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DETERMINATION OF THE COMPONENT COMPOSITION OF PHENOLIC EXTRACTS FROM THE PURIFICATION OF PETROLEUM OILS

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ABSTRACT

The paper studies samples of phenolic extracts of aromatic hydrocarbons from the purification of medium, heavy, and residual oils of an oil refinery. The component composition of phenolic extracts was studied using physicochemical research methods. The group composition of the hydrocarbon part obtained after the removal of resins and distillation of petroleum ether was determined by the adsorption method. To separate the fractions of the phenol extract, the physicochemical constants were determined, and a structural-group analysis of the aromatic fractions was carried out. In aromatic concentrates after phenolic purification of oils, the amount of aromatic hydrocarbons was 49-57%, n-paraffin - about 6%, and isoparaffin-naphthenic - 23-30%. To separate the hydrocarbon mixture into the paraffin-naphthenic and aromatic parts, silica gel was used. Based on the results obtained, the average number of aromatic rings in the molecules of the two aromatic fractions increases from 1.8 to 2.8, which indicates the presence of naphthalene derivatives with an increase in the number of carbons in the side chain from 9 to 15. The completeness of separation of aromatic hydrocarbons on synthetic zeolites of the CaX and NaX types was studied. The results of the conducted research allow us to establish a new approach to the rational use of large-tonnage waste–phenolic extract, which allows for the beneficial use of polycyclic aromatic hydrocarbons and resinous substances.

Keywords: Phenolic Extract, Petroleum Oil, Fraction, Aromatic Hydrocarbons, Zeolite.

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INTRODUCTION

Currently, oil refining products are among the main pollutants of water bodies, soil, and air. No other pollutant can compare with waste and emissions from oil refining in terms of the breadth of distribution and the magnitude of the load on the components of the natural environment.[1,2] A special place in the range of petroleum products is occupied by oils used for lubricating mechanisms to reduce friction between solid surfaces and prevent wear of materials. To use oil fractions of petroleum as finished lubricating oils, they must be thoroughly purified from unwanted and harmful impurities, while preserving in their composition the components that impart lubricating ability and viscosity.[3-5]

The purification of oil raw materials with phenol is based on its ability to dissolve unsaturated and aromatic hydrocarbons with short side chains and resinous substances well. A characteristic feature of phenol as a selective solvent is its ability to remove naphthenic acids from the purified distillate and reduce the sulfur content, which is especially interesting for processing oil from some fields into oils.[6,7] After cleaning the oil feedstock, it is necessary to regenerate phenol from the raffinate and extract solution. The yield and quality of the raffinate obtained during the cleaning of the oil feedstock depend on the quality of the distillate taken for processing, the temperature regime of the process, and the ratio of phenol to the purified feedstock. The extract from the cleaning of petroleum oils formed in this process is a large-tonnage waste of the oil refining industry. Due to the lack of rational methods of disposal and the inefficiency of existing processing methods, the phenol extract is mainly sent to sludge collectors.[8] One of the industrial methods of purifying oil fractions is their selective purification with phenol. Phenol, as a selective solvent, has medium selectivity and high dissolving capacity.[9] Unsaturated and aromatic hydrocarbons with short side chains, as well as resinous, sulfurous, and oxygen-containing compounds, which will be removed first during the purification of oil distillates, dissolve well in phenol. Oil purification with phenol is carried out in a continuous process in an extraction column using counter-current extraction. As a result, two phases are formed in the column: the upper, raffinate phase contains a solution of purified oil in phenol, and the lower phase contains a phenol solution with aromatic, sulfurous, and oxygen-containing components removed from the raw material. Phenol is separated from the raffinate and extracted by step distillation. Oils are obtained from the raffinate, the regenerated phenol is again used for purification, and the aromatic concentrate, no longer containing phenol, but with an admixture of resins, sulfur compounds, and naphthenic acids, has not yet found a qualified application.[10,11] The issue of the rational use of aromatic hydrocarbons from extracts from phenolic oil refining is very relevant, since these wastes are large-tonnage. The annual output of the extract at typical oil refineries is about 20% of the weight of the oil.[12,13] In most cases, phenolic extracts (PE) are used as fuel, while it would be possible to extract components valuable for both lubricating oils and petrochemical synthesis.[14,15] Today, the vast majority of current scientific and technological research in the field of oil refining is devoted to the development of principles for improving the quality and volumes of produced and promising commercial petroleum products.[16,17,18] However, there is little work in this area. It was of great interest to apply modern adsorbents and analytical methods to the study and separation of high-boiling aromatic hydrocarbons, in particular those obtained during the purification of oils with phenol. The present study aims to determine the component composition of phenolic extracts using physicochemical research methods.

EXPERIMENTAL

Sampling of Phenolic Extracts

Samples of phenolic extracts of aromatic hydrocarbons from the purification of medium, heavy, and residual oils of an oil refinery were selected as the object of the study. Four samples of phenolic extracts were studied: FE-1 - II+III fractions; FE-2 - III fraction; FE-3 - residual; FE-4 - residual. The studied samples of extracts from phenolic refining of oils were, in appearance, dark, viscous, resinified oil with a specific gravity of about 350. The phenol content in the extract was 0.000-0.003%, water was absent.[19,20]

Adsorption, Purification, and Separation of Aromatic Extracts

Adsorption, purification, and separation of aromatic extracts were carried out in large glass three-stage columns 1.5 m high and with internal stage diameters of 4, 2.5, and 1 cm, respectively. The extracts were purified from resins and naphthenic acids on aluminum oxide (stick for chromatography) in a solution of petroleum ether at 40-60^{0}C. The adsorbent was poured into the column, and a solution of the extract in petroleum ether was added and eluted with petroleum ether until pure petroleum ether was obtained. The resins were desorbed with acetone.[21,22]

The group composition of the hydrocarbon portion obtained after removing resins and distilling off petroleum ether (total content of aromatic hydrocarbons, n-paraffin, and isoparaffin + naphthenic) was determined by the adsorption method. To determine the clarity of separation of alkanes from aromatic hydrocarbons, 0.5 g of the paraffin-naphthenic part was dissolved in 25 ml of cyclohexane and passed through 10 g of silica gel (the degree of purity was determined by the cryoscopic method).[23]

Structural-Group (Ring) Analysis of Phenolic Extracts

To separate the fractions of the phenol extract, physicochemical constants and structural-group analysis were determined using the ring analysis method. The ring analysis method of high-boiling fractions is based on determining n_D^{20} and the molecular weight of hydrocarbon mixtures, preliminarily separated on silica gel into paraffin-naphthenic and aromatic concentrates. The method includes calculation of the average number of rings in one molecule, the average number of carbon atoms in a ring, and the average weight percentage of carbon in a ring for carbon mixtures. The average algebraic deviations between calculations and theoretical values are 11.5 wt.% +0.02 rings in one molecule, +0.09 ring carbon atoms in one molecule +0.06 wt.% ring carbon atoms.[24]

RESULTS AND DISCUSSION

The study of the component composition of phenolic extracts showed that the amount of resins in phenolic extracts from the purification of residual oils is twice as large as in phenolic extracts from the purification of oils of II and III fractions, and the hydrocarbon part is correspondingly smaller. The results of the study are presented in Table-1.

Table-1: Component Composition of Phenolic Extracts (wt.%)

Sample No.	Resins			Hydrocarbons
	Total	Desorbed with acetone	Non-desorbed	
FE-1	16.18	11.89	4.19	83.82
FE-2	15.09	12.17	2.92	84.91
FE-3	33.57	20.44	13.13	66.43
FE-4	31.75	23.00	8.75	68.78

The group composition of the hydrocarbon portion obtained after removal of resins and distillation of petroleum ether, determined by the adsorption method, is presented in Table-2. As can be seen from the table, in aromatic concentrates after phenolic purification of oils (II and III fractions), the amount of aromatic hydrocarbons is 49-57%, n-paraffin - about 6%, and iso-paraffin + naphthenic - 23-30%.

Table-2: Group Hydrocarbon Composition of Phenolic Extracts (wt.%)

Sample No.	Total hydrocarbons	Aromatic hydrocarbons		n-paraffin hydrocarbons		Isoparaffinic + naphthenic hydrocarbons	
		Σ hydro-carbons	Initial extract	Σ hydro-carbons	Initial extract	Σ hydro-carbons	Initial extract
FE-1	83.82	58.33	48.89	6.25	5.23	35.42	29.70
FE-2	84.91	67.02	56.90	5.55	4.71	27.43	23.30
FE-3	66.43	70.03	49.85	5.22	3.48	24.75	16.70
FE-4	68.78	72.88	50.14	8.45	5.81	18.67	12.83

To separate the hydrocarbon mixture into the paraffin-naphthenic and aromatic parts, silica gel LPG (large-porous granular) was used. Silica gel (350 g) was poured into a large column; the hydrocarbon mixture was dissolved in light petroleum ether (bp=40°C); (7.0 g of hydrocarbon mixture in 100 ml of light petroleum ether), passed through silica gel, and eluted with the same ether. The end of separation was determined by the refractive index of pure petroleum ether and by a positive formol reaction. Petroleum ether was distilled from the filtrate**,** and the paraffin-naphthenic part of the hydrocarbons (18.64 g) obtained in the residue was dried to a constant weight. The paraffin-naphthenic part is a solidified oil with a specific gravity of 0.7909, a refractive index of 1.4905 (drum index - 40.5)**,** and a molecular weight of 277, boiling point - 400°C. Silica gel LPG can likely adsorb some amount of naphthenic hydrocarbons. The above data showed that silica gel LPG does not adsorb naphthenic hydrocarbons at this boiling point range, and also that there are no aromatic hydrocarbons (AH) in the paraffin-naphthenic part. The aromatic hydrocarbons remaining on the silica gel in the large column after washing out the naphthenic-paraffin part were desorbed with ethanol and sulfuric ether. The solvents were distilled off, and the remaining mixture of aromatic hydrocarbons was brought to a constant weight.

The degree of purity of the isolated aromatic hydrocarbons, equal to 100%, was determined by the adsorption-cryoscopic method using silica gel LPG. The results of the analysis of aromatic hydrocarbons using synthetic zeolites were presented in Fig.-1, Fig.-2, and Fig.-3.

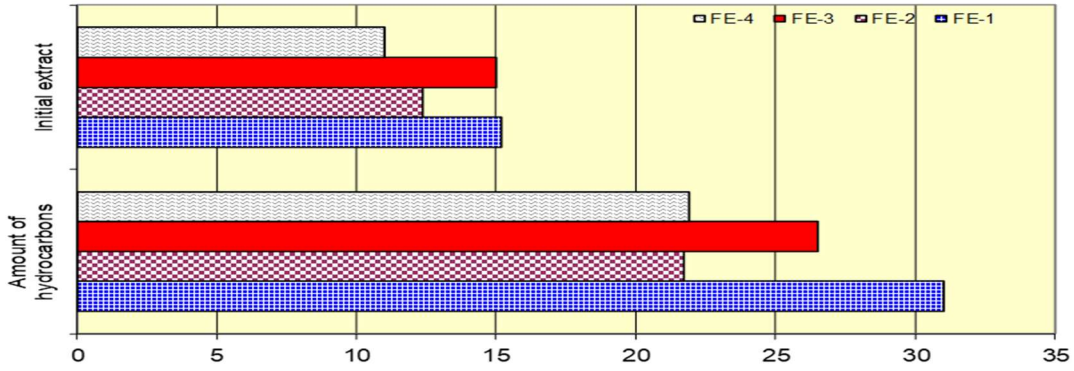

Fig.-1: Composition of Aromatic Hydrocarbons (wt.%): Fraction A-1 (adsorbed on CaX)
With sizes up to 0.8 nm of Molecules

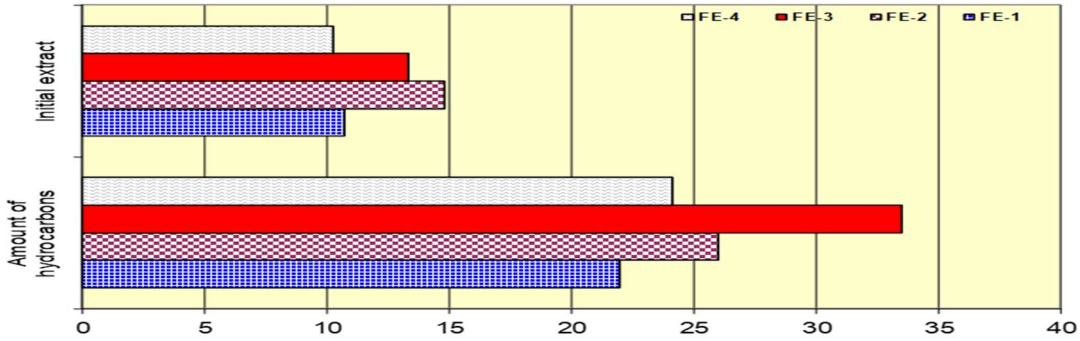

Fig.-2: Composition of Aromatic Hydrocarbons (wt.%): Fraction A-2 (adsorbed on NaX)
With sizes of Molecules 0.8-0.9 nm

Analysis was also done on aromatic hydrocarbons from additional phenolic extract samples. Table-3 shows the results, which show that the percentage of molecules with a critical diameter decreases from 20% to 30% in all situations, up to 22–33% for molecules between 0.8 and 0.9 nm and 40–54% for the largest molecules larger than 0.9 nm.

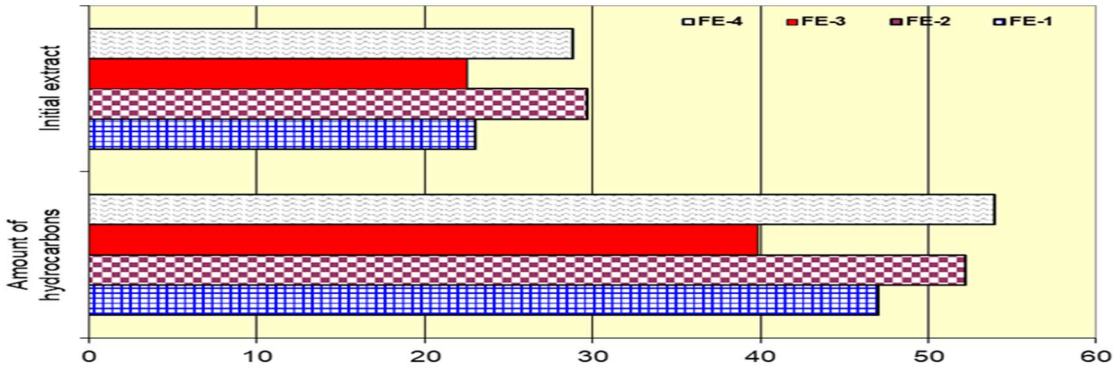

Fig.-3: Composition of Aromatic Hydrocarbons (wt.%): Fraction A-3 (not adsorbed on either NaX or CaX)
with Sizes of Molecules > 0.9 nm

The degree of purity of the separated fractions A-1, A-2, and A-3 was checked. In case of clear and complete separation, fraction A-1 should be completely adsorbed on the zeolite CaX, fraction A-2 on the zeolite NaX**,** and not adsorbed on the zeolite CaX, and fraction A-3 should not be adsorbed on the zeolites NaX and CaX, according to the literature data.[25,26,27] As can be seen from Table-3, the sum of aromatic hydrocarbons from the phenolic extract is divided into fractions by the sizes of molecules, which gives

grounds to speak about the use of these fractions as molecular probes for determining the sizes of pores in type X zeolites, i.e., for their distinction.[28-30]

Table-3: Checking the Completeness Separation of the Sum Aromatic Hydrocarbons on Synthetic Zeolites Type X

Fractions	Zeolite		t_1, °C	t_2, °C	t_3, °C	% of adsorbed aromatic hydrocarbons
	Type	Size of pores in Å				
A-1 (< 0.8 nm)	CaX	10	6.40	5.29	6.40	100
A-2 (0.8-0.9 nm)	CaX	10	6.40	4.20	4.22	0.9
A-2 (0.8-0.9 nm)	NaX	13	6.40	4.20	6.40	100
A-3 (> 0.9 nm)	CaX	10	6.40	4.42	4.42	0
A-3 (> 0.9 nm)	NaX	13	6.40	4.42	4.44	1.01

To separate the fractions of the phenol extract, the physicochemical constants and structural group analysis of the aromatic fractions were also determined. Physicochemical constants of aromatic fractions are shown in Table-4. The results also revealed that the average number of aromatic rings in the molecules of aromatic fractions A-1, A-2, and A-3 increases from 1.8 to 2.8, which indicates the presence of naphthalene derivatives with an increase in the number of carbons in the side chain from 9 to 15. The third fraction already contains a mixture of bi- and tricyclic hydrocarbons. Aromatic hydrocarbons were identified using ultraviolet absorption spectra taken on an SF-4 spectrophotometer.[31,32] Ultraviolet spectra of aromatic hydrocarbons of fractions are shown in Fig. 4. The spectra showed a maximum at 3200 Å with a shift in the spectral maxima toward longer wavelengths from A-1 to A-3, which corresponds to naphthalene derivatives with an increasing number of substituents in the side chains.[33]

Based on the composition of phenolic extracts, it is advisable to raise the issue of isolating aromatic hydrocarbons (48-56%) from them, which are valuable as raw materials for petrochemistry, and returning the remaining hydrocarbons (n-paraffin 4-6%, isoparaffin 13-30%) to oil refining processes, and sending the resins (15-34%) to the production of bitumen. The main amount, as expected, falls to the share of aromatic hydrocarbons (48-57%) with a composition from C_{19} to C_{29}, represented by a mixture of mono-, bi, and tricyclic aromatic hydrocarbons (in the boiling temperature range of about 350-430 °C).

Table-4: Physicochemical Constants of Aromatic Fractions

Fractions	Output, wt.%		Output, wt.%		Refractive index at temperature		Refractometer indicator-ons	Relative dispersion	Mr	Boiling point According to the nomogram, °C
	Sum of AH	Initial concentrate	70°C (exp.)	20°C (calc.)	70°C (exp.)	20°C (calc.)				
A-1	22.0	11.0	0.9569	0.9597	1.5380	1.5580	35	31.5	258	345
A-2	24.0	12.0	0.9857	0.9885	1.5560	1.5760	36	29.0	296	390
A-3	54.0	27.0	0.9948	0.9976	1.5620	1.5820	37.5	28.3	341	427

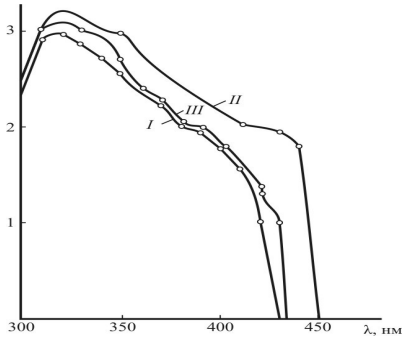

Fig.-4: Ultraviolet Spectra of Aromatic Hydrocarbons of Fractions: I - A-1; II - A-2; III - A-3

CONCLUSION

Thus, the composition and the most important properties of FE were studied using physicochemical research methods. It was found that it is advisable to use silica gel LPG for the extraction of aromatic hydrocarbons from FE. The silica gel LPG has a total dynamic capacity of -1.45% for benzene and 3.91%

for naphthalene. The physicochemical constants required for separating FE fractions were determined using structural group analysis. UV absorption spectra also confirmed the presence of aromatic HC in the range of 300 to 450 nanometers.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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