Functional Group Composition of Ingredients of Mongolia Oils

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Abstract

Results of complex research of sweet, tarry, high-wax oils that occur in lower Cretaceous horizons at Zuunbayan, Tsagan-Els, and Tamsagbulag fields (Mongolia) are presented. With the use of results of physicochemical and radiospectrometric analysis, average values of structural parameters have been calculated for hydrocarbons and high molecular weight hetero-organic compounds inherent in oils.

INTRODUCTION

More than half a century ago, commercial reserves of oil have been found in the territory of East and Southeast Mongolia. Geological descriptions and certain geochemical characteristics of oil fields are given in works [1, 2]. Oils that are made here are still not clearly understood chemically: only individual, random samples of Zuunbayan and Tamsagbulag oils became, in effect, subjects of detailed research [3–6]. Employing modern analytical methods, we have thus far investigated oils from 13 various holes that yield production from lower Cretaceous horizons that occur at 1000–1300 m depth at Tsagan-Els and Zuunbayan fields (East Gobi petroliferous province) and in an interval of 2300–2500 m at Tamsagbulag field (Tamsag province). Results of the completed research are summarized in this message.

EXPERIMENTAL

Samples of oils upon their dehydration and clearing from trace amounts of mechanical impurities were separated into basic fractions (oils, resins, and asphaltenes) by strictly unified methods [3, 4, 7, 8] so that discrepancies be avoided that could come about from the reported dependence of yields and composition of high molecular mass heteroatomic compounds (HMMHC) of oil on their extraction conditions [9].

Asphaltenes were precipitated by diluting oil with 40-fold volume of n-hexane. Deasphaltenized oils spread onto ASC silica gel; the mixture was loaded into a Soxhlet apparatus and then we consecutively extracted oils by n-hexane, resins by mixture benzene + ethanol (1 : 1 by volume).

Functional group analysis (FGA) of crude oils and resins that were extracted from them was performed by the procedure that was based on the combined use of insights into the elemental composition, average molecular weights, and data of PMR spectrometry [9]. A content of C and H in the elemental analysis of products was found using traditional methods of burning; concentration of nitrogen was determined by means of Pokrovskii reactor and a content of sulphur, by the double burning method [10]. Molecular mass of substances were measured by cryoscopy in naphthalene with a microcalorimeter “Krion” that has been designed in Institute of Petroleum Chemistry, SB RAS (Tomsk). PMR spectra were written with AVANCE-AV-300 Fourier spectrometer (solvent – deuterochloroform, the internal standard – hexamethyldisiloxane) under conditions that are favourable for suppression of the processes of association and spatial organization of molecules, *i.e.* at elevated temperature (60 °C) and with small (1 mass %) concentrations of HMMHC in the analysed solution, according to recommendations of [11].

This message applies the same notation of structural parameters that were in use previously in works [3, 4, 6, 9]; if necessary, they are additionally explained further in the text.

RESULTS AND DISCUSSION

Insights into general characteristics of oils of Zuunbayan, Tsagan-Els, and Tamsagbulag fields are given in Table 1. It is evident that deeply occurring Tamsagbulag oils contain less quantity of high molecular mass heteroatomic compounds (5–7 mass %) than East Gobi oils (9–12 mass %), and consequently they show smaller density (830–845 *vs.* 860–900 kg/m^3 at 20 °C) and mean molecular mass (270–380 *vs.* 300–460 atomic mass units). All the studied oils are high wax and they contain no less than 11 mass % of solid hydrocarbons. All the studied Mongolian oils are of very low sulphur content (no more than 0.2 mass %); Tamsagbulag oils feature the same low concentration of nitrogen, but it is somewhat higher (0.20–0.45 %) in oils of Zuunbayan field. Mass fraction of asphaltenes in all these oils did not exceed 1 %; therefore, we failed to extract them in quantities large enough for a structural study, and we did not conduct FGA of oil HMMHC of this type.

TABLE 1

Physicochemical and structural characteristics of oils from Tsagan-Els, Zuunbayan, and Tamsagbulag fields

Indices	Tsagan-Els							Zuunbayan	Tamsagbulag				
Hole number	142	1410	A-2	14	147	145	A-1	XIX-3	13	12	14	329	3
Mean occurrence depth, m	1007	1170	1280	1290	1300	1308	1355	1372	2311	2355	2376	2440	2480
Density (20 °C), kg/m^3	862.0	921.2	868.3	887.5	904.1	863.4	882.2	903.5	829.1	827.5	831.2	834.0	845.5
Mean molecular mass	297	459	360	397	428	312	304	371	272	340	381	298	295
Content, mass %:													
Asphaltenes	0.15	1.00	0.56	0.22	0.08	0.46	0.00	0.00	0.10	0.19	0.93	0.73	0.29
Gums	8.70	7.85	9.76	11.67	10.96	10.87	11.47	9.92	7.05	5.00	5.23	4.54	4.68
Oils	91.15	91.15	89.68	88.11	88.96	88.68	88.53	90.08	92.85	94.81	93.84	94.73	95.03
Paraffin	18.1	14.3	19.6	11.1	14.6	16.2	24.2	15.0	16.6	17.8	17.2	16.7	21.0
Elemental composition, mass %:													
C	85.15	85.37	85.89	86.28	85.93	85.79	85.81	86.32	86.33	86.40	85.48	86.47	86.56
H	13.02	12.21	12.28	12.23	12.78	12.81	12.31	13.10	13.43	13.13	13.21	12.88	12.83
N	0.23	0.34	0.27	0.46	0.40	0.16	0.46	0.33	0.18	0.20	0.10	<0.01	0.05
S	0.19	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.05	0.06	0.20	0.12
O	1.76	2.08	1.56	0.93	0.89	1.24	1.42	0.25	0.02	0.38	1.09	0.45	0.44
Distribution of C atoms, %:													
f_a	14.0	19.0	17.9	19.1	14.3	12.7	16.6	16.5	3.7	5.7	6.0	7.7	6.7
f_n	36.4	27.7	26.9	25.1	33.0	33.4	33.2	29.5	46.1	42.2	42.2	47.6	52.4
f_p	49.6	53.3	55.3	55.8	52.7	53.9	50.2	54.0	50.2	52.1	51.8	44.7	40.9
f_p/f_n ratio	1.36	1.92	2.06	2.22	1.60	1.61	1.51	1.83	1.09	1.24	1.23	0.94	0.78
Ring composition:													
K_o	2.04	2.58	2.40	2.69	2.27	1.99	2.31	2.05	2.10	2.59	2.29	2.63	2.77
K_a	0.17	1.13	0.80	0.94	0.53	0.21	0.59	0.15	0.12	0.25	0.29	0.29	0.25
K_n	1.87	1.45	1.70	1.75	1.74	1.78	1.72	1.90	1.98	2.34	2.00	2.34	2.52
Oil base according to [13]	M-N	M-N	M	M	M	M-N	M-N	M-N	M-N	M-N	M-N	N-M	N-M

According to the classification, the described oils should be classed with type A[1] [4] based on their concentration of n-alkanes and isoprenanes [12], and when typified on their proportion of shares of carbon atoms that are inherent in paraffin and naphthenic molecular structures (f_p/f_n) of all ingredients of oil in general, as it is offered in work [13], all East Gobi samples are methane or methane-naphthenic ones. From oils of Tamsagbulag field, the oils that occur at depths up to 2380 m fall into methane-naphthenic type; more embedded horizons show a little domination of naphthenic structures over paraffin ones in their abundance in molecules, and the oil base changes into naphthene-methane.

Having calculated mean gross formulae of oils on evidence of Table 1, one can see that no more than 13 % of molecules in oils of the Tsagan-Els area and as much as 5 mol % in the remaining studied objects are due to nitrogen-bearing compounds; sulphur atoms are present only in 1–2 % of molecules, the mole fraction of oxygen compounds among them, as a rule, falls short of 20 %. When making these estimates, we took into account that molecules of an overwhelming majority of the nitrous and sulphur compounds of oils contain only on one atom N and S, and oxygen-containing substances that are most abundant in oils (carboxylic acids, esters) each include two oxygen atoms [14]. It is obvious that the main ingredients of Mongolian oils are the hydrocarbons (HC) that amount 88–95 % of mass of their lube cuts. It is apparent that the mean magnitudes of the structural parameters that have been found for oils in general should define in satisfactory approximation structural features of molecules of oil HCs.

The received quantitative values have revealed significant distinctions in composition of oils of the two considered petroliferous provinces of Mongolia.

Oils of East Gobi are much richer in aromatic HCs than are oils of Tamsag region. An extent of aromatics f_a of oily components for oils of Tsagan-Els and Zuunbayan fields varies within the limits of 14–19 % whereas it does not exceed 8 % for oily fraction of Tamsag oils. Alicyclic fragments are less developed in HC molecules of East Gobi oils: no more than one third of the total number of carbon atoms

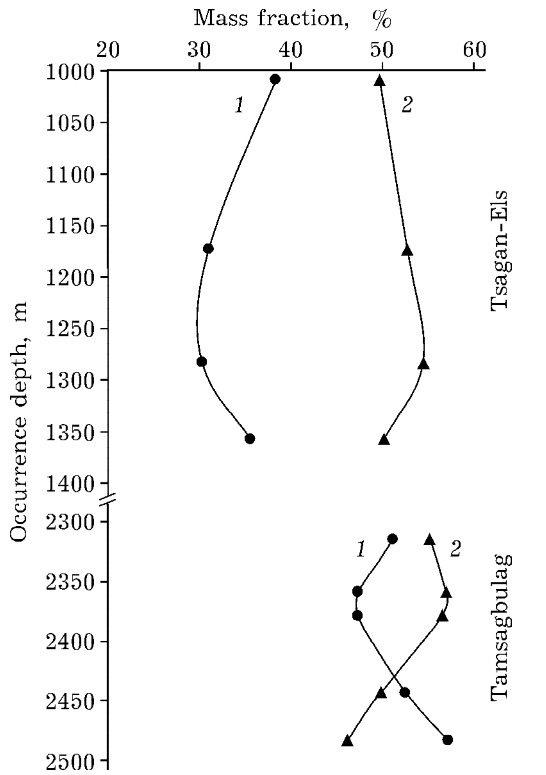

Fig. 1. Variation in proportions of carbon atoms in naphthenic *(1)* and paraffin *(2)* structures in "average molecules" of oils *vs.* their occurrence depth.

(f_n = 33 %) are grouped in these fragments; this magnitude is tangibly higher (42–52 %) in HC of Tamsag oils. Meanwhile, the variation of proportions of naphthenic carbon atoms with their occurrence depth in oils of both provinces is of qualitatively identical nature, although productive horizons are located on different "oil-bearing capacity floors" in them, *i.e.* on much dissimilar hypsometric marks (Fig. 1).

As oil fields dip down, these proportions first appreciably drop, but they start rising again in the deepest horizons. It is reasonable that in so doing, proportions of paraffin carbon atoms in oils (f_p) vary in the opposite way. Aliphatic structures are developed more strongly in all Mongolian oils we investigated, than are naphthenic and the more so aromatic; they aggregate 41–56 % of the total number of carbon atoms in each oil. In both provinces, the oils that are richest with paraffin fragments are confined to inner cross-sections, and they are impoverished a little with those fragments as the fields approach both to the top and to the bottom edge of their productive stratum.

TABLE 2

Physicochemical and structural characteristics of tarry ingredients of oils from Tsagan-Els, Zuunbayan, and Tamsagbulag fields

Indices	Tsagan-Els							Zuunbayan	Tamsagbulag				
Hole number	142	1410	A-2	14	147	145	A-1	XIX-3	13	12	14	329	3
Mean molecular mass	1025	1610	1770	1230	1485	1175	1380	1290	745	730	845	745	760
Elemental composition, mass %:													
C	84.22	85.32	84.88	85.36	85.34	85.94	85.91	84.48	84.13	85.90	83.16	85.30	86.35
H	10.50	10.40	10.57	10.21	10.31	10.91	10.63	9.65	9.79	10.72	9.07	10.26	9.73
N	1.33	1.70	1.53	1.35	1.19	1.13	0.91	0.87	1.19	1.37	1.29	1.54	1.28
S	0.36	0.20	0.36	0.50	0.44	0.41	0.32	0.34	0.28	0.21	0.31	0.45	0.44
O	3.59	2.38	2.66	2.58	2.72	2.43	2.23	4.66	4.66	1.80	6.17	2.45	2.20
Parameters of "average molecules":													
C^*	71.8	114.5	90.5	87.5	105.8	84.1	98.8	96.7	52.1	52.2	58.6	53.0	54.7
C_n^*	30.6	44.2	40.6	22.2	38.4	37.2	36.7	20.6	11.5	21.4	4.5	18.3	6.4
f_a	25.4	26.4	26.5	23.5	26.5	23.8	24.1	27.2	26.3	27.3	26.3	29.0	27.6
f_n	32.1	35.0	28.6	51.2	37.2	32.0	38.7	50.1	51.8	31.7	66.0	36.6	60.8
f_p	42.5	38.6	44.9	25.3	36.3	44.2	37.2	22.7	21.9	41.0	7.8	34.5	11.6
Parameters of molecular blocks:													
m_a	1.80	2.40	2.18	1.98	2.40	1.98	2.10	2.20	1.54	1.55	1.66	1.62	1.60
K_o^*	5.40	6.62	5.53	7.85	6.72	5.80	6.90	7.60	6.23	4.65	7.81	5.06	7.06
K_a^*	2.40	2.92	2.67	2.50	2.80	2.50	2.60	2.70	2.06	2.08	2.23	2.20	2.14
K_n^*	3.00	3.70	2.86	5.35	3.92	3.40	4.30	4.90	4.17	2.57	5.58	2.86	4.92
C^*	39.8	44.5	41.5	44.2	44.0	43.8	46.6	43.9	3.8	33.7	35.3	32.7	34.2
C_p^*	12.6	16.6	11.9	22.5	16.4	13.6	18.2	20.6	7.4	13.8	2.7	11.3	4.0
C_α^*	5.3	5.6	5.1	5.0	6.2	5.4	5.8	6.2	3.8	3.8	4.0	3.6	4.3
C_γ^*	2.0	2.7	2.4	2.6	2.2	2.3	2.7	2.0	2.8	2.8	2.7	1.9	2.1
σ_a	0.70	0.70	0.64	0.70	0.74	0.70	0.70	0.80	0.54	0.53	0.56	0.49	0.58
N^*	0.53	0.80	0.64	0.60	0.53	0.50	0.40	0.36	0.41	0.46	0.47	0.51	0.43
S^*	0.05	0.04	0.07	0.10	0.08	0.07	0.07	0.05	0.05	0.03	0.05	0.06	0.06
O^*	1.28	1.00	0.98	1.00	1.05	0.91	0.91	1.68	1.40	0.53	1.96	0.70	0.70

Ring composition of oily fraction from the described oils is in agreement with these parameters of distribution of carbon atoms between aromatic and naphthenic structures and with the nature of the variation of these parameters with depth. Naphthenic rings, certainly, are the dominating type in oils; their median number (K_n) in molecules of East Gobi oils is not over 1.9 and it is just a little higher in Tamsag oils (K_n = 2.0–2.5).

Table 2 gives composition and structural characteristics of petroleum tars that have been found by experimental and calculation methods.

Molecules of petroleum tars for oils that correspond to Zuunbayan and Tsagan-Els fields are on average larger by comparison to Tamsagbulag oils (the respective molecular mass of 1025–1770 and 730–845, the respective mean quantities of carbon atoms in molecules comprise 72–115 and 52–59). Gums of Tamsagbulag oils consist predominantly of mono and two-block molecules in proportions from 1 : 1 up to 1 : 2 (the number of blocks in molecules (m_a) changes from 1.5 up to 1.7). Contributions of single-block molecules to gums from East Gobi oils are much more less; no less than 80 % of particles constitute two- and three-block structured molecules of (m_a = 1.8) and as much as 40 %, and possibly more, from the total number of molecules comprise three-block particles (m_a = 1.8–2.4).

Biarene nuclei considerably dominate ($K_a^* = 2.1-2.2$) among aromatic nuclei in structural blocks of molecules of gums from Tamsagbulag oils, whereas in gums from Tsagan-Els field, triarene nuclei comprise no less than 40 % ($K_a^* = 2.4$) and in specific cases (when K_a^* reaches the value of 2.80–2.92) may be equal to 92 %.

Naphthenic patterns in molecules of gums from oils of both petroliferous provinces are strongly developed: $K_n^* = 2.9-5.4$ and 2.6–5.6 of naphthenic rings in each structural unit of molecules of gums from oils of Tsagan-Els and Tamsagbulag floor spaces, respectively. As a consequence, the total cyclicity of molecules of gums is very high: the cumulative number of rings in these gums, with a single exception (Tamsagbulag oil, the hole No. 12), is more than five. Based on this fact, the composition of tarry components of the oils in question may be thought of as including individual polycyclane blocks that are free of an aromatic nucleus. Previously, by means of thermal degradation it was found that such base units are even present as constituents of asphaltenes in many polytypic oils [15].

Large alkyl chains are typical for molecules of gums of oils of East Gobi province. The number of carbon atoms in these chains is $C_p^* \approx$ 12–22, calculated per one block. A very small number of terminal methyl groups ($C_\gamma^* = 2.0-2.7$) is indicative of linear or weakly branched nature of these chains. Analogous aliphatic fragments are also detected in gums from two oils of Tamsagbulag floor space (the hole No. 12 and 329, $C_p^* = 11.3-13.8$). Alkyl groups in gums from the other Tamsag gums are constructed of no more than 8 carbon atoms, and HMHC in oil from the hole No. 14 contain merely CH_3 groups as substituents, since $C_p^* = C_\gamma^* = 2.7$ in these gums.

No interrelations between comparative abundance of naphthenic and paraffin structures in tarry and hydrocarbon (oily) parts of the described oils were observed. A distinguishing characteristic is that both maximally, and minimally developed aliphatic structures occur in gums that contain the greatest number of naphthenic cycles. This is observable in oils of the both petroliferous provinces in point.

From 40 to 60 % (and sometimes more) of aromatic nuclei in molecules of gums contain nitrogen atoms, *i.e.* include pyridine or pyrrole cycles.

SUMMARY

1. Mesozoic depositions in the fields of East and Southeast Mongolia are typified by aggregations of high wax, nonsulphurous or sweet oils. Oils from Tsagan-Els and Zuunbayan fields constitute medium tarry oils, and those from Tamsagbulag are low tarry oils; all oils from East Gobi provinces belong to methane-naphthenic or methane type in terms of their hydrocarbon composition. Oils of Tamsag province are also methane-naphthenic, except for those oils that occur in the horizons embedded by more than 2400 m that contain more carbon atoms in naphthenic patterns, rather than in those of paraffin nature, *i.e.* that belong to naphthene-methane type. As it can be seen, the composition of the studied oils of Mongolia has been shaped practically without involvement of biodegradation processes.

2. Tarry components of Tamsag oils are made up of molecules of considerably smaller size on average and include predominantly bicycloaromatic nuclei as constituents of their structural blocks in comparison with gums of oils from East Gobi provinces that contain much more condensed triarene nuclei.

3. In contrast to typically exhibited tendency to "methanization" of oils (*i.e.* to the growth of a contribution of aliphatic hydrocarbons and fragments of molecules to the composition of hydrocarbon oils with an increase in their age and in the occurrence depth of the adjacent strata), the oils on the studied fields of Mongolia, oily cuts of which are richest in paraffin and are, accordingly, impoverished with naphthenic structures, are confined to inner rather than bottom parts of the cross-section of their productive stratum. Parameters of distribution of carbon atoms between aliphatic and alicyclic fragments in molecules of tarry substances from the same oils vary oppositely with depth.

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