DISTRIBUTION OF ACIDS AND PHENOLS IN AZERBAIDZHAN CRUDES

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It is known that oxygen-containing acidic compounds have a corrosive effect on process equipment in petroleum refining and also have an adverse effect on the service properties of the products. At the same time, these compounds offer promise as a source of raw material for the chemical and petrochemical industries. Investigation of their distribution in crudes from various fields is extremely important in terms of establishing correlations between physicochemical characteristics and the contents of their components. Statistical treatment of such data will be of assistance in establishing relationships that were previously unknown.

Previous studies [1] dealt mainly with the determination of the potential content of oxygen-containing acidic compounds in a number of Azerbaidzhan crudes. Data had been reported in [2] on the distribution of acids and phenols in crudes from new fields: Tarsdalayer, Dzhafarly, Darwin Bank, 28 April, and Neftyanye Kamni. Here we are reporting on a study of the distribution of acids and phenols in crudes from both new and old fields, including some that had not been investigated previously (Table 1).

TABLE 1

Production site and field	Depth of occurrence, m	Density at 20°C, kg/m^3	Content, wt. %				
			wax	silica gel resin	asphalteness	sulfur	nitrogen
Low-wax crudes							
Onshore							
Balakhany (lube, commercial)	750	876,0	0,94	10,2	0,27	0,23	0,104
Balakhany (heavy, commercial)	1800	919,0	0,54	11,6	0,62	0,26	0,139
Binagady (commercial)	700	902,7	0,36	12,0	0,25	0,18	0,164
Naftalan (Well 88)	403—366	937,6	0,001	16,7	0,37	0,10	0,151
Offshore							
Neftyanye Kamni (commercial)	400—2600	885,1	1,3	9,25	0,43	0,34	0,180
Artem Island (commercial)	700—3000	920,5	0,35	12,8	1,81	0,27	0,210
Darwin Bank (commercial)	1000—1200	924,7	0,70	16,0	0,80	0,40	0,245
28 April (commercial)	3450—4282	861,0	1,75	7,13	0,62	0,20	0,125
Medium- and high-wax crudes							
Onshore							
Dzhafarly (Well 1)	4020—3901	870,1	3,0	5,30	7,28	0,10	0,151
Tarsdallyar (Well 1)	3800—2625	870,1	9,9	6,70	2,24	0,17	0,178
Shikhbagi (Well 28)	2672—3957	881,8	12,9	15,50	2,60	0,61	0,170
Shirvan (commercial)	1200—3400	895,4	3,88	13,20	5,48	0,30	0,157
Karachukhur (commercial)	2400	808,0	6,28	2,54	0,90	0,39	0,051
Offshore							
Sangachaly Sea (commercial)	4950—2400	875,9	7,89	6,31	1,52	0,24	0,080
Kaverochkin (commercial)	2883—2844	855,6	6,8	9,15	1,46	0,44	0,078
Bulla Sea (Well 61)	4610	816,9	9,7	5,32	0,02	0,18	0,073
Lam Bank (Commercial)	2625—3800	838,7	12,8	5,32	0,263	0,24	0,140

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TABLE 1 (continued)

Production site and field	Depth of occurrence, m	Density at 20°C kg m^{-3}	Content, wt. %				
			wax	silica gel resins	asphaltenes	sulfur	nitrogen
26 Baku commissars (Well 1)	2810—2768	850,3	3,9	5,40	0,13	0,47	0,090
Crudes from other fields [4]							
Samotlor	1750—1756	879,9	0,0	6,52	0,79	1,16	0,030
West Siberian (pipeline)	1639—2925	864,6	6,6	11,50	1,24	1,28	0,180

TABLE 2

Field	Acid number, mg KOH g	Total acidic compounds, wt. %	Acids, wt. %			Phenols, wt. %		
			total	free	combined	total	free	combined
Balakhany, commercial			Low-wax crudes					
lube	1,54	0,860	0,162/18,8	0,069/8	0,093/10,8	0,698/81,2	0,008/0,9	0,69/80,3
heavy	1,87	0,964	0,15/15,6	0,051/5,3	0,099/10,3	0,814/84,4	0,01/1	0,804/83,4
Binagady (commercial)	1,38	0,920	0,174/18,9	0,076/8,2	0,098/10,6	0,746/81	0,016/1,7	0,73/79,3
Naftalan (Well 88)	1,41	0,966	0,117/12,1	0,107/11,1	0,01/1	0,759/78,6	0,019/1,9	0,74/76,6
Neftyanye Kamni (comml.)	1,70	0,849	0,259/30,5	0,084/9,9	0,175/20,6	0,59/69,5	0,11/12,9	0,48/56,6
Artem Island (commercial)	1,50	1,180	0,24/20,2	0,046/3,9	0,192/16,3	0,94/79,7	0,009/ 9,8	0,932/78,9
Darwin Bank (commercial)	2,73	1,183	0,099/8,4	0,034/2,8	0,065/5,49	1,084/91,6	0,373/31,5	0,711/60,1
28 April (commercial)	1,08	0,284	0,174/61,3	0,129/45,4	0,045/15,8	0,11/38,7	0,014/4,9	0,096/33,8
			Medium- and high-wax crudes					
Dzhafarly (Well 1)	0,034	0,024	0,008/33,3	0,003/12,5	0,005/20,8	0,016/66,7	0,003/12,5	0,013/54,2
Tarasdallyar (Well 1)	0,05	0,051	0,017/33,3	0,006/11,8	0,011/21,5	0,034/66,7	0,01/19,6	0,024/47,1
Shikhbagi (Well 28)	0,12	0,147	0,074/50,3	0,032/21,8	0,042/28,5	0,073/49,7	0,032/21,8	0,041/27,9
Shirvan (commercial)	0,27	0,055	0,018/32,7	0,007/12,7	0,011/20	0,037/67,3	0,007/12,7	0,03/54,6
Karachukhur (commercial)	0,142	0,069	0,015/21,7	0,006/8,7	0,009/13	0,054/78,2	0,011/15,9	0,043/62,3
Sangachaly Sea (commercial)	0,32	0,143	0,068/47,5	0,019/13,3	0,049/34,2	0,075/52,4	0,014/9,8	0,061/42,6
Kaverochkin (commercial)	0,136	0,089	0,026/29,2	0,007/7,9	0,019/21,3	0,063/70,8	0,007/7,8	0,056/62,9
Bulla Sea (Well 61)	0,061	0,063	0,053/84,4	0,041/64,5	0,012/19,6	0,01/15,8	0,005/7,9	0,005/7,9
Lam Bank (commercial	0,08	0,063	0,015/23,8	0,008/12,7	0,007/11,1	0,048/76,2	0,004/6,3	0,044/69,8
26 Baku Commissars (Well 1)	0,42	0,184	0,074/40,2	0,041/22,3	0,033/17,9	0,11/59,9	0,043/23,3	0,067/36,6
			Crudes from other fields					
Samotlor	0,00	0,008	0,005/62,5	0,004/50	0,001/12,5	0,003/37,5	0,002/25	0,001/12,5
West Siberian (pipeline)	—	0,028	0,012/42,9	0,01/35,7	0,002/7,2	0,016/57,1	0,012/42,8	0,004/14,3

Note. First value is referred to crude, second value to total oxygen-containing acidic compounds.

The acids and phenols were recovered from the crudes by alkaline extraction with aqueous solutions of 5% sodium bicarbonate and 10% sodium hydroxide, followed by hot saponification with a water—alcohol caustic solution. The results from functional analysis of the oxygen-containing acidic compounds in these crudes are presented in Table 2.

It will be seen that the low-wax crudes occurring at depths below 2000 m have high contents of these acidic components (0.85-1.18% by weight). The medium- and high-wax crudes occurring at depths of 2000-4950 m differ greatly from the low-wax crudes in acid number and in the contents of acids and phenols. The total oxygen-containing acidic compounds in these crudes is no greater than 0.184%. No correlation between acid number and density can be observed. In comparison with the low-wax crudes, we may observe that for the medium-wax crudes with intermediate or high density (above 840 kg/m^3), i.e., the Dzhafarly (Well 1), Tarsdallyar (Well 1), Shikhbagi (Well 28), Shirvan commercial, Kaverochkin, and Sangachaly Sea crudes, the acid numbers are lower (0.034-0.32 mg KOH/g).

For the medium-wax crudes from the Middle Eocene deposits that are produced onshore from the Tarsdallyar and Dzhafarly fields, the acidities are considerably lower than for the low-wax crude produced offshore in the 28 April field from Pliocene deposits. With increasing content of wax (above 3% by weight), the total quantity of oxygen-containing compounds and the quantity of acids taken separately drop off by an order of magnitude. Also, for the low-wax crudes, the total of the oxygen-containing acidic compounds depends on their content of silica gel resins and asphaltenes; for the medium- and high-wax crudes, this relationship breaks down.

With increasing quantity of resins and asphaltenes in the Dzhafarly, Shikhbagi, Shirvan, and Kaverochkin crudes, the total of the oxygen-containing acidic compounds drops off sharply. For the low-wax crudes, as the content of asphaltenes increases, the total phenols increase as a result of an increase in the content of combined phenols, which are apparently recovered upon rupture of acid–base bonds in high-molecular-weight esters after hot saponification of the crude with a water–alcohol caustic solution [3]. An exception is the low-wax 28 April crude, in which we found only 0.11% phenols, with an asphaltene content of 0.62%. For the low-wax crudes, we could not establish any correlation between the asphaltene content and total acids.

According to the data of Table 2, even a small increase in the contents of sulfur and nitrogen in the crude lead to an increase in the quantity of phenols. In contrast to crudes from other regions [4, 5], the phenols in the Azerbaidzhan crudes predominate considerably over the acids (by a factor of 2-7) [2]. An exception may be found in the offshore crudes 28 April, Bulla Sea, and 26 Baku Commissars.

In the 28 April crude, occurring at a depth of 3450-4282 m and classified as light (861 kg/m^3), low-resin (7.13% resins), and low-wax (1.75% wax), we found 0.129% acids in the free form (45.4% of the total oxygen-containing acidic components). Only in the Shikhbagi crude were acids and phenols found in equal quantities.

The major part (54.5-93.7%) of the acids and phenols in these crudes exists in the combined form, i.e., as esters.

Our data are consistent with results reported in [4, 5] for West Siberian crudes; i.e., the same relationship is maintained between the contents of oxygen-containing acidic compounds, resin content, and density of the crudes, regardless of where they are produced. The total content of oxygen-containing acidic compounds depends on the age of the enclosing rock, owing to depth factors, i.e., the mechanism of their formation [4].

Thus, we have established the following: the quantitative distribution of oxygen-containing acidic compounds in crudes from 18 Azerbaidzhan fields, including old fields; the qualitative and quantitative composition of these compounds, and also the contents of acids and phenols, in particular the predominance of phenols over acids; the contents of free and combined acids and phenols; a direct correlation between the content of oxygen-containing acidic compounds and resin/asphaltenes; a quantitative correlation among the contents of acids, phenols, and wax; higher contents of acids and phenols in low-wax and medium-wax crudes from new fields, the same as in the previously investigated fields (crudes with up to 3% wax).

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