP-5 capillary quartz columns, helium as a carrier gas, injector temperature of 320 ℃, source temperature of 250 ℃, and ionizing voltage of 70 eV. The HC fraction was kept at 100 ℃ for 4 min and then was heated to 290 ℃ at a rate of 4 ℃/min and kept at this temperature for 30 min.

The composition of mono-, di-, and triaromatic HCs was determined by chromatography–mass spectrometry analysis of corresponding HC fractions on a GSMS-QP5050 Shimadzu quadruple system equipped with a DB5-MS capillary quartz column. The analysis was performed in the following thermal mode: The temperature was increased from 80 to 290 ℃ at a rate of 2 ℃/min and was kept constant for 25 min. Helium was used as a carrier gas.

Individual HCs were identified from mass fragmentograms *m/z* 57, 71, 183, and 253 for alkanes, *m/z* 69, 83, 109, 123, 177, 191, 217, and 218 for cyclanes, *m/z* 91, 105, 119, and 133 for alkylbenzenes, *m/z* 118, 145, 159, 213, 212, 226, 253, and 365 for naphthene-benzenes, *m/z* 128, 142, 156, 170, and 184 for alkylnaphthalenes, *m/z* 153, 165, 195, 209, and 223 for naphthene-naphthalenes, *m/z* 178, 192, 206, 220, and 234 for alkylphenanthrenes, *m/z* 231, 257, 342, and 356 for naphthene-phenanthrenes, and *m/z* 136, 135, 148, 163, 176, and 188 for adamantanes, using the NIST11, NIST02, and Willey229 mass spectrum databases.

The structural-group analysis of resins and asphaltenes was carried out by the technique elaborated at the Institute of Petroleum Chemistry, Tomsk, which is based on the use of elemental-composition data, average molecular weights, and PMR spectroscopy data (Golovko et al., 2012).