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CLASSIFICATION OF CRUDE OILS PRODUCED BY *in situ* COMBUSTION

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It was shown in [1, 2] that oil from the Karazhanbas field undergoes thermal and thermooxidative conversions in the course of production by *in situ* combustion (ISC). The degree of such conversions depends on the distance from the combustion front and on the penetration of hot air and hydrocarbon vapor through cracks into regions that are quite distant from the front. It has been proposed that crudes produced by this method should be assigned to three classes — those that have been subjected to thermal action only, those that have been subjected to thermooxidative action, and unconverted (native) crudes [2].

This sort of classification is necessary in resolving questions of logical mixing of crudes, transportation, storage, and subsequent processing. A thermooxidized crude should be processed by means of a special scheme; it cannot be mixed with crudes that have been subjected to thermal action only, or with unconverted crudes [2]. The classification is based on data obtained in IR spectroscopic studies of crude oil samples (group composition) and determinations of their physicochemical characteristics (density, viscosity, distillation, etc.).

Crudes with high contents of paraffinic hydrocarbons and low contents of aromatic hydrocarbons and oxidation products typically have lower viscosities and densities and higher contents of light fractions in comparison with native crudes; they are assigned to the class of crudes that have been subjected to thermal action only.

The reasoning behind this assignment is that a purely thermal action results in splitting of the weakest C—C bonds to form hydrocarbons with lower molecular weight (including olefins) and in condensation of resins to asphaltenes and of the asphaltenes to carbenes and carboids, which are deposited in the formation as a consequence of the lowering of oil viscosity.

Crudes with increased contents of aromatic hydrocarbons, oxidation products, and asphaltenes typically have higher densities and viscosities and lower initial boiling points in comparison with native crudes; they are assigned to the class of oils that have been subjected to thermooxidative action. As our studies have shown, the resins of Karazhanbas crudes — which were previously classed as crudes that had been subjected to purely thermal action — are characterized by a higher degree of oxidation in comparison with the resins of crudes that had been previously classed as thermooxidized.

Here we are reporting on a comparative analysis of the composition and properties of the resins in Karazhanbas crude produced by natural influx and also by ISC; on the basis of these results, we have refined the previous classification of such crudes and defined more precisely the nature of conversion of the oil in the course of ISC.

We have investigated the benzene—pentane, benzene, and alcohol—benzene resins of crudes produced by natural influx (oil 2160_4), subjected to thermal action close to the combustion front (oil 2118_5), and subjected to thermooxidative action (oil 54_4). The physicochemical characteristics of these crudes are listed in Table 1.

The resins were recovered from the oil samples by the following sequence of operations: 1) deasphalting of the crude oil with *n*-hexane; 2) liquid adsorption separation (on silica gel) of the hydrocarbon part from the deasphalted oil (1:20); 3) segregation of the resins. The benzene—pentane resins were eluted with a 15:85 mixture of benzene and pentane, the benzene resins with benzene, and the alcohol—benzene resins with a 1:1 mixture of ethanol and benzene.

In taking the IR spectra of the resins, it was difficult to obtain layers of the test samples with identical thickness, owing to the high viscosity of the resins. Therefore, in comparing the IR spectra of the different resins, we used as a criterion the ratio of optical density D of characteristic absorption bands in the spectrum of each resin to the optical density of the absorption band at 1460 cm^{-1}. In Table 2 we have listed the wavenumbers of the principal absorption bands in the IR spectra of the resins, and in Table 3 the relative optical densities D of the characteristic absorption bands in comparison with the optical density of the 1460 cm^{-1} band.

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TABLE 1

Oil*	Density, kg/m^3	Viscosity, mPa·sec	Content of asphaltenes, %	Group composition (based on spectroscopic data using a procedure given in [2]), wt. %			
				hydrocarbons			oxidation products
				paraffins	naphthenes	aromatics	
2160$_4$	935	586	4	69,4	8,2	19,6	2,8
54$_4$	938	634	5,33	63,5	8,7	23,3	4,5
2118$_5$	919	49	-	70,2	8,0	19,0	2,8

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*The oil identification includes the well number (for example, 54), and the sequence number of the sample (for example, 4). The wells were sampled, on the average, every 6-8 months.

TABLE 2

Wavenumber, cm^{-1}	Assignment of absorption band	Wavenumber, cm^{-1}	Assignment of absorption band
720	Vibrations of chain of CH_2 groups, with the number of such groups $n \geq 4$	1650	Vibrations of carbonyl group of oxygen-containing aromatic compounds (acids, ketones)
750	Disubstituted aromatic compounds	1700-1720	Vibrations of carbonyl group of saturated oxygen-containing compounds (acids, ketones)
810	Condensed aromatic compounds	3000 3038	Stretching vibrations C_{aliph}—H
870	Polysubstituted benzenoid hydrocarbons	3075 3095	Stretching vibrations C_{arom}—H
970 1035	Vibrations of carbon skeleton of naphthenic hydrocarbons	3300 3440	Intermolecular hydrogen bonds
1370	Bending vibrations of C—H bonds in CH_3 groups (symmetric)	3475 3540	Intramolecular hydrogen bond; compounds with one bridge
1460	Bending vibrations of C—H bonds in CH_2 groups (symmetric)		
1600	Vibrations of carbon skeleton of aromatic ring		

Benzene—Pentane Resins. As can be seen from Table 3, the D/D_{1460} ratio is very little dependent on the type of oil. For all of the bands in the IR spectrum of the resins from oil 2118_5, the ratio is slightly greater than the corresponding ratios in the IR spectra of the resins from oils 2160_4 and 54_4. The IR spectra of these resins are characterized by very weak absorption bands >3000 cm^{-1}, indicating a high degree of substitution of the aromatic rings.

Benzene Resins. The IR spectra of the resins from oils 2118_5 and 54_4, in contrast to that of the resins from oil 2160_4, contain absorption bands at 3038, 3075, and 3095 cm^{-1}. The ratio of the corresponding optical densities to the optical density of 1460 cm^{-1} is 2.0-2.5 times greater for the resins for oil 54_4 in comparison with the resins of oil 2118_5. The same picture is observed for the ratios D_{3440}/D_{1460}, D_{3475}/D_{1460}, and D_{750}/D_{1460}.

The ratio D_{720}/D_{1460}, which characterizes the content of hydrocarbons with a long, unbranched alkyl chain, is higher for the resins of oil 2160_4 in comparison with the resins of oil 2118_5. The ratios D_{750}/D_{1460}, D_{810}/D_{1460}, and D_{870}/D_{1460} (aromatic compounds) and D_{970}/D_{1460} for the resins of oil 2118_5 are higher than for the resins of oil 2160_4; this difference is explained by the significant effect of thermal action on the 2118_5 oil. The ratios D_{1650}/D_{1450} and D_{1700}/D_{1460}, which characterize the degree of oxidation, are identical for the resins of oils 2160_4 and 2118_5.

The benzene resins of oil 54_4 are a special case. They are characterized by higher values of the ratios D_{720}/D_{1460}, D_{750}/D_{1460}, D_{810}/D_{1460}, D_{870}/D_{1460}, D_{1600}/D_{1460}, D_{1650}/D_{1460}, and D_{1700}/D_{1460} in comparison with the resins of oils 2118_5 and 2160_4. The apparent cause of this difference is the severe oxidation to which oil 54_4 has been subjected, which supports its assignment to the class of thermooxidized oil.

TABLE 3

Characteristic absorption band, cm^{-1}	D/D_{1460} in IR spectra of resins								
	benzene—pentane resins from indicated oil			benzene resins from indicated oil			alcohol—benzene resins from indicated oil		
	2160_4	2118_5	54_4	2160_4	2118_5	54_4	2160_4	2118_5	54_4
720	0,156	0,169	0.142	0,166	0,151	0,225	0,162	0,220	0,161
750	0,220	0,247	0,190	0,196	0,223	0,272	0,147	0,230	-
810	0,228	0,276	0,202	0,191	0,230	0,278	0,141	0,218	0,152
870	0,169	0,190	0,155	0,171	0,178	0,252	0,138	0,230	-
970	0,083	0,097	0,078	0,102	0,148	0,185	-	-	0,154
1035	0,202	0,246	0,189	0,244	0,297	0,431	0,344	0,512	0,340
1376	0,58	0,57	0,54	0,61	0,57	0,64	0,60	0,68	0,62
1460	1	1	1	1	1	1	1	1	1
1600	0,157	0,184	0,151	0,203	0,200	0,293	0,230	0,350	0,260
1650	0,053	0,064	0,057	0,075	0,069	0,166	0,198	0,298	0,240
1700	0,042	-	0,063	0,1	0,093	0,196	0,23	0,38	0,27
3000	-	-	-	-	-	-	-	-	-
3038	-	-	-	-	0,3307	0,841	-	-	-
3075	-	-	-	-	0,1905	0,4628	-	-	-
3095	-	-	-	-	0,1480	0,4122	-	-	-
3300	-	-	-	-	-	-	0,1814	0,2882	0,182
3440	-	-	-	0,0870	0,0888	0,2096	-	-	-
3475	0,033	-	-	0,0856	0,0789	0,1921	-	-	-
3540	-	-	-	0,0514	0,0523	0,131	-	-	-

Alcohol—Benzene Resins. The ratios of optical densities of the bands in the 720-1700 cm^{-1} interval to that of the 1460 cm^{-1} band for the resins of oil 2118_5 is 1.3-1.6 times the ratio for the resins of oils 2160_4 and 54_4. The difference is particularly marked for the bands that are characteristic for aromatic structures (750, 810, 870, and 1600 cm^{-1}), oxygen-containing compounds (1650 and 1700 cm^{-1}), and the $-\underset{|}{\mathrm{S}}\rightarrow \mathrm{O}$ group (1035 cm^{-1}).

In Table 4 we present data on the group composition of resins from all of the types of oil, calculated on the basis of IR spectroscopic data using a procedure given in [3]. As can be seen from these data, the benzene—pentane resins from the different oils are very similar in composition, with the exception of a 2.4% content of oxidation products in the resins of the 54_4 oil.

The compositions of the benzene resins differ considerably from oil to oil, and from the corresponding benzene—pentane resins. These differences are the greatest for the benzene resins of the 54_4 oil, somewhat less for the resins of the 2118_5 oil. Attention is directed to the significant increases in the content of oxidation products in the resins of oils 2118_5 and 54_4 (5.2% and 9%, respectively), and also the decrease in content of paraffinic structures in the resins of the 54_4 oil.

The alcohol—benzene resins of the 2118_5 oil differ sharply from the resins of the 2160_4 and 54_4 oils in having a lower content of paraffinic structures, a higher content of aromatic structures and a particularly high content of oxidation products (increased up to 16%), which contradicts the previously accepted viewpoint that oils analogous to the 2118_5 should be classed as oils that have been subjected to thermal action only.

An analysis of the IR spectroscopic data on the petroleum resins leads to the following conclusions:

1. In the case of the unconverted oil 2160_4, as the change is made from benzene—pentane resins to alcohol—benzene resins, there are uniform decreases in the contents of paraffinic and aromatic structures and increases in the content of oxidation

TABLE 4

Compounds	Content (%) in resins								
	benzene—pentane resins of indicated oil			benzene resins of indicated oil			alcohol—benzene resins of indicated oil		
	2160_4	2118_5	54_4	2160_4	2118_5	54_4	2160_4	2118_5	54_4
Hydrocarbons									
paraffins	63,92	60.35	63.88	61.71	57,24	49.84	58,89	46.49	51,47
naphthenes	7.46	8.54	7,15	8.45	9,89	11,53	11,52	12,53	14,31
aromatics	28,62	31,11	26.57	26,43	27,70	29,26	21,92	25.10	20,41
Oxygen-containing									
aromatics	–	–	2,40	3,41	2,06	4,14	7,61	6.66	5,90
aliphatics	–	–	–	–	3,11	5,23	–	9,22	7,91

Note. The error in calculating the structural-group composition of the alcohol—benzene resins may be as great as 2-3% (abs.), since the 1035 cm^{-1} absorption band corresponds not only to naphthenic structures, but also to the sulfoxide group.

products. The apparent increase of the naphthene content (calculation based on bands at 970 and 1030 cm^{-1}) may be due to a contribution of the $-\underset{|}{S}\rightarrow O$ group (1030 cm^{-1}).

2. All of the resins of the 54_4 oil, which is classed as a thermooxidized oil [2], exhibit uniform increases in the content of oxidation products as the change is made from benzene—pentane resins (2.4%) to alcohol—benzene resins (14%), along with decreases in the contents of paraffinic and aromatic structures.

3. In the case of the 2118_5 oil, which had previously been assigned to the class of oils that had been subjected to thermal action alone [1], the content of oxidation products, even in the benzene resins, is considerably higher than for the 2160_4 oil (5.2% vs 3.4%); and in the alcohol—benzene resins, the content of oxidation products is higher than for the 54_4 oil (16% vs 14%).

Thus, the 2118_5 oil was apparently subjected to not only thermal but also oxidative action in the course of ISC. Along with this, the 2118_5 and 54_4 oils differ substantially in physicochemical properties. The 2118_5 oil is characterized by the very nearly complete absence of asphaltenes.

In the process of ISC, apparently, the 54_4 and 2118_5 oils were subjected to a strong oxidative action. However, the 2118_5 oil was closer to the combustion front; and as a consequence of the higher temperature, profound thermooxidative conversions took place in this oil: the hydrocarbons were subjected, along with cracking, to oxidation and oxidative condensation to form resins that were then converted to asphaltenes, carbenes, and carboids that were deposited in the formation as a consequence of the low oil viscosity. As a result, this crude was enriched in hydrocarbons, and the contents of resins and asphaltenes decreased.

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