

CURRENT PROBLEMS NEW SOLUTIONS

EXTRACTION TECHNOLOGY FOR PRODUCTION OF ENVIRONMENTALLY CLEAN DIESEL AND JET FUELS

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Increasingly rigorous environmental requirements are being imposed on diesel and jet fuels abroad: the concentration of aromatic hydrocarbons in diesel fuel must not exceed 5 – 10 wt. % [1], and the concentration of naphthalene hydrocarbons in the most widely used jet fuel, Jet A-1, must be below 3 wt. % with a minimum smoke point of 26 mm [2]. Restrictions on the concentration of aromatic hydrocarbons in fuels are also being introduced in Russia: for example, it must be no greater than 20 wt. % in DLECh-V diesel fuel and no greater than 10 wt. % in T-6 ultrasonic jet fuel [3].

The emission of solid particles and smoke content in exhaust gases increase with an increase in the concentration of aromatic hydrocarbons in the fuels [4]. The danger of aircraft accidents increases in fouling in the engines. Aromatic hydrocarbons, especially bi- and polycyclic hydrocarbons, decrease the cetane number of diesel fuels, which should be within the limits of 49 – 53 for RF-03-A-84 standard diesel fuel and a minimum of 49 for standard fuel whose production is organized by the All-Russian Scientific-Research Institute of the Petroleum Industry based on Russian standard TU 38.401-58-96—94 [5].

In hydrotreating fuels, only heteroatomic compounds can be removed sufficiently efficiently, while aromatic hydrocarbons are insignificantly hydrogenated. The concentration of aromatic hydrocarbons in diesel fuel can be reduced to 20 wt. % by single-stage hydrocracking under a pressure of 10 – 14 MPa on nickel catalysts or two-stage hydrocracking under a pressure of 8.3 – 10.5 MPa using catalysts based on noble metals in the second stage [6].

In comparison to hydrotreating, the investments are doubled and the power consumed increases by 65 – 77% [7]. Obtaining fuels with a concentration of aromatic hydrocarbons under 10 wt. % requires constructing new hydrocracking plants designed for pressures up to 25 – 30 MPa [8], but only production of hydrocracking reactors for operating under a pressure of less than 15 MPa are produced in Russia [9].

The concentration of aromatic hydrocarbons in fuels can also be reduced to the required level by extraction with selective solvents [10]. However, the use of such comparatively highly selective and high-boiling extractives as sulfolane, di- and triethylene glycol, and propylene carbonate, proposed for dearomatization of kerosene [11] and diesel [12] fractions, is complicated by the impossibility of regenerating them by fractionation, which is due to the formation of azeotropic mixtures with the components of the feedstock.

The extractants used for selective treatment of oil fractions (N-methylpyrrolidone, furfural, phenol) have boiling points close to the components of middle distillates so that complex process schemes and re-extraction methods must be used.

Low-boiling polar organic solvents (acetone, methanol, acetonitrile, etc.) are easily regenerated by

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TABLE 1

Indexes	Jet fuel fraction	Denormalize from Parex unit	Hydrotreated diesel fuel fraction	Atmospheric gasoil
Distillation, °C				
IBP	140	218	222	257
10%	166	226	244	290
30%	178	245	262	307
50%	190	260	289	316
70%	201	274	315	327
90%	222	286	360	360
EP	239	300	375	390
Refractive index	1.4417	1.4656	1.4700	1.4609
Density at 20°C, kg/m ³	791	839	841.4	862.2
Viscosity, mm ² /sec				
at 20°C	1.43	—	6.22	11.1
at 50°C	6	—	2.97	4.69
Concentration, wt. %				
aromatic hydrocarbons	23.3	27.5	27.1	29.45
sulfur	0.9	—	0.03	1
Aromaticity factor	0.104	0.111	0.122	0.132

fractionation, but have comparatively low group selectivity with respect to aromatic hydrocarbons [13] and a low density, which complicates separation of extract and raffinate phases.

Extraction with these solvents, even on addition of water to increase the selectivity, does not guarantee a high separation factor and production of highly concentrated aromatic extracts. In dearomatization of heavy gasoline and kerosene fractions with acetone with 9 – 13 wt. % water, the concentration of aromatic hydrocarbons in the extract is only 38 – 50 wt. % versus a concentration of 15 – 25 wt. % in the feedstock [14].

The concentration of aromatic hydrocarbons in the extract and the separation factor can be increased in extraction with polar and nonpolar washing solvents, where pentane was selected as such a solvent. The role of pentane is similar to the role of recirculated products in units for extraction of C₆ – C₈ aromatic hydrocarbons from reforming catalyzate; pentane dissolves better in a polar solvent than the saturated hydrocarbons of middle distillates and displaces them from the extract phase.

As determined in studying liquid-liquid phase equilibrium in the model systems decane-*sec*-butylbenzene-polar solvent (acetonitrile or 2-methoxyethanol), in the presence of pentane, the slope of the nodes changes and the binodal curve is shifted to the apex of the triangular diagram corresponding to the polar solvent [15, 16]. This causes an increase in the separation factors, distribution factors, and concentration of aromatic hydrocarbons in the extract remaining after removal of the solvents from the extract phase by fractionation.

In addition, pentane decreases the density of the raffinate phase, which allows using low-density extractants – acetone and acetonitrile. In this case, the difference in the phase densities becomes sufficient (100 kg/m³ and higher) for rapid separation of the system. Pentane, which has a lower viscosity than the polar extractant and feedstock, also decreases the viscosity of the system, which increases the efficiency of the plates in the extraction column and number of theoretical extraction stages.

Extraction of aromatic hydrocarbons from the jet fuel fraction with aqueous acetone [17], from the diesel

TABLE 2

Indexes	Extraction of aromatic hydrocarbons from					
	jet fuel fraction with acetone* and pentane	Parex unit denormalize with 2-methoxyethanol** and pentane	hydrotreated diesel fuel fraction		atmospheric gasoil	
			with 2-methoxyethanol* and pentane	with acetonitrile and pentane	with acetonitrile*** and pentane	with dimethylacetamide*** and pentane
<i>Process conditions</i>						
Concentration of water in polar solvent, wt. %	20	5	3	2	3	3
Pentane: feedstock (wt.)	0.5:1	-/0.75:1	0.75:1	1:1	1.5:1	1.5:1
Temperature, °C	25	40/40	20	30	30	30
Number of theoretical stages	5	5/5	3	5	5	5
Yield of raffinate, wt. %	88	67.8/72.3	86.4	83	78.8	75.6
<i>Characteristics of raffinate</i>						
Refractive index n_D^{20}	1.4381	1.4560/1.4508	1.4641	1.4610	1.4682	1.4642
Density at 20°C, kg/m ³	784	823/818	835.6	828.9	—	836.2
Viscosity, mm ² /sec						
at 20°C	1.40	—	6.04	6.00	—	10.18
at 50°C	5.04****	—	3.13	3.04	—	4.57
Concentration, wt. %						
aromatic hydrocarbons	13.1	11/3.2	18.2	14.3	14.2	9.64
sulfur	0.12	—	0.016	0.003	—	0.24
Aromaticity factor	0.085	-/0.022	0.085	—	—	—
<i>Characteristics of extract</i>						
Refractive index n_D^{20}	1.4872	1.5010/1.5060	1.5173	1.5178	1.5450	1.5640
Density at 20°C, kg/m ³	842	873/895	921.8	922.7	—	956.9
Concentration, wt. %						
aromatic hydrocarbons	98.1	62.8/89.6	83.9	89.8	86.1	90.8
sulfur	6.62	—	0.12	0.16	—	3.35
Degree of extraction of aromatic hydrocarbons, wt. %	50.5	73.5/90.3	42	56.2	62	75.3
Aromaticity factor	—	0.335/0.373	0.359	—	—	0.49
Notes. * For a solvent : feedstock weight ratio of 3:1. ** In the numerator: for a solvent : feedstock weight ratio of 3.46:1; in the denominator: 5.77:1. *** For a solvent : feedstock weight ratio of 5:1. **** At -40°C.						

fraction with acetonitrile and 2-methoxyethanol [18], from the 200 – 320°C dewaxed fraction (denormalize: product of removal or conversion of straight-chain paraffins) with 2-methoxyethanol [19], and from atmospheric gasoil with acetonitrile and dimethylacetamide was investigated using pentane as the washing solvent.

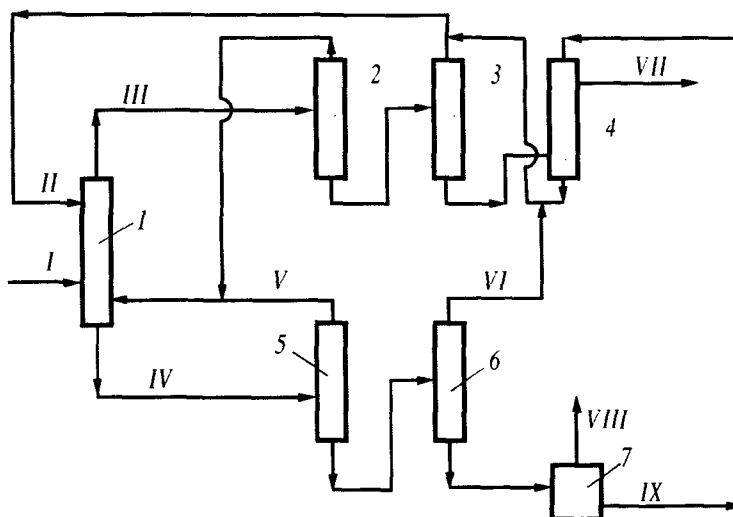


Fig. 1. Skeleton scheme of extraction of aromatic hydrocarbons from the jet fuel fraction with aqueous acetone and pentane: 1) extractor; 2, 3) fractionation columns for regeneration of pentane and acetone from the raffinate phase; 4) column for aqueous washing of acetone from raffinate; 5, 6) fractionation columns for regeneration of pentane and acetone from extract phase; 7) separator; I) feedstock; II) aqueous acetone; III) raffinate phase; IV) extract phase; V) pentane; VI) acetone; VII) raffinate; VIII) extract; IX) water.

Elimination of formation of azeotropes with the components of the feedstock was the condition for selection of selective solvents for each type of feedstock [20]. Of the above solvents, only acetone for the jet fuel fraction containing C_8 hydrocarbons and acetonitrile and 2-methoxyethanol for the diesel fraction and denormalize with C_{10} hydrocarbons satisfy this condition. For atmospheric gasoil containing C_{13} saturated hydrocarbons, a higher-boiling solvent, dimethylacetamide, can be used.

The investigated middle distillates obtained at the Kirishinefteorgsintez Industrial Association are characterized in Table 1. The aromaticity factor f_a , which characterizes the fraction of aromatic carbon atoms in an "average molecule" in the fraction, was calculated with data from the ^{13}C NMR spectra obtained on a Bruker AM-500 NMR spectrometer.

The jet and diesel fuel fractions and the denormalize and atmospheric gasoil with distillation similar to the diesel fraction do not satisfy foreign and future Russian environmental requirements. The smoke point of the jet fuel fraction is 19 mm, which is also much lower than the required values (25 – 26 mm).

The parameters for extraction of aromatic hydrocarbons from the different fractions and the results of the process are reported in Table 2. In extraction from denormalize from a Parex unit, addition of a washing solvent – pentane – significantly increases the concentration of aromatic hydrocarbons in the extract and the degree of their extraction, increases the yield of raffinate, and decreases the concentration of aromatic hydrocarbons in the raffinate to a level corresponding to the most rigorous environmental requirements for diesel fuels. However, the ratio of 2-methoxyethanol to denormalize was increased from 3:1 to 5:1 (vol.) or from 3.46:1 to 5.77:1 (wt.) to increase the degree of extraction of aromatic hydrocarbons.

Organosulfur compounds are removed even more efficiently in extraction of aromatic hydrocarbons from the jet fuel fraction: the degree of extraction is 88.3 wt. %. The raffinate obtained corresponds to TS-1 jet fuel without hydrotreatment with respect to the concentration of sulfur and to both TS-1 and Jet A-1 with respect to the smoke point (30 mm). It also satisfies the other requirements for TS-1 jet fuel – with respect to the kinematic viscosity, density, distillation, flash point (closed cup) (34°C), and the initial crystallization temperature (below –67°C).

The process skeleton scheme of extraction of aromatic hydrocarbons from the jet fuel fraction is shown in Fig. 1. The pentane and acetone from the raffinate and extract phases can be regenerated by fractionation. The

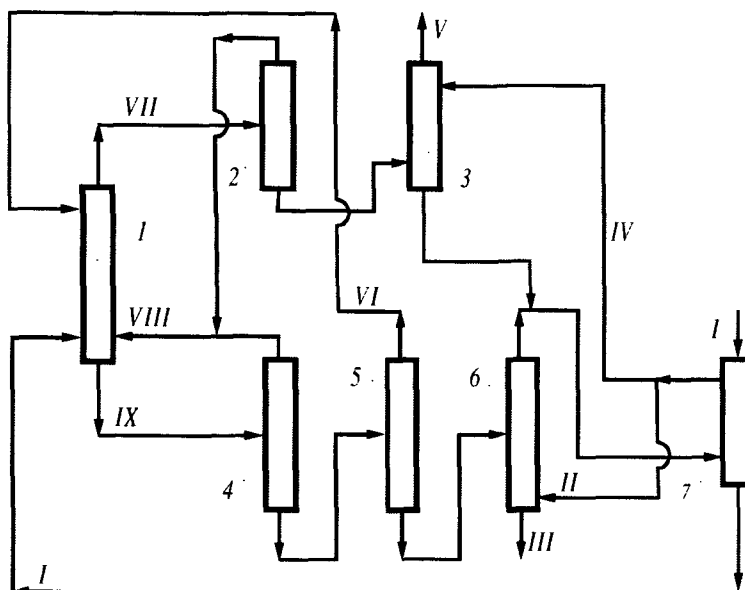


Fig. 2. Skeleton scheme of extraction of aromatic hydrocarbons from middle distillates with 2-methoxyethanol and pentane: 1) extractor; 2, 4) pentane fractionation column; 3) extractor for aqueous washing of 2-methoxyethanol from raffinate phase; 5, 6) fractionation columns for regeneration of 2-methoxyethanol; 7) 2-methoxyethanol absorber; I) feedstock; II) livesteam; III) extract; IV) water; V) raffinate; VI) aqueous 2-methoxyethanol; VII) raffinate phase; VIII) pentane; IX) extract phase.

water remaining in the extract phase after distillation of pentane and acetone is separated from the extract in a separator and used as extractant for the small amount of acetone remaining in the raffinate. When the proposed scheme is used, a closed water cycle is executed and no power has to be consumed for evaporating the water contained in the aqueous acetone.

After hydrotreatment, the separated extract can be used for production of aromatic solvents of the Nefras AR-120/200 type, the petroleum solvents Solvesso 100 and Solvesso 150, widely used in paint and varnish coatings, detergent compositions, solvents for extraction of metals, adhesives, developers, and in compositions for removal of tar-asphaltene and paraffin deposits in oil field equipment [21].

A high-quality detergent mixture of sulfonaphthenic acids with a high concentration of sulfonic acids, an effective industrial detergent, can be obtained by sulfonation of the extract without preliminary hydrotreatment. This detergent is also the base for PO-1 foaming agent used in extinguishing fires. Alkylaromatic lubricants can be obtained by alkylation of the extract with olefins.

Denormalizate from Parex units is a higher-boiling fraction than the jet fuel fraction with a high concentration of aromatic hydrocarbons due to removal of liquid *n*-paraffins by adsorption on zeolites. The saturated hydrocarbons in denormalizate are represented by naphthenes and isoparaffins which are more soluble in polar extractants than *n*-paraffins.

For this reason, it is more difficult to extract aromatic hydrocarbons from denormalizates than from mixtures with *n*-paraffins or from straight-run fractions with a high concentration of them. Extraction was thus conducted with a more selective solvent – 2-methoxyethanol, with a high ratio of both the polar extractant and pentane with the feedstock.

The skeleton process scheme for extraction of aromatic hydrocarbons from middle distillates (Parex unit denormalizate or diesel fraction) with 2-methoxyethanol and pentane is shown in Fig. 2. Pentane is easily regenerated from the equilibrium phases by fractionation. Regeneration of 2-methoxyethanol from the raffinate phase is possible by re-extraction with water. Most of the 2-methoxyethanol can be removed from the extract phase by simple fractionation, and the residual solvent can be removed by fractionation with live steam. It is

recommended that 2-methoxyethanol from a mixture with water vapors be absorbed by the feedstock.

In extraction of aromatic hydrocarbons from hydrotreated diesel fraction, the best results are obtained by using acetonitrile with 2 wt. % water and pentane. The raffinate obtained satisfies the requirements for DLECh-V fuel on all indexes. Raffinate containing less than 10 wt. % aromatic hydrocarbons and satisfying the environmental requirements for foreign diesel fuels can be obtained by increasing the ratio of acetonitrile and feedstock.

With respect to the concentration of sulfur, 0.003 wt. %, the raffinate obtained with a 3:1 ratio of acetonitrile to feedstock satisfies the requirements for diesel fuel for urban conditions used, for example, in Great Britain and containing less than 0.005 wt. % sulfur [22]. The skeleton process scheme of extraction of aromatic hydrocarbons by acetonitrile with pentane is similar to the one shown in Fig. 2.

The aromatic extract separated from the denormalizate is more efficient as a hydrocarbon base for cutting fluids for industrial media than as diesel fuel: the running time for a lubricant film using the extract is two times lower. The detergent power of dissolving-emulsifying agents based on the aromatic extract obtained from denormalizate is higher than for the corresponding technical detergents based on *p*-xylene [23].

The extracts separated from the denormalizate and diesel fraction can be used for manufacturing aromatic solvents of the Nefras AR 150-300, Solvesso 200, and Cyclosol 73 types, widely used in detergents, paints and varnishes, and solvents for pesticides, for extraction of oil, as collector reagents in flotation of coals and other mineral resources, etc. [21].

In extraction of aromatic hydrocarbons from atmospheric gasoil using dimethylacetamide with pentane, better results were obtained than with acetonitrile (see Table 2). This is due to the higher selectivity of dimethylacetamide [13], which allows obtaining a raffinate that satisfies the environmental requirements for diesel fuel with respect to the aromatic hydrocarbon content for a moderate ratio with the feedstock. When atmospheric gasoil is used as catalytic cracking or hydrocracking feedstock, it is also important to reduce the aromatic hydrocarbon content to reduce carbonization and increase the yield of naphtha fractions [24, 25].

Extraction of aromatic hydrocarbons from middle distillates with low-boiling selective solvents and pentane thus allows obtaining environmentally clean jet and diesel fuels and highly concentrated aromatic extracts with comparatively low ratios of solvents and feedstock.

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