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RESEARCH INTO KEROSENE FRACTION DEAROMATIZATION PROCESS BY MEANS OF ION-LIQUID EXTRACTION

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Abstract: *In paper the results of extraction purification of the kerosene fractions with use of ionic liquid based on acetic acid as a selective solvent have been presented. The influence of various factors on process of the selective purification has been investigated and the optimal conditions of dearomatization have been determined. The advantage of ion-liquid extraction dearomatization of the kerosene fractions in comparison with acidic-contact purification has been shown.*
Keywords*: kerosene fraction, extraction purification, ionic liquid, extract, raffinate, dearomatization*
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Introduction

The kerosene is one of the widely used products in the oil refining industry prepared by direct oil distillation or rectification.

Depending on the area of application, specific requirements are complied with physical and chemical properties of kerosene. In particular, the aviation kerosene is meant to have anti-wear and low-temperature properties, high specific combustion heat and thermal-oxidative stability as well. It should be noted that the technical kerosene is used as a raw material for preparation of ethylene, propylene and aromatic hydrocarbons by pyrolysis method. In everyday life, the kerosene is mainly used in kerosene lamps, kitchen stoves (kerogaz, kerosene stove, primus) as a means for cleaning and washing, degreasing composition, and it is desirable that the composition does not contain carcinogenic substances, primarily aromatic hydrocarbons.

Consequently, to remove carcinogenic substances, including aromatic hydrocarbons, the kerosene, if necessary, is subjected to selective purification.

Depending on extraction place and conditions of the oil distillation in the once-run kerosene fraction, the content of aromatic hydrocarbons varies in the range of 14-35% mass.

An industrial method of decrease in the concentration of aromatic hydrocarbons in the kerosene composition is the method of hydropurification, or acidic-contact purification [1-3]. There are also known the methods of extraction purification of the kerosene with the use of a number of organic compounds – sulfolan, phenol, morpholine, furfural, N-methylpyrrolidone, etc. as a selective solvent [4-6].

In recent years, with the aggravation of ecological situation in order to create ecologically safe technologies, a substitution of toxic organic solvents with ionic liquids in line with "green chemistry" requirements is one of the topical issues of oil refining [7-10].

In the paper, the results of research into selective purification of the kerosene fraction through the use of extraction method by means of ionic liquid – N-methylpyrrolidone acetate synthesized by interaction of acetic acid and N-

methylpyrrolidone as a selective solvent were presented [11].

Experimental part

The process of selective purification of the studied kerosene fractions was carried out at different mass ratios of ionic liquid to raw material one-stage, and also in stages at a temperature of 20-25 ° C. The experiments were carried out in a three-necked flask equipped with a mechanical stirrer and a thermometer. At the end of the extraction process, the raffinate phase was separated from the extract solution by settling for 30 minutes, and the upper raffinate phase was separated by draining the lower extract phase.

Discussion of the results

High efficiency of the use of N-methylpyrrolidoneacetate as a selective solvent in the processes of extraction purification of oil fractions, in particular, in the purification processes of diesel distillate of various composition [12, 13], oily distillates of different viscosity [14, 15],etc. was shown by means of systematic investigation cycle carried out at IPCP ANAS.

In the course of the analysis, three samples of kerosene fraction differing with boiling ranges and content of aromatic hydrocarbons were used as raw material (Table 1).

Table 1. Physical-chemical properties of kerosene fractions

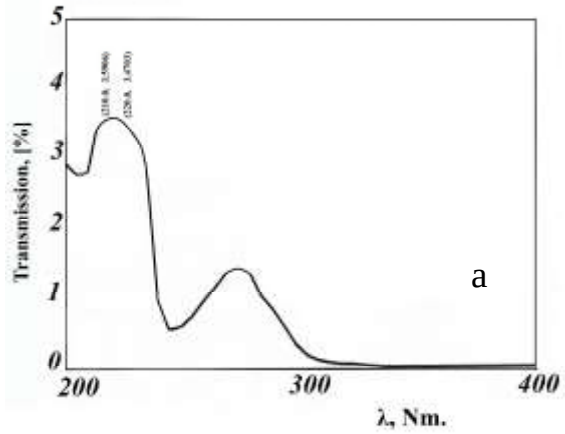
Name of indices	Kerosene fractions		
	Samp. № 1	Samp. № 2.	Samp. № 3.
Density at 20°C, kg/m^3	0,796	0,775	0,780
Fractional composition: initial boiling temperature, °C	136	145	185
10%- distilled at	162	170	195
50%- distilled at	190	200	220
98%- distilled at	237	245	245
End boiling	240	250	250
Molecular weight	153	134,4	139
Mass fraction of aromatic hydrocarbons, %	12	16,5	17
Acidity, mg KOH per 100cm^3 of fuel	0.04	0.042	0.045
Refractive index at 20°C	1.440	1.442	1.445

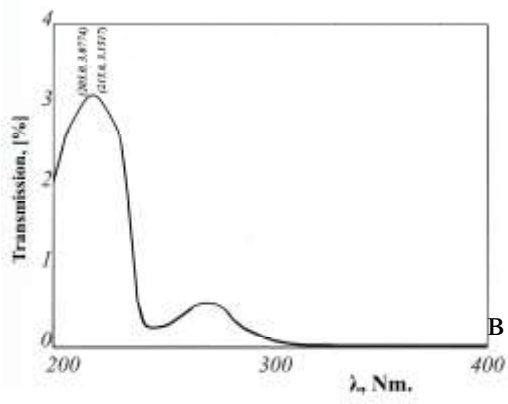
The group hydrocarbon composition of the studied kerosene fractions was determined by UV spectral analysis carried out on a JENWAY UV / Vis 6850 spectrophotometer. In the spectra of the absorption band with wavelengths 195 - 215; 220; 255 and 275 nm correspond to benzene, naphthalene, phenanthrene and anthracene hydrocarbons. The quantitative composition of the investigated samples of the kerosene fractions has been calculated on known method [16].

It was established that the kerosene fraction with a boiling point range of 145-250 ° C is characterized by a relatively high content of monocyclic aromatic hydrocarbons - benzene derivatives, as well as bicyclic, naphthalene hydrocarbons. The kerosene fraction with a boiling point of 136-240 ° C is characterized by a low content of anthracene hydrocarbons - only 0.04% mass (Table 2, Fig. 1).

Table 2. Group hydrocarbon composition of analyzed kerosene fractions

Samples of kerosene	Boiling ranges, °C	Benzene derivatives, %	Naphthalenes, %	Phenanthrenes, %	Anthracenes, %	Total aromatics, %
№ 1	136-240	6.3	5.7	1.0	0.04	13.22
№ 2	145-250	9.41	6.13	2.62	1.04	19.2
№ 3	185-250	8.33	5.76	2.10	1.12	17.3





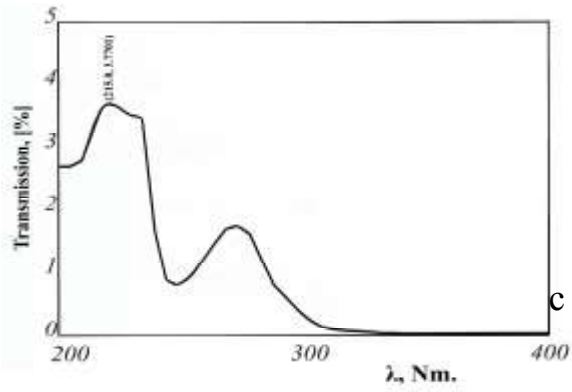


Fig. 1. UV-spectra of samples of initial kerosene fractions; with boiling temperature of 136-240°C- (a), 145-250°C- (b) and 185-250°C- (c)

Removal of aromatic hydrocarbons from the composition of analyzed samples of kerosene fractions in keeping with ion-liquid extraction purification was carried out both in one-stage and step-by-step. The extraction purification of kerosene samples in one stage was carried out at a room temperature (22-25°C) with mass ratio of ionic liquid to raw materials equal to 2.5:1.0 and contact time of components for 2 h. In this case, a yield of raffinate varied in the interval 81.2-86.4% mass, a residual content of aromatic hydrocarbons in the composition of the prepared raffinates determined by means of sulphurization on GOST 6994-74 was 1.0-2.0% mass (Table 3).

Table 3. Dependence of degree of dearomatization of the kerosene on conditions of extraction

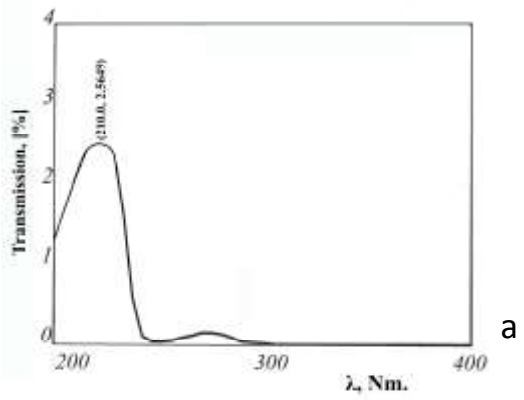
Kerosene fractions	Mass ration IL:kerosene	Quantity of stages	Contact time of components, hour	Yield, % mass	Indices of raffinate		
					n_D^{20}	d_4^{20}	Aromatics content

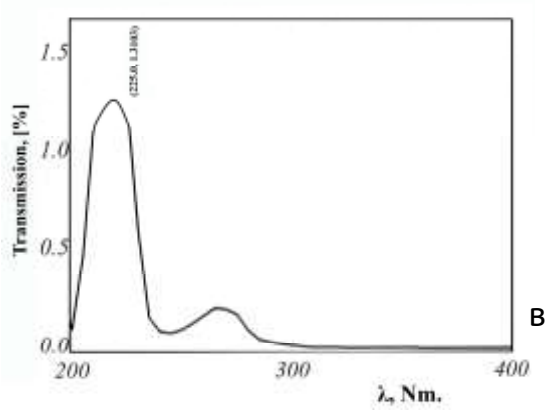
Sample №1	2.5:1	I	2.1	86.4	0.772	1.4350	1.0
	1:1	II	1.0	87.3	0.7715	1.4355	-
	1:1		1.0	85.0	0.7709	1.4348	1.0
Sample №2	2,5:1	I	2.0	82.1	0.7730	1.4363	2.0
	1:1	II	1.0	85.0	0.7718	1.4365	-
	1:1		1,0	81.0	0.7709	1.4353	1.0
	1:1	III	1.0	84.3	0.7720	1.4361	-
	1:1		1.0	81.0	0.7700	1.4350	-
	1:1		1.0	80.0	0.7694	1.4335	2.0
Sample №3	2,5:1	I	2.0	81.2	0.7755	1.4364	2.0
	1:1	II	1.0	85.3	0.7771	1.4358	6.0
	1:1		1.0	82.1	0.7760	1.4340	4.0

The purification of the kerosene fractions step-by-step has been also carried out at temperature 22-25°C, at equal weight ratio of extractant to raw materials and contact time of components for 1 h at each stage. In this case a residual content of aromatic hydrocarbons in purified kerosene depending on composition of the initial raw material is decreased to 1.0-4.0% mass

Determination of group hydrocarbon composition made of raffinate through UV-spectral analysis revealed that at ion-extraction purification of kerosene fractions was followed by a complete removal of anthracenes contained in raw material.

At one stage treatment of the kerosene with boiling ranges 145-250°C (samp. 2) with 2.5 multiple excess, and also at three-stage treatment with equal quantity of extractant at each stage, it is observed a complete removal from the composition and phenanthrene (Table 4, Fig. 2).





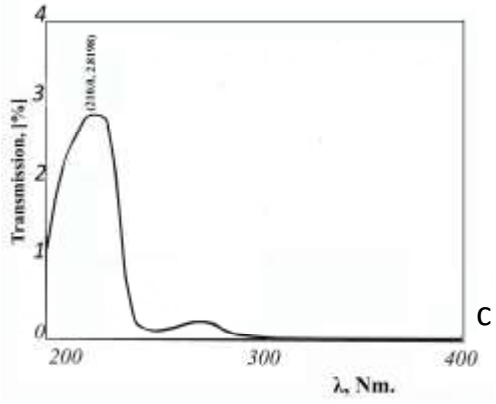


Fig. 2. UV-spectra of kerosene fractions with boiling range at 145-250°C after one- (a); two- (b) and three-stage (c) purification by ionic liquid

As quantity of the stages of extraction purification of raw materials with ionic liquid grows, there is a drop both in residual quantity of benzene derivatives and total quantity of aromatic hydrocarbons in raffinate (Fig. 3).

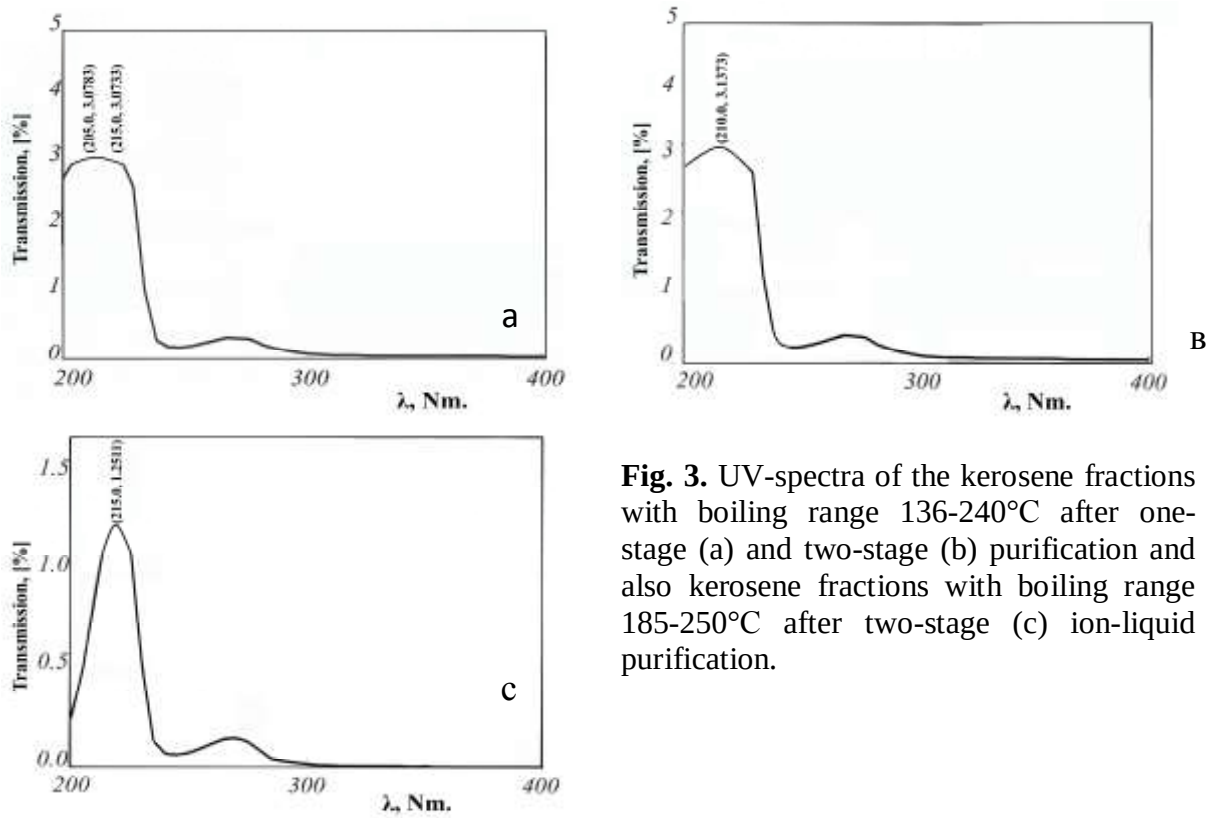


Fig. 3. UV-spectra of the kerosene fractions with boiling range 136-240°C after one-stage (a) and two-stage (b) purification and also kerosene fractions with boiling range 185-250°C after two-stage (c) ion-liquid purification.

After two-stage selective purification the kerosene fraction with boiling ranges at 136-240°C was characterized by the lowest content of residual aromatics (0.62% mass) (Table 4). According to UV-spectral analysis, the content of monocyclic aromatics compounds in raffinate was 0.41% mass against 6.3% mass in the initial kerosene, bicyclic 0.17% mass against 5.7%, tricyclic - phenanthrene 0.04% against 1.0% mass, so anthracenes were completely removed.

To compare, the dearomatization of kerosene fractions with boiling ranges at 145-250°C and 185-250°C was also carried out by the method of acidic-contact purification. The UV-spectral analysis of the prepared raffinates shows comparative results of acidic-contact and ion-liquid purification. The content of residual aromatics in the prepared raffinates was 2.14% and 0.97% mass, respectively (Fig. 4).

Table 4. Group hydrocarbon composition of aromatic hydrocarbons of kerosene fractions before and after ion-liquid extraction purification

Kerosene fractions	Molecular weight of sample	Group composition of aromatic hydrocarbons, %				
		benzene derivatives	naphthalenes	phenanthrenes	anthracenes	total content of aromatics

Sample №1 purification in I stage purification in II stage	153.0 147.0 144.0	6.3 1.1 0.41	5.7 0.42 0.17	1.0 0.15 0.04	0.04 - -	13.22 1.68 0.62
Sample №2 purification in I stage purification in II stage purification in III stage	134.4 134.0 133.5 133.5	9.41 0.44 0.8 0.5	6.13 0.31 0.9 0.4	2.62 traces traces traces	1.04 traces traces traces	19.2 0.75 1.7 0.9
Sample №3 purification in II stage	139.0 138.7	8.33 1.0	5.76 0.6	2.1 traces	1.12 traces	17.31 1.6
*Sample №2	130.0	1.2	0.8	0.14	-	2.14
*Sample №3	140.0	0.91	0.052	-	-	0.96

*Note: samples purified by a method of acidic-contact purification

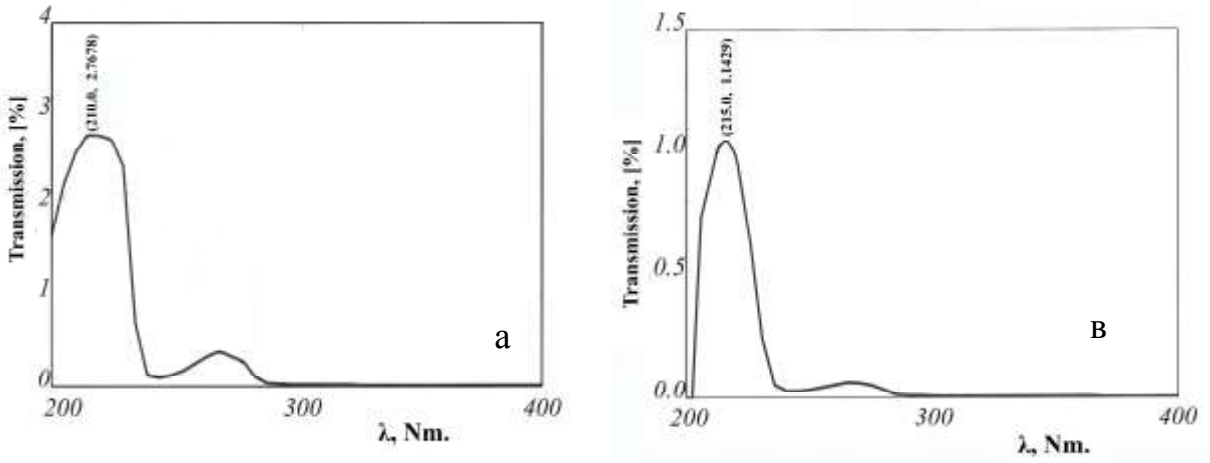


Fig. 4. UV-spectra of the kerosene fractions with boiling range 145-250°C (a) and 185-250°C (b) after acidic-contact purification

Conclusion

Thus, the conditions of dearomatization of the kerosene fractions by a method of extraction purification with use of N-methylpyrrolidone acetate as an extractant of ionic liquid have been determined by carried out investigations.

The efficiency and advantage of ion-liquid extraction of the kerosene fractions is determined as by simplicity of the process, as well as by possibility of regeneration of ionic liquid and its recycling as an extractant without considerable decrease of the efficiency. The use of ion-liquid extractant favors the elimination of the ecological problems arising from acidic-contact treatment: formation of non-utilizable products – acid tar and waste water polluting the environment.

References

1. Yurkina O.V., Kraev Yu.L., De Vekki A.V. Hydroaromatization of kerosene fractions. *Oil Processing and Pertochemistry*. 2003, no. 1, pp. 24-26.
2. Kovalenko Yu.A. Investigation of the process of hydrotreating the kerosene fraction. *Jurnal Mirovaya Nauka.* 2018, no. 2 (11), pp. 27-29. (In Russian).
3. Mohammad F. Abid, Shakir M. Ahmed, Waleed H. Abohameed, Salah M. Ali. Study on hydrodesulfurization of a mixture of middle distillates. *Arabian Journal For*

Science And Engineering. 2018, vol. 43, issue 11, pp. 5837–5850.
4. Somov V.E., Zalishchevsky G.D., Gaile A.A., et al. Method for the extraction of aromatic hydrocarbons from a kerosene fraction. Russian patent, 2150450, 2000
5. Knyazkov A.L., Nikitin A.A., Lagutenko N.M., Karasev E.N., Bubnov M.A., Borisanov D.V. The method of demercaptanization of kerosene fractions. Russian patent, 2436838, 2011.
6. Extraction dearomatization of oil fractions. Ed. A.A. Gaile, and V.E. Somonova. St. Petersburg: Publishing house St. Petersburg University, 2002, 324 p.
7. Pletnev I.V., Smirnova S.V., Zernov L.V. The use of ionic liquids in extraction. *Russian Journal of General Chemistry*. 2004, vol. 48, no. 5, pp. 51-58.
8. Jonchen E., Wasserscheid P., Jess A. Deep desulfiration of oil refinery streams by extraction with ionic liquids. *Green Chem.*, 2004, no. 7, pp. 316-322.
9. Reshetov S.A., Frolkova A.K. Ionic liquids as separating agents. *Theoretical Foundations of Chemical Technology.* 2009, vol. 4, no. 3, pp. 27-44.
10. Azizov A.G., Asadov S.G., Akhmedova G.A. Ionic liquids and their use. Baku: Elm Publ., 2010, 578 c.
11. Ibragimova M.D., Nagiev V.A., Pashaeva Z.N., Seidova S.A., Abdullaeva F.M., Akhmedbekova S.F., Abdullaeva H.A. Synthesis of ionic liquids based on formic and acetic acid and physicochemical methods for their study. *Journal of Caucasus University,* 2016, no. 1, pp. 101-107.(In Azerbaijan).
12. Ibragimova M.D., Seidova S.A., Aliyeva S.G., Huseynov G.D., Nagiev V.A., Halilov A.B., Akhmedbekova S.F., Huseynova S.Sh. Extraction refinement of diesel distillate and narrow fractions based on it. *Azerb.Chem.Journal.*, 2018, no. 4, pp. 60-68.
13. Ibragimova M.D., Seidova S.A., Huseynov G.J., Abbasov V.M., Nagiev V.A., Alieva S.A., Dzhafarova R.A., Akhmedbekova S.F. Study of the structural-group composition of raffinate and extract obtained by dearomatization of a mixture of straight-run diesel fraction with products of secondary oil refining. *Oil Processing and Pertochemistry.* 2018, no. 8, pp. 14-20.
14. Ibragimova M.D., Abbasov V.M., Aliyeva S.G., Khalilov A.B., Guseinov G.D., Nagiyev V.A., Seidova S.A., Alizade A.E. Selective purification of oil fractions using an ionic liquid based on N-methylpyrrolidone acetate as an extractant. *Processes of Petrochemistry and Oil Refining.* 2018, no. 3, pp. 302-314.
15. Mirzoeva L.M., Ibragimova M.D., Nagiev V.A., Yunusov S.G., Andryushchenko N.K., Guseinov G.D. The use of ionic liquids for the desulfurization of gasoline fractions. *Chemistry and Technology of Fuels and Oils*. 2018, vol. 608, no. 4, pp. 28-32.
16. Mamedov A.P., Dzhafarova R.A., Najafova M.A., Salmanova Ch.K. Spectral-luminescent properties, EPR and photochemistry of petroleum products. Baku: Elm Publ. 2014 .- 328 p.

KEROSİN FRAKSİYASININ İON MAYE EKSTRAKSİYA ÜSULU İLƏ AROMATİKSİZLƏŞDİRİLMƏSİ PROSESİNİN TƏDQİQİ

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Məqalədə seçici həlledici kimi sirkə turşusu əsasında sintez edilmiş ion maye tərkibdən istifadə etməklə kerosin fraksiyasının ekstraksiya üsulu ilə təmizlənməsi prosesinin nəticələri əks olunmuşdur. Ekstraksiya prosesinə müxtəlif faktorların təsiri tədqiq olunmuş və aromatiksizləşdirmə prosesinin optimal şəraiti müəyyən edilmişdir. Aparılan tədqiqatlar əsasında ion-maye ekstraksiya üsulu ilə kerosin fraksiyasının aromatiksizləşdirmə prosesinin turşu-kontakt üsulu ilə təmizlənmə prosesindən effektiv olduğu müəyyən edilmişdir.

Açar sözləri: *kerosin fraksiyaları, ekstraksiya üsulu ilə təmizlənmə, ion maye, ekstrakt, rafinat, aromatiksizləşmə*

ИССЛЕДОВАНИЕ ПРОЦЕССА ДЕАРОМАТИЗАЦИИ КЕРОСИНОВОЙ ФРАКЦИИ МЕТОДОМ ИОННО-ЖИДКОСТНОЙ ЭКСТРАКЦИИ

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В статье изложены результаты экстракционной очистки керосиновых фракций с использованием в качестве избирательного растворителя ионной жидкости на основе уксусной кислоты. Исследовано влияние различных факторов на процесс селективной очистки и определены оптимальные условия деароматизации. Показано преимущество ионно-жидкостной экстракционной деароматизации керосиновых фракций по сравнению с кислотно-контактной очисткой.

Ключевые слова: *керосиновая фракция, экстракционная очистка, ионная жидкость, экстракт, рафинат, деароматизация*