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SELECTIVE PURIFICATION OF TRANSFORMER OIL BY THE METHOD OF IONIC LIQUID EXTRACTIVE PURIFICATION

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Abstract- The paper represents comparative results of selective purification of transformer oil distillate by the method of extractive purification using ionic liquids of various compositions as selective solvent, providing environmental friendless of the process technological solution and a complex of physicochemical properties of purified transformer oil. Taking into account the relatively high yield of raffinate in extractive purification in comparison to acid contact purification, it is shown that ionic liquid extractive purification is promising in order to create "green chemistry" technologies.

Keywords: Green Chemistry, Distillate, Transformer Oil, Ionic Liquid, Raffinate, Physicochemical Properties.

1. INTRODUCTION

Transformer oil production, like other insulating oils, is mainly based on the use of acid contact purification method of the corresponding distillates [1]. According to this method, for the purpose of obtaining the target product, purification process of raw materials is carried out by multiple treatment of raw materials with 95-97% sulfuric acid, taken in the amount of 5-20% wt., depending on the raw materials composition, via neutralization by 5-10% aqueous solution of sodium hydroxide, washing with water until neutral reaction and further by blow drying at 70-95 °C. As is evident, the purification process is characterized by a number of significant disadvantages. In particular, acid contact purification is a multistage method, the use of concentrated sulfuric acid causes the formation of a large amount of hard-to-dispose industrial waste - acid tar and waste water that pollutes the environment and premature corrosion of equipment.

Creation of eco-friendly technologies for obtaining petroleum products for various purposes is an urgent task of petrochemistry and oil refining taking into account increasing requirements for environmental protection [2-4]. In this aspect, from scientific and practical points of view, it's interesting to develop new, alternative methods for purification of petroleum fractions, differing in environmental safety, simplicity in technological execution, as well as a high yield of the target product.

The industrial method for liquid extraction of petroleum fractions is a promising and widely used one for removing undesirable components, in particular aromatic hydrocarbons, as well as resinous compounds from the composition of petroleum distillate, improving the quality of the target product. However, the toxicity of the selective solvents used in the process conducted via extractive purification method requires the development of new approaches to the selective purification of petroleum distillates, in particular, replacement of traditionally used organic solvents by eco-friendly compositions - ionic liquids.

This class of compounds, due to the complex of physicochemical properties - high solubility of various classes of compounds, low vapor pressure, non-toxicity, non-volatility, thermal and chemical stability, etc., has found application to create green chemistry technologies as a solvent and catalyst in organic synthesis reactions, selective solvent in selective purification processes of analytical chemistry, as well as oil refining.

Effectiveness of ionic liquids as selective solvent in selective purification processes of petroleum fractions for various purposes was established by systematic studies carried out at the Institute of Petrochemical Processes of the National Academy of Sciences of Azerbaijan. Effectiveness of ionic liquid compositions in the processes of selective purification of diesel distillates of various compositions [5-7], catalytic cracking gasoline [8, 9], transformer oil distillates, oil fractions of various viscosities, hydraulic liquid was established by a cycle of studies. Ionic liquids synthesized by interaction of formic or acetic acid with various amines - morpholine, N-methylpyrrolidone, di-, triethylamine, aniline, etc. were used as extractant in the studies. All synthesized compounds are colorless and transparent liquids at room temperature, the structure was confirmed by IR and NMR spectral analyzes.

The results from selective purification of petroleum fractions for various purposes proved the feasibility of using ionic liquids as selective solvent, ensuring production of fuels and higher quality base oils.

In particular, the use of the ionic liquids on the basis of formic acid and morpholine - morpholinformate, or aniline - anilineformate, and also on the basis of acetic acid and N-methylpyrrolidone - N-methylpyrrolidoneacetate provides the possibility of obtaining transformer oil meeting the requirements of the standard for transformer oils (GOST 982-80).

Study of various factors influence - the ratio and contact time of the components, extraction temperature on the yield and the quality of the transformer oil obtained by ionic liquid extraction allowed determination of optimal conditions for extractive purification by the use of the above ionic liquids as selective solvent:
- morpholinformiate - mass ratio of extractant:feedstock - 2.5:1.0; extraction temperature 60 ° C, contact time of the components - 2.5 h; raffinate yield - 85% wt;
- anilineformiate - mass ratio of extractant: feedstock - 2.5:1.0; extraction temperature 60° C, contact time of the components - 2.5 h; raffinate yield - 83% wt;
- N-methylpyrrolidoneacetate - mass ratio of extractant: feedstock 2.0:1.0 wt., extraction temperature 60 °C, contact time of the components - 2 h; raffinate yield - 81.2% wt.

As is evident, similar results were achieved by the use of all three above-indicated ionic liquid compositions and the yield of transformer oil raffinate (81.2-85% wt.) was much higher than the results of acid contact (76.7 wt%) purification.

At this temperature, regardless of the composition, the yield of raffinate and residual amount of aromatic hydrocarbons decrease by an increase in the amount of ionic-liquid extractant in relation to the distillate that confirms an increase in the degree of purification of the hydrotreated diesel distillate (Tab.1).

Distillate color change from 40 to 10 CNT during ionic-liquid extractive purification, determined by the method of NPA proves removal of resinous compounds from the distillate composition.

Table 1. Dependence of extractive purification process of transformer oil distillate on the ratio of components. Extraction conditions: temperature 60 °C, contact time of components - 2.5 h

Mass ratio of IL: TOD	Yield, % mas.		Raffinate parameters				
	raffinate	extract	Density at 20 °C, kg/m^3	Refractive index, n_D^{20}	Residual arom.hydroc.content., %	Acid number, mg KOH per 1 g oil	Color, un. CNT
IL: Morpholineformiate							
1.5: 1.0	95.5	4.5	872.4	1.4810	15.0	0.08	1.0
2.0: 1.0	94.9	5.2	871.3	1.4800	10.0	0.05	1.0
2.5: 1.0	93.4	6.6	870.1	1.4780	8.0	0.002	1.0
3.0:1.0	93.35	6.65	870.0	1.4775	6.0	0.01	1.0
IL: N-methylpyrrolidoneacetate							
1.5: 1.0	92.0	18.0	879.6	1.4910	14.0	0.05	1.0
2.0: 1.0	81.15	17.075	877.3	1.4860	9.6	0.005	1.0
3.0: 1.0	75.6	24.1	876.0	1.4843	6.0	0.005	1.0
3.5: 1.0	74.5	25.5	875.0	1.4800	6.0	0.005	1.0
IL: Anilineformiate							
1.5: 1.0	86.0	14.0	875.3	1.4895	12.1	0.04	1.0
2.0: 1.0	83.0	17.0	878.5	1.4860	10.0	0.02	1.0
2.5: 1.0	81.2	18.8	873.9	1.4852	9.0	0.02	1.0
3.0:1	79.8	21.2	871.2	1.4843	7.0	0.01	1.0

Comparative results of physicochemical parameters of raffinates obtained by extractive purification using ionic liquids of various compositions are represented in Tab. 2. After the treatment of raffinate samples at 120 °C for 1 h with bleaching clay - 5% mas. of gumbrin, transformer oil samples were characterized by the tangent of dielectric loss angle at 90 °C from 0.31 to 0.41. As is seen, the results prove the feasibility of the method of ionic liquid extractive purification of transformer oil distillate.

The possibility of regeneration and reuse of ionic liquid compositions as extractant in the process of selective purification of transformer oil distillate also proves the efficiency of ionic liquid extractive purification of raw materials.

The results of the studies on hydrocarbon composition of transformer oil samples obtained by acid contact method and ionic liquid extractive purification are set into Table 2. Silica gel ASK was used as an adsorbent in the studies (GOST 11244-76); desorption of naphthene-paraffinic hydrocarbons was carried out in the presence of heptane as a solvent, but aromatic hydrocarbons and resinous compounds by sequential supply of solvent mixtures - heptane + 5% benzene, heptane + 15% benzene, 100% benzene.

The possibility of regeneration and reuse of ionic liquid compositions as extractant in the process of selective purification of transformer oil distillate also proves the efficiency of ionic liquid extractive purification of raw materials [18].

The results of the studies on hydrocarbon composition of transformer oil samples obtained by acid contact method and ionic liquid extractive purification are set into Table 3. Silica gel ASK was used as an adsorbent in the studies (GOST 11244-76); desorption of naphthene-paraffinic hydrocarbons was carried out in the presence of heptane as a solvent, but aromatic hydrocarbons and resinous compounds by sequential supply of solvent mixtures - heptane + 5% benzene, heptane + 15% benzene, 100% benzene.

Table 2. Physicochemical properties of transformer oil obtained by ionic liquid extraction

Properties	Morpholineformiate	Anilineformiate	N-methylpyrrolidoneacetate	Transformer oil distillate	T-1500 according to GOST 982-80
Fractional composition: initial boiling point, °C final boiling point, °C	 250 405	 250 405	 250 405	 250 405	 - -
Density at 20°C, kg/m^3	881.8	884.0	878.0	885.9	no more than 885
Kinematic viscosity, mm^2/s, at 50°C at 30°C	 6.76 10.0	 6.74 9.94	 6.81 9.95	 7.17 -	 no more than 8.0 no more than 11.0
Refractive index, n_D^{20}	1.4840	1.4840	1.4780	1.4920	
Acid number, mg KOH/g	0.0	0.0	0.0	3.8	no more than 0.01
Flash point, °C in a closed crucible	138	136	137	137	no less than 135
Freezing point, °C	-53	-52	-52	-53	-45
Colour, on the method NPa	+1.0	1.0	1.0	4.0	no more than 3.5
Low molecular weight volatile acids content, mg/KOH to 1 g of oil	0.04	0.04	0.02	-	0.04
Acid number, mg KOH/g	0.02	0.02	0.02	0.02	0.2
Transparency at 5 °C	transparent	transparent	transparent	-	transparent
Dielectric loss tangent at 90 °C	0.31	-	0.41	-	no more than 0.5
Mechanical impurities content, %	none	none	none	none	none
Sodium test, points	0.18	0.20	0.19	-	0.4
Ash content, %	0.005	0.005	0.005	-	0.005
Sediment	none	none	none	-	none

Table 3. Group hydrocarbon composition of transformer oil purified by acid contact and ionic liquid purification

Hydrocarbons	Transformer oil distillate		Acid contact purification		Ionic liquid extraction					
					Morpholineformiate		N-methylpyrrolidoneacetate		Anilineformiate	
	n_D^{20}	yield, %	n_D^{20}	yield, %	n_D^{20}	yield, %	n_D^{20}	yield, %	n_D^{20}	yield, %
Naphthene-paraffinic	1.4795	88.25	1.4868	92.5	1.4723	93.5	1.4731	93.8	1.4728	90.0
Aromatic: the I group	1.5000	4.54	1.5240	4.1	1.4853	0.45	1.4894	0.3	1.4890	0.8
the II group	1.5835	5.04	1.5320	3.4	1.4968	6.05	1.4985	5.9	1.4973	9.2
the III group	1.5900	0.26	-	-	-	-	-	-	-	-
Resinous compounds	>1.5900	1.91	-	-	-	-	-	-	-	-
Total		100		100		100		100	-	100

Analysis of structural group composition indicates that, regardless of ionic liquid composition used as an extractant, the content of naphthene-paraffinic hydrocarbons in the composition of the purified samples varies in the range of 90-93.8 wt%, and aromatic hydrocarbons - 6.2-10 wt%. In particular, transformer oil obtained by extractive purification of the distillate of anilineformiate ionic liquid consists of 90 wt% of naphthene-paraffinic ($n_D^{20} \leq$ 1.48) and 10 wt% of aromatic hydrocarbons ($n_D^{20} \geq$1.49). The sample obtained by ionic-liquid extractive purification using N-methylpyrrolidone acetate was characterized by the content of 93.8 wt% of naphthene-paraffinic and 6.2 wt% of aromatic hydrocarbons, as well as the sample obtained by transformer oil distillate purification using morpholineformate by the content of 93.5 wt% of naphthene-paraffinic and 6.5 wt% of aromatic hydrocarbons.

Thus, the analysis of the results of ionic liquid extractive purification of transformer oil distillate by the use of ionic liquids as selective solvent, differing in both anionic and cationic fragments, proves that this purification method is promising in comparison with acid contact purification. In particular, ionic liquid extractive purification has a number of advantages:

- high yield of raffinate (81.2-85 wt%) against 76.7 wt%. in acid contact purification
- a high degree of removal of aromatic hydrocarbons and resinous substances: 44.68-47.23% wt. by ionic liquid extraction against 36.17% wt. by acid contact purification;
- possibility of regeneration and reuse of ionic liquids in the process of extractive purification;
- absence of environmental problems observed in acid contact purification, formation of industrial non-utilized waste - acid tar and wastewater polluting the environment is not observed in ionic liquid extractive purification;
- prevention from premature corrosion of equipment;
- transformer base oil, obtained by ionic liquid extractive purification, is characterized by significantly higher properties and meets the requirements of GOST 982-80.

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