

The Composition and properties of Straight-Run and Mechanoactivated 360-400°C Distillate from Yakut Petroleum

P.A.Pikula, A.K.Golovko*, V.F.Kamyarov

Institute of Petroleum Chemistry, Russian Academy of Sciences, Siberian Branch
3, Academichesky Av., 634021, Tomsk, Russia

Abstract

The group hydrocarbon composition of 360-400°C straight-run distillate of the petroleum from Talakanskoye oil-field (Yakutia – Republic of Saha) has been studied in detail using clathrate formation, liquid adsorption chromatography, thermodiffusion methods and mass spectrometric analysis of obtained thermodiffusion fractions. The fundamental physical constants of all isolated narrow hydrocarbon fractions were measured. The regularities of thermodiffusion separation of saturated hydrocarbons having different amounts of rings in molecules as well as the relations between properties and composition of the concentrates obtained were traced.

It is established that a mechanoactivation of petroleum distillate leads to a change of its hydrocarbon composition, first of all to a decrease of its paraffin content, as well as to respective changes of its physical-chemical characteristics (to a decrease in pour point and an increase in density and viscosity values).

Introduction

The properties of oil fractions are depending mainly on their hydrocarbon composition, without sufficient knowledge of which it is impossible to understand and explain the behaviour of oil products under conditions of their manufacturing and application. The only way to working out true notions about correlations between physical-chemical and operational properties and a composition of oil products consists in carrying out the profound investigations basing on modern methods of separation of hydrocarbon mixtures and instrumental analysis of isolated narrow concentrates. The mixtures of high-boiling isoalkanes and naphthenes obtained after deparaffinization and dearomatization of straight-run oil distillates may be considered as the objects submitting to preparative separation hardly than other ones. One of the most effective methods of such mixtures' separation is a thermodiffusion, which was widely used in a practice of petroleum analysis during the last several decades. Some results of application of this method for separation of vacuum distillates from different petroleum were summarized, e.g., in monographs [1, 2].

In this study a thermodiffusion, along with other fractionation methods, was used for separation of oil 360-400°C distillate from the first petroleum commercially extracting at the comparatively new and insufficiently explored Yakut oil-bearing province.

A search of new physical ways for coercion upon petroleum fractions with the purpose of changing their composition and properties is an actual scientific and technical task. In this connection we have studied the influence of mechanical treatment (mechanoactivation) of the same petroleum distillate on its properties and group hydrocarbon composition. The consequences of carrying out this operation are also discussed in present report.

Experimental

As an object of investigation we chose the 360–400°C vacuum distillate isolated by rectification in ARN–2 apparatus (GOST 11011) from the light ($d^{20} = 0.842$), paraffinaceous (3.7 wt % of free paraffin), low-sulfurous (0.44 wt % of S), methanic by hydrocarbon composition petroleum extracted from Lower Cambrian layer at Talakanskoye oil-field (Nepsko-Botuobinsk oil-bearing region).

n-Paraffin hydrocarbons (HC) were isolated from

*corresponding authors. E-mail: golovko@ipc.tsc.ru

crude distillate in form of clathrates with carbamide by well-known procedure [3]. The compounds that did not form the clathrates were subjected to liquid chromatographic separation on ASK silicagel via successive elution of saturated HC (isoalkanes+naphthenes) by *n*-hexane, concentrates of mono-, bi-, and tricycloaromatic HC – by hexane+benzene mixtures 95:5, 85:15 and 1:1 (by volume) respectively. The separation process was completed by elution of polyarenes and nitrogen-, sulfur- and oxygen-bearing compounds (resins) with benzene.

After distilling the solvent off, the first chromatographic eluate – the mixture of isoalkanes and naphthenes – was feeded into thermodiffusion column of ATR-4 apparatus designed and made in Institute of heat and mass exchange (Republic of Belarus, Academy of Sciences, Minsk). Apparatus was equipped with Melpolder type columns [4] (with spirals in the working clearance) having the following main characteristics: mean diameter of inter-tube clearance – 1.5 cm, width of clearance – 0.45 mm, volume of charging sample – 36 cm³. The internal tube was heated with water steam superheated up to 130°C, and external one was bathed with water warmed up to 30°C, which provided maintenance in the clearance of temperature gradient of about 220 grad/mm. After 18-hour separation ten fractions were picked out, each of 3.6 cm³ by volume, which were subjected to physical-chemical and mass-spectral analyses (MH 1310 mass-spectrometer, energy of ionizing electrons – 12 or 70 eV, linearly programmed

heating of evaporator up to 200°C). Mass-spectra obtained were subjected to analytical treatment using the methods described in [5].

Mechanoactivation of initial distillate was carried out for 5 min at room temperature in the air with centrifugal planetary mill of AGO-2 type, which provided an acceleration of forcing bodies (steel balls of 8 mm in diameter) about of 80 g. The product obtained was separated by means of clathrate formation and adsorption chromatography, analogously to the procedure described above for crude distillate.

Physical-chemical analysis of all products isolated was accomplished by standard methods [3, 6].

Results and discussion

14.53 wt % of *n*-paraffin HC were extracted from straight-run distillate as the inclusions in carbamide crystals (clathrate compounds). The fraction of paraffin-cycloparaffin (PCP) HC, being virtually the mixture of isoalkanes and naphthenes, the concentrates of monocycloaromatic (MCA), bicycloaromatic (BCA), tricycloaromatic (TCA), and the mixture of polycycloaromatic (PCA) HC and heteroatomic (resinous) substances were isolated in the course of further liquid adsorption separation of deparaffinized product. The contents of HC groups isolated calculating both on initial and on deparaffinized distillates, as well as physical-chemical characteristics of these fractions are shown in Table 1.

Table 1

Characteristics of initial, deparaffinized and mechanoactivated distillates and of their chromatographic fractions.

Indices	Whole distillate	PCP	MCA	BCA	TCA	PCA
		Hydrocarbons				
Straight-run distillate						
Yield, wt %	100	78.47	10.92	4.02	4.10	2.48
d ²⁰ , kg/m ³	877.2	866.2	899.6	951.7	997.3	998.7
n _D ²⁰	1.4864	1.4742	1.4980	1.5370	1.5752	1.5629
v ₄₀ , cSt	22.5	19.3	28.4	39.2	99.0	242.8
v ₁₀₀ , cSt	4.40	4.12	5.23	6.50	9.23	13.1
Pour point, °C	7	9	-34	-27	-12	-6
Deparaffinized distillate						
Yield, wt %	100	75.34	12.51	4.61	4.70	2.84
d ²⁰ , kg/m ³	885.9	868.0	901.0	951.9	997.3	998.7

Table 1
Continued

Indices	Whole distillate	PCP	MCA	BCA	TCA	PCA
		Hydrocarbons				
Deparaffinized distillate						
n_D^{20}	1.4892	1.4764	1.4994	1.5376	1.5752	1.5629
v_{40} , cSt	22.1	19.0	28.4	39.2	97.7	241.4
v_{100} , cSt	4.53	4.24	5.25	6.51	9.24	13.1
Pour point, °C	-16	-38	-36	-29	-14	-8
Mechanoactivated distillate						
Yield, wt %	100	78.67	11.01	3.65	4.09	2.58
d^{20} , kg/m ³	879.8	883.2	911.8	952.1	998.8	996.8
n_D^{20}	1.4921	1.4708	1.4934	1.5326	1.5740	1.5634
v_{40} , cSt	22.9	19.5	28.4	39.1	98.7	242.5
v_{100} , cSt	4.42	4.16	5.26	6.53	9.25	13.2
Pour point, °C	1	3	-37	-28	-11	-7

Free paraffins extracted from distillate contained, apparently, little admixtures of isoalkanes, mono- and bicyclic HC having sufficiently long linear substituents in molecules because such compounds can to form clathrates with carbamide too [7]. That confirms by slight alterations of physico-chemical characteristics of corresponding fractions as a result of operation performed.

Isoalkano-naphthenic (IN) HC presented two thirds of deparaffinized distillate by mass (≈ 64 wt % calculating on initial straight-run matter). MCA HC prevailed essentially among arenes that was generally characteristic of paraffinaceous petroleums [8]. The concentrations of individual HC groups on the whole diminished when a number of rings in molecules increased. Pour points, densities, refraction indices n_D^{20} , and kinematic viscosities of chromatographic fractions (the lasts measured at 40 and 100°C, i.e. v_{40} and v_{100}) rised in the same sequence.

As it has been expected, the removing of *n*-paraffins resulted in sharp decrease of pour point of straight-run distillate (from +7 to -16°C) and especially of its IN part (from +9 to -38°C).

Thermodiffusion (TD) fractions obtained from IN part of the distillate differed significantly by all physico-chemical parameters (Table 2). Densities, refraction indices and viscosities increased, and pour point values decreased regularly from first (upper) to last

(lower) TD fractions. Certainly, that is stipulated by the changes of hydrocarbon composition of separation products.

According to mass-spectral data, isoalkanes are predominant components of most TD fractions except the two lasts. Total content of these HC calculating on whole IN mixture is about 43.0 wt %. The weight concentration of isoalkanes reaches two thirds in the first and falls down to ≈ 15 wt % in the tenth TD fraction. The quotas of naphthenes with the equal amounts of rings in molecules increase in the same direction from the minimal values in the first to the maximums in the tenth or, more rarely, ninth fraction. It was established that IN part of the distillate includes naphthenes containing from one to six cycles in molecules, i.e. mono- (15.8 wt %), bi- (14.0 wt %), tri- (16.3 wt %), tetra- (5.4 wt %), penta- (4.1 wt %) and hexa- (1.4 wt %) -cyclanes. It is significative that tricyclanes stand out against a background of general tendency towards a diminution of sum concentrations of individual IN HC groups when a number of rings in their molecules rises: tricyclanes prevail quantitatively not only over bi-, but also over monocyclanes. It is noteworthy that similar (though much weaker pronounced) predominance of tricyclic compounds over bicyclic ones is observed also in the case of aromatic HC groups isolated by means of chromatography (Table 1).

Table 2
Characteristics of thermodiffusion fractions from isoalkane-naphthenic part of distillate.

Indices	Number of fraction									
	1	2	3	4	5	6	7	8	9	10
	9.62	9.66	9.62	9.64	9.80	9.93	10.12	10.22	10.59	10.81
d^{20} , kg/m ³	818.9	819.2	820.4	821.8	834.2	845.1	861.1	870.3	901.1	919.9
n_D^{20}	1.448	1.452	1.454	1.462	1.468	1.470	1.481	1.484	1.487	1.490
v_{40} , cSt	12.3	12.6	13.2	15.6	18.7	20.5	29.1	43.2	67.1	144.8
v_{100} , cSt	3.32	3.37	3.44	3.77	4.15	4.35	5.26	6.55	8.45	13.6
	-23	-23	-24	-29	-38	-45	-48	-49	-50	-50
Content, wt %, of										
isoalkanes	66.6	62.4	58.0	54.0	48.6	43.2	36.9	30.4	22.1	14.7
monocyclanes	13.1	13.6	14.1	13.3	14.7	15.3	16.4	17.1	18.7	20.8
bicyclanes	9.3	9.6	10.0	10.8	11.5	12.5	13.7	15.5	20.1	24.1
tricyclanes	7.3	9.4	11.4	13.5	15.4	17.6	19.9	22.1	22.6	22.3
tetracyclanes	2.5	2.9	3.5	4.4	5.4	6.4	7.5	8.3	7.4	6.0
pentacyclanes	1.2	2.1	3.0	3.7	4.0	4.4	4.6	4.9	5.7	7.0
hexacyclanes	0	0	0	0.3	0.4	0.6	1.0	1.7	3.4	5.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
K_m	0.70	0.83	0.96	1.13	1.28	1.44	1.62	1.82	2.05	2.26

As it was mentioned above, physical-chemical characteristics of TD fractions are predetermined naturally by their hydrocarbon composition. As generalized quantitative representation of the HC composition one can use, for example, a value of product's mean «cyclic degree» which is quantitatively equated with an average number of rings in all molecules of fraction components K_m . Calculated values of K_m for every fraction are given at the last line of Table 2. The presence of clear interdependences between physical-chemical constants and K_m values is demonstrated visually in Fig. 1. Computer-assisted analysis has shown that these interdependences may be described with high reliability (correlation coefficients $r = 0.985-0.996$) by the following simple (trinomial) equations:

$$d^{20} = 830.05 - 45.742 \cdot K_m + 38.323 \cdot K_m^2$$

$$(r = 0.992)$$

$$n_D^{20} = 1.4127 + 0.05392 \cdot K_m - 0.008534 \cdot K_m^2$$

$$(r = 0.985)$$

$$\log(v_{40}) = 1.2948 - 0.5769 \cdot K_m + 0.41885 \cdot K_m^2$$

$$(r = 0.996)$$

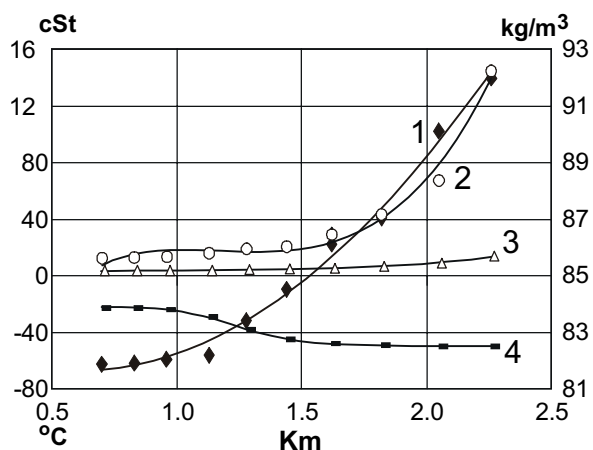


Fig. 1. Physical constants of thermodiffusion fractions depending on average number of cycles in molecules. 1 - Density at 20°C, d^{20} , kg/m³; 2 - Viscosity at 40°C, v_{40} , cSt; 3 - Viscosity at 100°C, v_{100} , cSt; 4 - Pour point, °C.

$$\log(v_{100}) = 0.6750 - 0.3888 \cdot K_m + 0.25717 \cdot K_m^2$$

$$(r = 0.994)$$

Mathematical correlations between pour points and mean «cyclic degrees» of TD fractions:

$$T = 16.317 - 58.650 \cdot K_m + 12.724 \cdot K_m^2$$

$$(r = 0.920)$$

is only a little weaker than foregoing ones.

Molecular-mass distributions of components in the every group of saturated HC found in the distillate studied are qualitatively similar. These distributions cover mainly the members of C₁₉-C₂₉ composition, though the compounds containing up to 32 carbon atoms in molecules were also discovered in very small amounts (less than 0.1 wt %) (Fig. 2). The series of penta- and hexacyclanes are limited from below by the members of C₂₁ and C₂₄ respectively, in conformity with structural features of petroleum hydrocarbons containing mentioned amounts of rings in the molecules. All hydrocarbon series found are unimodal, the HC of C₂₁-C₂₆ composition presenting in the largest amounts. The positions of maximums in considering interval of the distributions shift to more high-molecular region as a number of rings in molecules increases, viz. from C₂₁-C₂₂ in isoalkane and monocyclane series to C₂₄-C₂₆ for hexacyclanes.

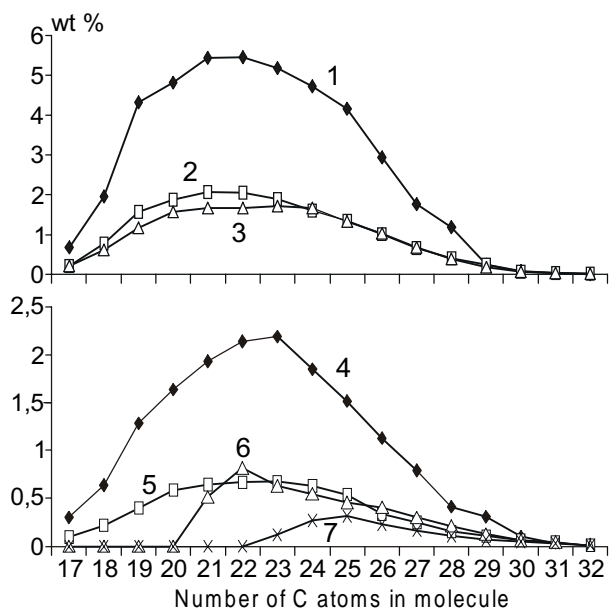


Fig. 2. Molecular-mass distributions of isoalkanes (1), mono- (2), bi- (3), tri- (4), tetra- (5), penta- (6) and hexa- (7) -cyclanes in isoalkane-naphthenic part of the distillate, wt %.

Mechanoactivation treatment of straight-run distillate results in appreciable changes of its composition and some physico-chemical properties. The most essential alternations came over pour points both of initial distillate and especially of its PCP part (decrease in pour point by 6°C, Table 1). The reason

of this effect was cleared up after carrying out the reaction of treated material with carbamide. It was found that the content of *n*-alkanes in the distillate diminished after the treatment from 14.53 wt % to 6.41 wt %, i.e. more than twice. At the same time, judging from the chromatographic data, the total content of saturated HC in the distillate became even somewhat bigger. Proceeding from general notions about a character of probable chemical transformations of the substances at mechanoactivation coercion, one can propose that the immediate objects of such force in the case considered were large paraffin macroparticles forming, undoubtedly, from *n*-alkane components of the distillate under its treatment conditions (*i.e.* at room temperature).

To all appearance, other components of crude distillate were also drawn into destruction reactions initiated by mechanoactivation, though to much smaller extent. The evidences of that are the appreciable changes of yields and physical-chemical constants not only of PCP but also of aromatic products of chromatographic separation. Now it is impossible to explain logically all observed effects. Thus, if an increase in the PCP fraction yield may be stipulated by a contribution of saturated compounds forming owing to destruction of alkylarenes, and a small accretion of PCA and resin content – by an material oxidation proceeding in the course of mechanoactivation treatment, then reasons of a recession in BCA HC concentration remain not properly understood for the present.

Practical significance of these results permitting to outline the ways towards creation of a new method for improvement operational qualities of oil products and compelled conditionality of data interpretation stipulated by a scarcity of an information about chemical conversions of petroleum components in the course of mechanoactivation processes are indicative of an expediency of extending the investigations in this prospective direction.

Conclusions

Group hydrocarbon composition of 360-400°C distillate from the first commercial Yakut petroleum was studied in detail with the use of clathrate formation, liquid adsorption chromatography, thermofusion as well as of the methods of general physical-chemical and mass-spectrometric analyses of isolated fractions.

The distillate consists of aromatic (21.5 wt %),

naphthenic (36.5 wt %) and aliphatic (42.0 wt %) hydrocarbons including 14.5 wt % of free paraffin. The concentrations of aromatic and naphthenic hydrocarbons diminish with an increase in number of cycles in their molecules. Only triarenes and tricyclanes disturb this general tendency standing out against a background on account of their higher concentrations. Molecular-mass distributions of hydrocarbons of all structural types in the distillate are unimodal and include mainly the components of C₁₉-C₂₉ composition.

The fundamental physical-chemical constants of saturated fractions of the distillate correlate with average number of cycles in molecules of components present, interdependences between these parameters being well reflected by deduced regression equations (correlation coefficients $r = 0.982-0.995$).

Mechanoactivation treatment of straight-run petroleum distillate leads to significant diminution of free paraffin content and consequently to essential decrease of pour point and therefore appears to be a new prospective method for improvement of operational qualities of petroleum oils.

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