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ABSTRACT

of the dissertation for the degree of doctors of philosophy

RESEARCH OF THE PROCESS OF ION-LIQUID EXTRACTION DEAROMATIZATION AND DESULFURIZATION OF DIESEL DISTILLATE

Specialty: 3321.01– Oil, gas and coal processing technology

Field of science: Chemistry

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GENERAL DESCRIPTION OF WORK

Relevance of the topic: One of the global problems facing humanity in the XXI century is environmental protection. In this regard, the creation of environmentally friendly production of organic synthesis, as well as oil refining, meeting the requirements of "green chemistry" is relevant.

The development of the oil refining industry, which is a strategic task of the domestic economy, is determined by both an increase in the depth of oil refining and an increase in the volume and quality indicators of manufactured commodity oil products.

Among all types of petroleum products, motor fuels, in particular diesel fuel, occupy a special place, since without fuel for diesel engines it is impossible to imagine the existing growth in the volume of fleets - freight, rail, agricultural machinery and, consequently, with an increase in the production of petroleum products, diesel fuel production is also growing, as all over the world, and in our republic. In 2018, 1 million 956,3 thousand tons of diesel fuel was produced in Azerbaijan[1]. According to statistics, in the january-february months of 2019, the production of petroleum products in the republic increased by 0,2% compared to the same period last year and amounted to 461,136 million tons, including diesel fuel by 3,4% (339,4 thousand tons)[2].

With the growth of diesel fuel consumption, at the same time, there is a tightening of requirements for its quality. Particular attention is paid to the content of sulfur-containing compounds in the fuel composition, aromatic, in particular polycyclic aromatic hydrocarbons, which is associated with the toxicity of their combustion products, as well as an indicator of the cetane number of the fuel.

Known methods for improving the quality of diesel fuels are based mainly on hydrogenation, adsorption and oxidation processes, as well as on extraction cleaning methods. Hydrogenation

[1] Azərbaycan Energetikası: (statistik məcmuə) / tərt.ed. V.Məmmədov – Bakı: 9 №-li kiçik müəssə, – 2018. – 160 s.
[2] URL: http://interfax.az/view/760611

purification methods require the use of expensive catalysts, a large consumption of hydrogen, harsh process conditions - high temperature and pressure. Adsorption and oxidation methods of cleaning diesel fuel are effective only for cleaning low-sulfur diesel fractions. Extraction methods of cleaning are distinguished by the ability to carry out the process at low temperature conditions and atmospheric pressure. However, almost all selective solvents used in liquid extraction processes are phenol, furfural, sulfolane, N-methylpyrrolidone, morpholine, etc. characterized by toxicity, corrosiveness, high dissolving power and relatively low selectivity, which necessitates the development of liquid extraction methods with the selection of more effective, environmentally friendly solvents.

In this aspect, it is of interest to develop processes for cleaning diesel distillates using environmentally safer solvents, which is the subject of the present dissertation.

Purpose of work. The aim of this dissertation work is to develop conditions for producing high-quality diesel fuel that meets the requirements of the European standard by ion-liquid extraction cleaning of diesel distillates of various compositions, in particular the straight-run fraction of diesel distillate produced at the Baku oil refinery named after G. Aliyev, hydrotreated diesel distillate, as well as a mixture of diesel fractions obtained by compounding a diesel distillate with products of secondary oil refining - light coking gas oil or light catalytic cracking gas oil. To achieve this goal, the extraction purification of the above diesel fractions was studied using ionic liquids based on acetic and formic acids as a selective solvent. In particular:

- conditions of dearomatization and desulfurization of straight-run diesel distillate and its narrow fractions are investigated;

-conditions for ennoblement diesel distillate after hydrotreating were investigated;

- the process of dearomatization and desulfurization of a diesel fraction obtained by compounding a diesel distillate with a light gas oil coking or a light gas oil catalytic cracking at a volume ratio of components of 70:30 , respectively was studied;

- technical and economic calculations were carried out to establish the benefits of ion-liquid purification.

Research methods. The reliability of the results obtained is determined by the use of modern methods of analysis in the research: IR, UV, luminescence and chromato-mass spectroscopy, as well as standart methods for analyzing the diesel fraction.

In this work, the following provisions have been protected:

– influence of conditions of ion-liquid extraction purification - temperature, ratio of raw materials to extractant and duration of contact of components on the output and quality of refined diesel fuel;

– the effects of the nature of the ion-liquid extractant, ie cation-anion combination on the efficiency of the extraction purification process of fuel;

– the influence of the fractional composition of diesel distillate on the degree of extraction of undesirable components during ion-liquid extraction cleaning;

– the results of studies of ion-liquid extraction purification of straight-run diesel distillate involving products of secondary oil refining;

– the rationale for the selection of the optimal composition of the ion-liquid extractant for the cleaning process of the diesel fraction.

The scientific novelty of the work.

For the first time, the process of extraction purification of diesel fractions was carried out using an ion-liquid composition as an environmentally friendly solvent. The efficiency and feasibility of ion-liquid extraction purification is shown.

Conditions have been developed for almost complete dearomatization and a decrease in the content of sulfur-containing compounds to 130 ppm by the method of ion-liquid extraction purification of a hydrotreated diesel fraction with a boiling range of 185-364°C obtained from the Baku Oil Refinery named after G. Aliyev.

The conditions have been developed for ion-liquid extraction purification of a straight-run diesel fraction with a boiling range of

191-350°C were obtained to produce diesel fuel with a cetone number of 51 against 45 of the feedstock.

Extractional purification of fractions with boiling limits of 191-250°C; 250-300°C and 300-345°C, isolated by distillation of straight run diesel fraction on the installation of Engler, the possibility and feasibility of ennoblement diesel distillate using N-methylpyrrolidonacetate as an ionic liquid as a selective solvent are shown.

An ion-liquid extraction purification of fractions with boiling limits of 191-300°C and above 300°C, isolated by distillation of straight run diesel fraction and differing in the content of aromatic hydrocarbons and sulfur-containing compounds, is proposed. Compounding the raffinates obtained by ion-liquid extraction purification of the above narrow fractions provides environmentally friendly fuels containing 3% mass of aromatic compounds and 348 ppm of sulfur compounds.

The conditions of ion-liquid extraction purification of a mixture of straight-run diesel distillate and a secondary product are proposed, which ensure the production of diesel fuel that meets the requirements of the European standard.

The practical value of the work.

- the proposed method of ion-liquid extraction cleaning of the diesel fraction provides the possibility of obtaining diesel fuel of improved quality using an environmentally friendly method;
- the effectiveness of the combined method of ion-liquid extraction purification of hydrotreated diesel distillate to obtain almost completely dearomatized diesel fuel is established;
- the technical and economic calculation method established an annual profit of 52 mln AZN for the extraction purification of a mixture of straight-run diesel fraction and light gas oil coking, a product of oil refining by ionic liquid synthesized based on acetic acid and N-methylpyrrolidone;
- the practical significance of the research is also determined by the possibility of repeated reuse of ionic liquid after regeneration.

As you can see, the results can be used to create an environmentally friendly process of extraction purification of oil

fractions for various purposes.

Aprobation work: The main results of the dissertation work were presented at international and national conferences:
The main results of the dissertation work were presented at international and national conferences: International conference on thermophysical and mechanical properties of advanced materials (Cesme-Izmir, 2014); Республиканская научно-практическая конференция, посвященная 100-летию академика С.Д.Мехтиева (Баку, 2014); Müasir biologiya və kimyanın aktual probremləri elmi-praktik konfrans (Gəncə, 2015); "XXI əsrdə ekologiya və torpaqşünaslıq elmlərin aktual problemləri" IV Respublika elmi konfransı (Bakı, 2015); XII Международная научно-практическая конференция «Advances in Science and Technology» (Москва, 2018); Международная научно-практическая конференция «Инновативные перспективы развития нефтепереработки и нефтехимии», посвященная 110-летию академика В.С.Алиева (Баку, 2018); Akademik Murtuza Nağıyevin 110 illik yubileyinə həsr olunmuş "Nağıyev qiraətləri" Beynəlxalq konfransı (Bakı, 2018); Beynəlxalq elmi konfrans "Müasir təbiət və iqtisad elmlərinin aktual problemləri" (Gəncə, 2018); Dedicated to the 96th Anniversary of the National leader of Azerbaijan, Heydar Aliyev «III International scientific conference of young researchers» (Baku, 2019); Ümummilli Lider Heydər Əliyevin anadan olmasının 96-cı ildönümünə həsr olunmuş doktorant, magistrant və gənc tətqiqatçıların «Kimyanın Aktual Problemləri» XIII Beynəlxalq Elmi Konfrans (Bakı, 2019); Международная научная конференция « Актуальные проблемы современной химии», посвященная 90-летию ИНХП имени академика Ю.Г.Мамедалиева (Баку, 2019); Kimya texnologiyası və mühəndisliyinin innovativ inkişaf perspektivləri Beynəlxalq elmi konfrans (Sumqayıt, 2019); Radiation and chemical safety problems «Internation Scientific-Practical» Conference (Baku, 2019).

Place of carrying out of dissertation work. The studies presented in this dissertation were carried out according to the program of scientific research of the Institute of Petrochemical Processes of ANAS 16/2016, 2016-2019 years (State registration

number 0106Az00017).

Published works on the dissertation: On the result of the dissertation, 28 scientific papers were published, of which 14 scientific articles in national and international journals, 14 abstracts.

Personal contribution of the applicant. The applicant was the responsible executor of all stages of work related to the setting of tasks, conducting experimental studies, analyzing the results, as well as the design of publications and dissertations.

Volume of dissertation: The work is presented on 163 pages of computer text and consists of an introduction - 7 pages, four chapters: a literature review –30 pages, a technique for conducting an experiment –14 pages, a discussion of the results (chapters 3 and 4) – 74 pages, conclusions- 2 pages, list of used literature, consisting of 272 bibliographic items – 32 pages. The dissertation includes 32 tables and 25 figures. The volume of dissertation work is 175290 symbols (without tables, figures and references).

In the introduction justifies the relevance of the work, formulates the purpose and objectives of the research, scientific novelty, and practical significance of the work.

The first chapter presents a literature review of the methods used to produce improved quality diesel fuel, as well as the use of ionic liquids in the extraction of undesirable components from the composition of fuels, in particular diesel fuel by extraction cleaning.

The second chapter is devoted to the description of the basic physical and chemical characteristics of raw materials - diesel distillates, as well as ionic liquids used as extractant. The results of determining the critical temperature of dissolution of a mixture of straight-run diesel fraction and light gas oil coking in the studied extractants are presented.

The third chapter is devoted to determining the optimal conditions for ion-liquid extraction purification of hydrotreated diesel fraction, as well as the results of studies on the refinement of straight-run diesel fraction and its narrow fractions with ion-liquid compositions based on formic and acetic acids. The results of IR and UV spectral analyzes of diesel fractions and raffinates obtained on their basis are presented.

The fourth chapter is devoted to the results of extraction purification of a mixture of straight-run diesel fraction and products of secondary oil refining using N-methylpyrrolidonacetate as an ionic liquid extractant. A technical and economic assessment of the extraction treatment of a mixture of straight-run diesel fraction with light gas oil coking is given.

The conclusions present the main results of the work carried out.

MAIN CONTENT OF WORK

In order to improve the environmental situation in recent years, one of the main challenges facing the oil refining industry is the production of high-quality diesel fuel. The use of extraction methods for cleaning the diesel fraction using ionic liquids as solvents, solvents that obey the principles of "green chemistry", is considered a promising way to solve this problem [1,25]. In the process of extraction purification of diesel distillates of various fractional composition, ionic liquids (IL), which differ in a cation-anionic combination, in particular N-methylpyrrolidonformate, N-methylpyrrolidonacetate and morpholinformate, were used as a selective solvent. These ionic liquids are synthesized by a known method by the interaction of an equimolar amount of components at a temperature of 50-60°C and a contact time of 2-3 hours. By the methods of IR and NMR spectral analysis, the structure of the synthesized ionic liquids was confirmed and the main physicochemical properties were determined [4,6].

In the conducted studies, the influence of various factors was studied, in particular, both the conditions of the process of ion-liquid extraction cleaning (temperature, ratio and contact time of components), and the fractional composition of diesel distillates used as raw materials, as well as the anionic-cationic combination of ionic liquids on the efficiency extraction process. It was found that the yield and quality of the raffinate depends on all the above parameters [5,7,9,13,14,17,27].

Ion-liquid extraction purification of hydrotreated diesel fraction

Extraction purification of hydrotreated diesel fraction (HDF) with a boiling point of 185-364°C, containing 16% mass of aromatic and 311 ppm sulfur-containing compounds was carried out using ionic liquids synthesized based on acetic acid and N-methylpyrrolidone (IL-1), formic acid and N-methylpyrrolidone (IL-2), as well as morpholine and formic acid (IL-3). The optimal conditions for the extraction purification of HDF were determined by studying the influence of temperature, the ratio of extractant - IL-1 to raw materials and the contact time of the components (tab.1). The extraction cleaning process was carried out both in one stage and in stages [3,8,9,10,12,15].

Table 1

The dependence of the yield and indicates of diesel fuel on the conditions for the selective purification of hydrotreated diesel fraction with N-methylpyrrolidonacetate ionic liquid

№	Ratio IL: HDF	Temperature, °C	Contact time, h	Raffinate yield, % mass	Degree of dearomatization, % mass	Degree of desulfurization, %mass	d_4^{20}, кg/m^3	n_D^{20}	Kinematic viscosity, at 20°C, mm^2/s	Cetane number
1	1:1	60	3	88,80	62,5	59,9	838	1,4659	5,35	49
2	2:1	60	3	81,34	75,0	54,7	832	1,4634	5,53	51
3	3:1	60	3	73,20	75,0	50,9	829	1,4615	5,8	52
4	1:1	20-25	3	89,00	56,2	53,1	836	1,4639	5,23	50
5	2:1	20-25	3	82,00	81,2	56,6	832	1,4633	5,40	51
6	2:1	20-25	1	80,50	100	58,2	831	1,4616	5,40	52
7	2:1	20-25	0,5	79,60	100	51,5	832	1,4615	5,34	51
8	in stages 1,5:1 1,5:1	60 -	1,5 1,5	80 70,4	- 75,0	- 59,2	- 832	- 1,4634	- 5.38	- 51

It was shown that during one-stage extraction purification of HDF under conditions of a threefold excess of ion-liquid extractant, at a temperature of 60°C and a contact time of components of 3 hours, as compared to the process under similar conditions, in two

stages, the output of the raffinate is relatively high, in particular, at 73,2% mass against 70,4% mass. Under these conditions, with a decrease in the amount of ionic liquid in relation to the feed, the best result was achieved with a twofold excess of extractant to the feed. The raffinate obtained under these conditions is characterized by a relatively high yield (81,34% mass). When the ratio of IL: HDF equal to 2: 1 with a decrease in the extraction temperature from 60°C to 20-25°C and contact time of the components from 3 hours to an hour, the degree of desulfurization increases (58 % mass) and almost complete dearomatization of diesel distillate is achieved (GOST 6994-74). The yield of raffinate is 80,5% mass, the residual sulfur content of 130 ppm (ASTM D- 4294).

Thus, diesel fuel after ion-liquid extraction purification according a number of indicators, such as cetane number, density, kinematic viscosity, to the Euro-5 standard, and twice exceeds the Euro-3 standard in sulfur content.

Under certain optimal conditions, the extraction purification of HDF was carried out using IL-2 and IL-3 as a selective solvent. In this case, a relatively low degree of dearomatization of the raw material was observed, in particular, in the case of IL-2, the degree of dearomatization was 62,5 % mass, in the case of IL-3 it was only 25 % mass (tab. 2).

Table 2

Dependence of the efficiency of the extraction purification of hydrotreated diesel fraction on the composition of the ion-liquid extractant

Ionic liquid	Ratio IL : HDF	Temperature, °C	Contact time, h	Raffinate yield, % mass	Content of aromatic hydrocarbons % mass	Content of sulfur, ppm	d_4^{20}, kg/m^3	n_D^{20}	kinematic viscosity, at 20°C, mm^2/s	Cetane number
İL-1	2:1	20-25	1	80,5	0	130	831	1,46160	5,40	52
İL-2	2:1	20-25	1	83,0	6	114	832	1,4618	5,51	51
İL-3	2:1	20-25	1	92,5	12	161	833	1,4663	5,47	51

In the IR spectra of HDF and raffinate, identical absorption bands are observed. However, in the raffinate, a decrease in the intensity of the absorption band is observed in the region of 1605cm^{-1}, which characterizes the C – C bonds of the substituted benzene ring. On the contrary, an increase in the intensity of the above absorption band is observed in the IR spectrum of the extract, which confirms the selective purification of HDF (fig. 1) [19].

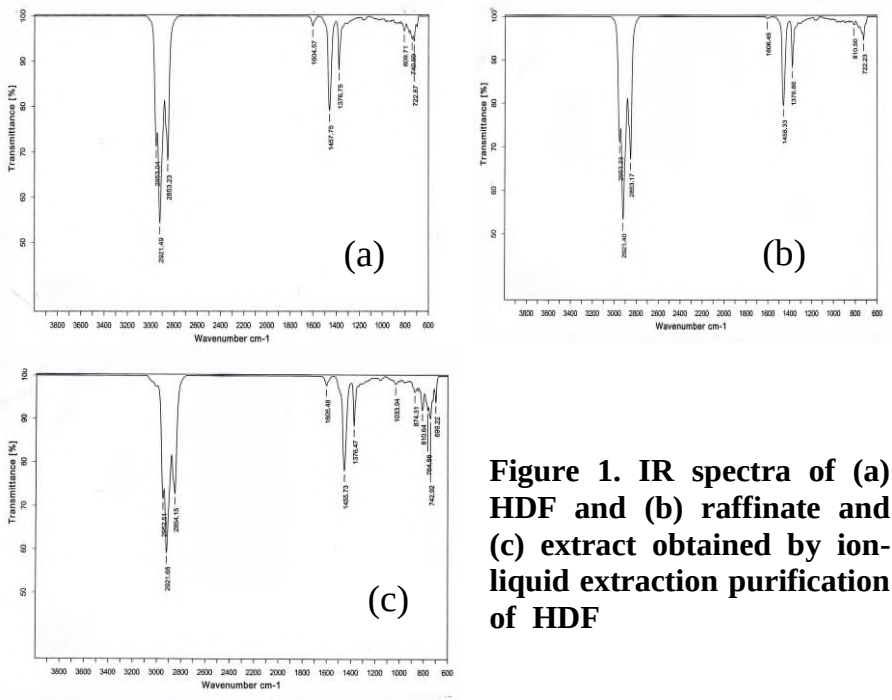

Figure 1. IR spectra of (a) HDF and (b) raffinate and (c) extract obtained by ion-liquid extraction purification of HDF

According to the results of UV spectral analysis, the residual content of aromatic hydrocarbons in the raffinate is 0,62% of the mass versus 18,82% of the mass in the original. The degree of dearomatization is 96,8% of the mass (tab. 3) [26].

Table 3

Results of UV spectral analysis of hydrotreated diesel fraction and raffinate obtained by ion-liquid extraction

Samples	Molecular weight of samples	The concentration of aromatic hydrocarbons,% mass				
		benzene derivatives	Naphthalenes	Phenanthrenes	Anthracenes	The amount of aromatic hydrocarbons
HDF	208	8,54	6,37	3,46	0,45	18,82
Purified by IL	192	0,47	0,15	—	—	0,62

Extraction purification of straight-run diesel distillate and its narrow fractions using ionic liquids as a selective solvent.

Also studied the ion-liquid extraction purification of a straight-run diesel fraction (SDF) with a boiling point of 191-350°C with a content of 12% mass of aromatic and 983 ppm sulfur-containing compounds using IL-1 and IL-3 as an extractant (tab.4) [2,13,16,17,18,22].

During two-stage extraction purification of SDF at an extraction temperature of 20-25°C and a contact time of components of one hour using equal mass amounts of IL-3 at each stage with respect to raw materials, the residual aromatic hydrocarbon content in the obtained raffinate was 5 % mass, sulfur-containing compounds - 483 ppm (yield of raffinate 87,5% mass) against 4 % mass and 470 ppm (yield of raffinate 84,08% mass), respectively, in the case of extraction purification of the specified composition of the distillate with IL-1. The results obtained indicated almost the same extraction ability of IL-3 and IL-1 during the extraction purification of straight-run diesel fraction.

Under similar conditions, the extraction purification of narrow fractions of diesel distillate with a boiling point of 191-300°C (aromatic hydrocarbon content of 10% mass, sulfur-containing compounds of 828 ppm) and above 300°C (aromatic hydrocarbon content of 16% mass, sulfur-containing compounds of 1535 ppm)

obtained by distillation was studied SDF on the installation of Engler with IL-1. Diesel fuel obtained by compounding raffinates based on the separated fractions after two-stage ion-liquid extraction purification was characterized by a relatively low content of aromatic hydrocarbons – 3% mass and sulfur-containing compounds - 348 ppm [2,13,16,17,18,22].

Thus, the resulting diesel fuel on content terms of sulfur and aromatic compounds corresponds to the European class.

Ion-liquid extraction purification of a mixture of straight-run diesel distillate with products of secondary origin

In order to expand the raw material base, there is a tendency to involve secondary refining products in the diesel fuel production cycle. With this in mind, we studied the extraction purification of the mixture of PDF with the products of the secondary oil refining — light gas oil coking (LGC) or light gas oil catalytic cracking (LGCC) with a volume ratio of 70:30, respectively [20]. An ionic liquid based on acetic acid and N-methylpyrrolidone was used as an extractant for the purification of mixed raw materials. During the extraction purification of a mixture of SDF and LGC containing 16% mass aromatic and 1265 ppm sulfur-containing compounds, the influence of various factors on the yield and quality of the obtained raffinate was studied (tab.4) [22,23].

It was found that with an increase in the amount of ion-liquid extractant relative to the feed, the degree of dearomatization and desulfurization increases. So, the raffinate obtained as a result of the extraction purification process at a temperature of 20-25°C, a contact time of 1 hour by processing the raw material with a twofold excess of extractant is characterized by a residual aromatic hydrocarbon content of 6% mass with a yield of 76,57% mass based on the raw materials. The content of sulfur-containing compounds in the obtained raffinate is reduced to 364 ppm. With an increase in the contact time of the components up to 2 hours, there is only a slight increase in the degree of desulfurization. (residual sulfur content of 362 ppm). With an increase in the amount of ion-liquid extractant in

relation to diesel distillate up to 3 times, the content of aromatic hydrocarbons decreases to 5% mass and the degree of dearomatization is 68,75% mass, the degree of desulfurazion is 72,88 % mass with a residual sulfur content in raffinate of 343 ppm. However, at the same time, there is a decrease in the yield of raffinate (71,6% mass), which indicates a decrease in the selectivity of the ion-liquid composition with an increase in its quantity with respect to raw materials. With an increase in the extraction temperature to 60°C, a practical change in the degree of dearomatization and desulfurization of the raw material was not observed.

When stage-by-stage cleaning of a mixture of SDF with LGC using an equal amount of extractant with respect to raw materials at each stage at an extraction temperature of 20-25°C and a contact time of 1 hour at each stage, the residual aromatic content in the raffinate after the first stage of purification is 10% mass against 16 % mass in the original. After the second stage of selective purification, the amount of aromatics in the raffinate composition is reduced to 8% mass, i.e. the degree of extraction of aromatic hydrocarbons is 50% mass. However, the degree of desulfurization is higher and amounts to 74,3% (residual sulfur content of 325 ppm), which indicates a deeper desulfurization during the process in stages. The yield of raffinate in this case is 75,6% for raw materials. Based on the results obtained, stepwise extraction purification of a mixture of diesel distillate of the specified composition was carried out using a twofold excess of extractant in the first stage and only an equal amount of extractant in the second stage. Moreover, as can be seen from the table, already at the first stage a high degree of refinement of the raw material is achieved and a relatively deep dearomatization with residual aromatic hydrocarbon content in the raffinate of 6% mass is observed. After the second stage of purification, the residual aromatic content in the raffinate is 5% mass, sulfur containing 285 ppm when the raffinate yield 72,3% mass on the feedstock.

Thus, it was found that upon ion-liquid extraction of a mixture of PDF and LGC raw materials with a twofold excess of extractant at a temperature of 20-25°C and a contact time of components of 1

hour, a rather high degree of refinement of the raw material is achieved to obtain diesel that meets the requirements of the European standard.

Under the found optimal conditions, extraction purification of a mixture of diesel distillate based on SDF and LGCC containing 29% mass of aromatics and 1132 ppm of sulfur-containing compounds was carried out. It was shown that during selective purification of raw materials with a twofold excess of IL at a temperature of 20-25 °C and a contact time of 1 hour, the degree of dearomatization is 79,3% with a residual aromatic content of 6%, and the degree of desulfurization is 72,4% with a sulfur content of 313 ppm. The cetane number of the purified distillate increases from 23 to 50 points with a yield of 62,34% mass.

The results showed that with an increase in the concentration of aromatic hydrocarbons in the feedstock, an increase in the degree of their removal under the same conditions of ion-liquid extraction purification is observed.

carried out using N-methylpyrrolidone (NMP) as the amine component, which in turn is an industrially used selective solvent in the extraction purification of oil fractions, we studied the selective purification of the studied diesel distillate compositions using N-methylpyrrolidone as an extractant.

It was found that during the selective purification of the mixture of SDF + LGCC of the above composition under similar conditions (mass ratio of raw materials to extractant equal to 2: 1, extraction temperature 20-25°C, contact time of components1 hour) using NMP yield of raffinate as an extractant was only 54,43% mass versus 62,34% mass in the case of extraction purification of the corresponding raw material by ionic liquid. It should be noted that the residual content of aromatic hydrocarbons (8 % mass) and sulfur-containing compounds (392 ppm) in the obtained raffinate is slightly higher and the degree of dearomatization is only 72,5 %, of the desulfurization is 65,4 against 79,3% and 72,4% mass, respectively, in the case of the implementation of the extraction purification process using as extractant IL synthesized based on acetic acid and NMP.

Table 4

Characterization of raffinates obtained on the basis of a mixture of straight-run diesel fraction with light gas oil coking and catalytic cracking

Mass ratio IL: mixed diesel distillate	Temperature ° C	Contact time of components, h	The yield of raffinate,% mass	The residual content of aromatic hydrocarbons in the raffinate,% mass	The residual sulfur content in the raffinate, ppm	d_4^{20}, kg/m^3	n_D^{20}	Kinematic viscosity, at 20 ° C, mm^2 / s	Cetane number
1:1	20-25	1	84,10	10	484	829,2	1,4618	5,44	52
2:1	20-25	1	76,57	6	364	822,6	1,4554	5,11	54
2:1	20-25	2	74,35	6	362	822,8	1,4559	5.11	54
3:1	20-25	1	71,60	5	343	821,9	1,4553	5,11	55
2:1	60	0,5	79,68	8	387	823,8	1,4597	5,12	54
2:1	60	1	75,25	7	368	823,1	1,4583	5,12	54
2:1	60	2	74,18	6	371	827,7	1,4556	5,12	53
in stages I stage 1:1 II stage 1:1	20-25	1 1	84,4 75,6	10 8,0	486 325	– 826	– 1,4604	– 5,20	– 53
I stage 2:1 II stage 1:1	20-25	1 1	78,5 72,3	6,0 5,0	373 285	– 820	– 1,4586	– 4,97	– 55
2:1*	20-25	1	62,34	6.0	313	837	1,4662	5,20	50

Note: * The result of extraction purification of the mixture of SDF and LGC

Given that synthesis the specified ion-liquid composition was

In the selective purification of a mixture of diesel distillate based on LGC, a relatively high dissolving ability of NMP low selectivity is also observed. The yield of raffinate was 61% mass

against 76,57% when cleaning said IL-1 feedstock. In this case, the residual content of aromatic hydrocarbons in the obtained raffinate is 7 % mass with a degree of dearomatization of 56,25% versus 62,5% mass during the implementation of the process with IL-1. The residual content of sulfur-containing compounds in the raffinate was 398 ppm with a degree of desulfurization of 68,46% mass versus 72,2% mass during ion-liquid purification [7,14].

The calculated values of the distribution coefficients of aromatic hydrocarbons and sulfur compounds during the extraction purification of a mixture of SDF and LGA using both IL and N-methylpyrrolidone as an extractant showed that in the case of ion-liquid extraction purification of the studied composition of diesel distillate, the distribution coefficient for aromatic and sulfur compounds (K_A = 8,46, K_S = 10,35) are almost two times higher than the values of these indicators during the extraction process using N-methylpyrrolidone (K_A = 4,45, K_S = 5,47) [24].

The results of extraction purification of a mixed diesel distillate obtained by introducing into the composition of secondary processing products were studied using IR, UV, luminescence, and chromato-mass spectral analyzes. In particular, by IR spectral analysis of the feedstock, as well as the raffinate and extract obtained by extraction purification with IL-1, as well as purification by NMP, a relatively low residual content of aromatic hydrocarbons in the raffinate obtained by ion-liquid extraction purification was established.

UV spectral analysis of the initial samples of diesel distillate, as well as raffinates obtained by extraction purification, indicate the difference in the hydrocarbon group composition of the mixture of diesel distillates obtained by introducing LGC or LGCC into the straight-run diesel distillate, as well as raffinates based on them (tab.5) [11,14].

So, in the composition of the mixture of DD obtained on the basis of SDF and LGC, the content of monocyclic aromatic hydrocarbons is three times higher (9,96% mass) than in the mixture of DD on the basis of SDF and LGC, where the aromatic content is 3,7% mass. It should be noted that the total content of aromatic

hydrocarbons in the initial mixture based on SDF and LGC is almost two times higher than in the mixture of DD based on SDF and LGC. In the latter composition of the content of bicyclic aromatic hydrocarbons (11,2% mass) is relatively higher, and this composition differs in the content of tricyclic aromatic hydrocarbons, in particular anthracenes, the content of which is 7,7% mass.

An analysis of the UV spectra of the initial samples and the raffinate obtained by ion-liquid extraction indicates a decrease in the concentration of total aromatics from 31,3% to 8,6% mass in the case of a mixture of DD based on SDF and LGCC and with 16,6% mass up to 8,84 % mass in the case of a mixture of DD based on LGC. In this case, complete removal of bicyclic aromatic hydrocarbons from the composition of DD based on a mixture with LGC, and phenanthrenes from a mixture of DD based on SDF and LGCC, is observed.

Table 5

Results of UV spectral analysis of raffinates obtained by extraction purification of a mixture of SDF with LGCC or LGC ionic liquid and N-methylpyrrolidone

Samples	Molecular weight	Aromatic hydrocarbon concentration, % mass					
		benzene derivatives	Naphthalenes	Phenanthrenes	Anthracenes	1,2 benzpyrene, 3,4benzanthracene, pyrene	The amount of aromatic hydrocarbons
SDF+ LGCC	227,5	3,7	11,2	8,7	7,7	traces	31,3
Purified by IL	195,01	1,1	7,1	—	0,4	—	8,6
Purified by NMP	197,56	1,3	8,2	0,98	0,62	—	11,1
SDF+ LGC	205	9,96	4,8	1,8	—	traces	16,6
Purified by IL	179,7	8,4	—	0,44	—	—	8,84
Purified by NMP	180,8	4,8	3,6	1,3	—	—	9,7

In the case of extraction purification of the investigated DD mixtures using NMP as the extractant, the residual content of bicyclic hydrocarbons in the composition of the purified distillate is

3,6% mass, with a degree of removal of 25% mass, and phenanthrenes – 1,3% mass, at the degree of removal of 27,78% mass in the case of a mixture of diesel distillate based on SDF and LGC. In the selective purification of a mixture of DD based on straight-run DD and LGCC, the degree of removal of bicyclic hydrocarbons is 26,78% mass, with a residual content of 8,2 % mass, tricyclic – 90,25% mass, in particular phenanthrenes 88,73% mass and anthracene 91,95% mass.

In order to provide more informative data on the composition of the raw materials, along with UV spectral studies, a luminescence analysis of a mixture of SDF and LGC and raffinates obtained by extraction cleaning of the specified composition was carried out (fig. 2).

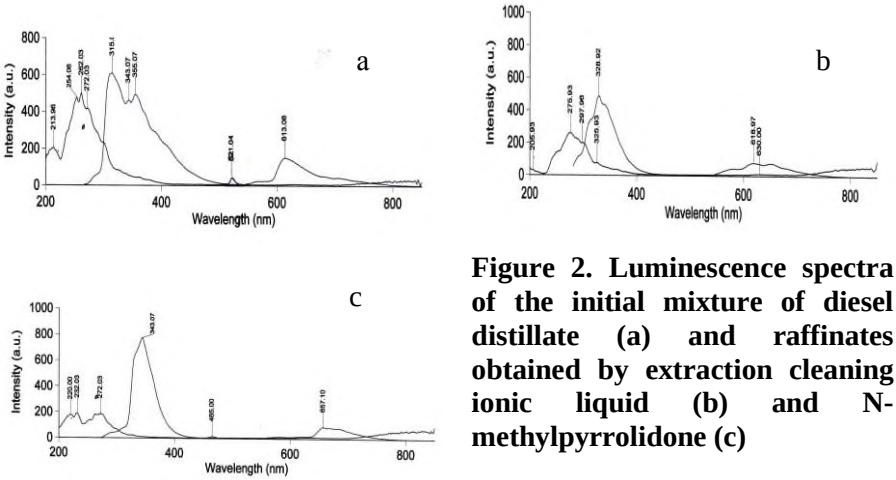

Figure 2. Luminescence spectra of the initial mixture of diesel distillate (a) and raffinates obtained by extraction cleaning ionic liquid (b) and N-methylpyrrolidone (c)

It was established that upon excitation of the feedstock and raffinate purified by ion-liquid extraction, the luminescence maxima of substituted benzene, naphthalene, and phenanthrene hydrocarbons decrease by 8,0; 10,0 and 3,2 times, respectively. In the spectrum of the indicated raffinate sample, the maximum luminescence of anthracene, 1,2 benzanthracene + 3,4 benzphenanthrene and pyrene was not observed.

In the luminescence spectrum of the raffinate sample obtained by purification with N-methylpyrrolidone, luminescence maxima of naphthalene and phenanthrene are observed, and the luminescence

maximum of the bicyclic hydrocarbon naphthalene is absent in the spectrum of the sample purified by ionic liquid.

The obtained results confirm the higher selectivity of the ion-liquid extractant with respect to the investigated raw materials - a mixture of diesel distillate.

The analysis of the group hydrocarbon composition of the feedstock obtained by compounding SDF and LGC, as well as the raffinates obtained by extraction purification of the indicated distillate with IL-1 and the industrial extractant N-methylpyrrolidone was also carried out by chromatography-mass spectroscopy.

The results of the chromato-mass spectral analysis of the studied samples show the expediency of ion-liquid extraction purification. Thus, a chromatographic analysis of the raffinates obtained by extraction purification of a mixture of SDF and LGC using IL-1 as a selective solvent, as well as an organic solvent, N-methylpyrrolidone, indicates a difference in the group hydrocarbon composition. In particular, the raffinate obtained by ion-liquid extraction purification of raw materials is characterized by a total aromatic hydrocarbon content of only 3,57% mass versus 5,69% during extraction purification of raw materials by N-methylpyrrolidone. The content of mono- and bicyclic aromatic hydrocarbons during ion-liquid extraction purification decreases from 10,73% mass to 3,37% mass, i.e. respectively 3,18 times, and during extraction purification with N-methylpyrrolidone it decreases only 1,89 times. Regardless of the nature of the extractant taken, three and tetracyclic aromatic hydrocarbons are completely removed during extraction purification [28].

One of the main requirements presented for selective solvents during extraction purification is the possibility of regeneration and reuse. The research cycle showed the possibility of IL-1 regeneration by adding to the extract solution 30% mass water from amount of extract solution with further rectification of the obtained aqueous extractant solution.

The possibility of using extracts obtained during the extraction purification of diesel fractions as a raw material in the process of obtaining plasticizing additives for concrete was investigated.

The feasibility study of the economic efficiency of the process of obtaining high-quality diesel fuel with a low content of aromatic and sulfur compounds was carried out by comparing the process of ion-liquid extraction purification with the hydrofining process and established the expediency of the extraction method. It is shown that fuel production by the developed method provides an annual profit of 52 mln AZN [21].

CONCLUSIONS

1. Conditions have been developed for obtaining improved quality diesel fuel by extraction cleaning of diesel fractions of various compositions using an environmentally friendly ionic liquid based on acetic acid and N-methylpyrrolidone - N-methylpyrrolidon acetate as a selective solvent.

2. It was found that the combination of methods for cleaning diesel distillate, in particular, hydrotreating and ion-liquid extraction purification, makes it possible to obtain almost completely dearomatized diesel fuel with a residual content of sulfur compounds of 130 ppm.

3. The expediency of two-stage ion-liquid extraction purification of narrow fractions of straight-run diesel distillate with boiling points of 191-300°C and above 300°C with subsequent compounding of the obtained raffinates has been established. It is shown that diesel fuel obtained in this way according to the basic physical and chemical characteristics meets the requirements of the European standard, in particular, the content of aromatic hydrocarbons and sulfur compounds is only 3% mass and 348 ppm.

4. In order to expand the raw material base of diesel fuel, ion-liquid extraction purification of a mixture of straight-run diesel fraction with products of secondary oil refining: light coking gas oil and catalytic cracking at a volume ratio of 70:30 was first studied for the first time.

5. It was found that during the extraction purification of the mixture of SDF and LGC with a twofold excess of extractant at a temperature of 20-25°C and a contact time of the components for one hour, the degree of dearomatization is 62,5%, desulphurization is

71,3% when the raffinate yield is 76,57% mass. The results obtained show the possibility of obtaining environmentally friendly diesel fuel with a simultaneous increase in the volume of diesel fuel due to the involvement of a secondary oil refining product in the extraction process.

6. It was shown that a similar result is observed during the extraction purification of a mixture of SDF and LGC. The possibility of producing diesel fuel with an aromatic hydrocarbon content of 6 % mass and sulfur compounds of 313 ppm by extraction cleaning of a mixture of straight-run diesel fraction and light catalytic cracking gas oil was established. Wherein, the degree of dearomatization and desulfurization is 79,31% and 72,4% mass, respectively.

7. It was established that the residual content of aromatic hydrocarbons in the raffinate obtained by ion-liquid purification (3,57% mass) is 1,6 times less than in the composition of the raffinate obtained by purification with N-methylpyrrolidone (5,69% mass).

8. The technical and economic calculation of the process of ion-liquid extraction purification of the mixture of SDF and LGA established an annual profit of 52 mln AZN.

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