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COMPOSITION OF OIL PRODUCTS AND METHODS OF SEPARATION OF INDIVIDUAL SUBSTANCES

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Abstract: The article examines the widespread use of chemical processes in the oil refining industry to obtain essential petroleum products and improve their quality. Currently, aromatic hydrocarbons are obtained from petroleum fractions included in the products of reforming and catalytic reforming, and from natural gas from pyrolysis waste - pyrolysis oil and by-products. The types of pyrolysis oils contained in secondary petroleum products, methods for their extraction, determination of composition and problems of their separation into separate parts are analyzed, optimal methods are identified. In addition to the classical method of separation and purification of organic substances, the advantages of using the extraction method for pure separation and analysis of compounds are described.

Keywords: Pirolysis oil, indene, naphthalene, oil, naphthene, toluene, xylene, petroleum products extraction, hexane, olefin, diesel fuel.

Introduction. Currently, aromatic hydrocarbons are extracted from petroleum fractions as part of reforming and catalytic reforming products, and from natural gas as waste from pyrolysis processes - oil and resin pyrolysis products. It is known that since the cost of petroleum products is high, this cost also affects the aromatic hydrocarbons obtained from them. The production of aromatic hydrocarbons in our republic has not yet been established. Oil is the main source of energy for the world economy and an integral part of modern life [1]. Most of the world's transport, industry and energy production depend on oil. However, due to the growing demand for oil and its increasing impact on the environment, the issue of oil refining and its efficient use is becoming increasingly important. Oil refining and its efficient use play an important role in solving these problems. The refining process involves separating crude oil into various types of fuel and other products. At present, aromatic hydrocarbons are obtained from oil fractions included in the products of reforming and catalytic reforming, and from natural gas from pyrolysis waste - pyrolysis oil and by-products. Oil in our country is extracted in small quantities, and all the extracted oil is processed, from which gasoline, diesel fuel, paraffin, bitumen are obtained, and our enterprises do not specialize in obtaining aromatic hydrocarbons. At the same time, industrial waste from a number of our enterprises, where the process of pyrolysis of natural gas takes place - pyrolysis distillate, pyrolysis oil and by-products - contain valuable organic compounds such as derivatives of indene, naphthalene, anthracene, fluorine and phenanthrene [1]. Despite the fact that pyrolysis waste is rich in aromatic hydrocarbons, their price is quite low. However, there is a problem of obtaining the necessary fractions from pyrolysis waste with a complex composition. Therefore, highly selective extractors are used in industry to separate compounds, which are easily regenerated and have a sufficiently high density compared to the separated raw material. In addition, it is necessary to take into account that the solvents selected as extractants are local, inexpensive and are used in other industries. Secondary liquid products of natural gas pyrolysis - pyrolysis oil and pyrolysis distillate - contain many aromatic compounds obtained by extraction in a mixture of dimethyl sulfoxide and diethylene glycol solvents. In the course of this study, it was found that pyrolysis oil and distillate contain benzene, toluene, xylene, styrene, indene, naphthalene, anthracene, phenanthrene and many other aromatic hydrocarbons [1]. Dimethyl sulfoxide (DMSO) is an important dipolar solvent. It is less toxic than dimethylformamide (DMF) and dimethylacetamide (DMAA), is widely used in organic synthesis, and is soluble in water. Diethylene glycol and dimethyl sulfoxide are good solvents. Of the aromatic hydrocarbons, n-paraffins and naphthenes dissolve poorly in them.

Results and discussion. It is obvious that the secondary products of the pyrolysis process include a wide range of organic substances of different classes and molecular weights. Therefore, their separation and analysis are difficult. Gas chromatography with mass spectrometry (GC-MS), elemental analysis, NMR and IR spectroscopy are mainly used to analyze these products. It is known that the results of determining the liquid pyrolyzate by these methods are insufficient for conclusions due to the overlap of peaks due to the multicomponent composition and their incorrect interpretation [2]. In a number of studies, the approach to the selection of extractants and conditions for obtaining oils by the pyrolysis method was carried out on an empirical basis [3].

In such works, there is a lot of information on the extraction of various compounds in a number of extraction systems in which methylene and other functional groups are summarized as a set of increments, as well as various organic substances, including pyrolysis methods for extracting oil and assessing distribution constants are described in [4, 5, 6]. In one of the works on the separation of pyrolysis oil into components and compositionalquantitative analysis by the chromatographic method [7], the extraction of individual substances from a hexane solution of pyrolysis oil using various selective solvents and reagents and extracted components by gas chromatographic mass spectroscopic analysis (GC-MS). Pyrolysis oil can be divided into low molecular weight, water-soluble polar solvents, including organic acids and bases, water-insoluble substances with polar functional groups in the molecule, polynuclear arenes with a condensed structure, aliphatic and naphthenic hydrocarbons. For this purpose, the hexane solution of pyrolysis oil is successively extracted with mineral acid or alkaline water, ethylene glycol, dimethyl sulfoxides, and then treated with oleum. When analyzing these fractions using the chromatographic distribution method, it was found that they contain aliphatic and unsaturated hydrocarbons, benzene derivatives, naphthalene, polycyclic aromatic hydrocarbons, phenols, etc.

Determining the chemical composition of liquid pyrolysates is important for finding an
effective method for their purification and subsequent use as fuel, as well as for assessing their toxicity. Pyrolysis oils are a complex mixture of hundreds of organic compounds. Their main classes are aromatic hydrocarbons, alkenes, alkanes [8]. Aromatic compounds in pyrolysis oil are compounds with one or more benzene rings and their alkyl derivatives: phenanthrene, pyrene, naphthalene, methyl-, dimethyl- and trimethylnaphthalenes [9]. There are several works in the literature devoted to the study of the composition of pyrolysis oils, each of them expresses its own methods and goals, and the results of their analysis differ from each other. For example, in the work of M.R. Islam et al. [10], only aromatic fractions were analyzed by the method of sequential elution chromatography and GX-MS of pyrolysis oils. S. Viriyaumpaivong [11] also ran pyrolysis oils and determined only the composition of the light fraction of naphtha with a boiling point of less than 160 ° C by GX-MS and elemental analysis, which is only 20 volume percent of the total oil content. Pyrolysis oils contain a large number of polycyclic aromatic hydrocarbons. It was found that these are toluene, dimethylcyclohexenes, ethylbenzene, xylene, styrene, methyloctene, ethylmethylbenzenes, methylethenylbenzenes and limonenes [12]. It should be noted that 15.7% toluene, 21.2% xylene, 6.9% limonene were found in the light fraction of naphtha, which is only ≈20% of the total amount of pyrolysis oil. The relative amount of toluene is 4.40%; xylene – 3.48, limonene – 5.12% [13, 14, 15, 16]. The targeted separation, identification and quantification of pyrolysis oil components are very complex. The results of pyrolysis oil analysis obtained by GX-MS are often ambiguous and lead to incorrect interpretation of the obtained data. The problem of chromatographic peak identification was also noted, in particular the presence of two peaks registered by the mass detector as limonene in the chromatogram of pyrolysis oil [17]. Several identical compounds with different retention times were detected, such as methylcyclopentene (7.57 and 7.99 min), trimethylpentane (11.02 and 11.98 min), dimethylcyclohexene (15.64, 15.82 and 16.41 min), etc. The reason for this is unknown. It is possible that this is due to the fact that the peaks are not individual substances, but their mixtures [18]. Pyrolysis oil contains various classes of organic compounds with a wide range of molecularweights (from C6 to C28). It is not surprising that compounds with different molecular weights and different polarities often have overlapping peaks even when using different columns. The problem of pyrolysis compounds determination is so complex that the development of reliable methods for pyrolysis oil analysis is very important. This problem can be solved by preliminary preparation of a pyrolysis oil sample. At the same time, it is impossible to accurately separate organic substances by classical methods, such as recrystallization and fractionation, which are widely used in chemical engineering and laboratory practice. It is known that extraction methods of separation and concentration are useful due to their simplicity, speed and efficiency. Meanwhile, the preparation of pyrolysis mixture samples and their use for subsequent GC analyses is of a separate, empirical nature. Thus, it is necessary to apply a targeted approach to the problem of determining the composition of pyrolysis products. The development of extraction methods for sampling pyrolysis

products allows us to determine the methods for extracting the main components of pyrolysis mixtures with various solvents, select optimal conditions for separating and concentrating components with similar properties, and their analysis using chromatograph mass spectrometry increases the efficiency and reliability of implementation. Extraction is known to be widely used in many areas of industry and laboratory practice. Currently, extractive sample preparation is practically not used in the analysis of pyrolysis oils. In a number of studies, the solvent-antisolvent extraction method was used to prepare an extraction sample of pyrolysis oils and analyze wood pyrolysis oil. For phase separation, the organic phases were separated from the pyrolysis oil by the simultaneous addition of a hydrophobic-polar solvent and water [19]. Since the addition of a hydrophobic polar solvent such as dichloromethane to the oil usually does not cause phase separation, a dichloromethane-water system was used to improve phase separation. Compared with traditional aqueous extraction, aqueous extraction with dichloromethane allows more organic compounds to diffuse from the oil into the organic phase. At the same time, analysis of the resulting extract is complicated by the fact that the peaks of different classes of pyrolysis mixture compounds are located close to each other on the chromatogram. Based on the expected chemical composition of pyrolysis oil, a sequence for preparing its extraction sample is proposed (Fig. 2).

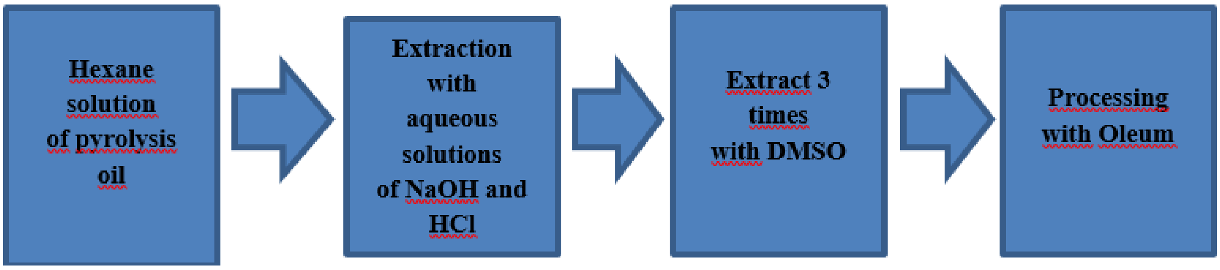

Figure 2. Pyrolysis oil extraction sample preparation sequence

As a result of such a sequence of preparation of extraction samples, the complex pyrolysis mixture contains relatively low-molecular water-soluble polar substances and separates, among other things, organic acids and bases; to water-insoluble substances with polar functional groups in the molecule; condensed polycyclic arenes; into aliphatic and naphthenic hydrocarbons that do not contain other classes of organic compounds. Similar results were obtained for various samples of pyrolysis oils. Comparison of the obtained data on the composition of pyrolysis oil and oil shows that they have a similar composition in the nature and molecular weight of hydrocarbons. Thus, pyrolysis oils can be used as fuel after preliminary treatment, for example, hydrotreating. Similar results were obtained for various pyrolysis oil samples. Comparison of the obtained data on the composition of pyrolysis oil and crude oil shows that they have a similarcomposition in the nature and molecular weight of hydrocarbons. Thus, pyrolysis oils can be used as fuel after preliminary treatment, such as hydrotreating. Extraction with water, an aqueous acid solution or an aqueous alkali solution removes hydrophilic bases and acids, extraction with ethylene glycol - weak hydrophobic compounds, extraction with dimethyl sulfoxide - condensed polynuclear arenes, treatment with oleum - unsaturated hydrocarbons from a hexane solution of pyrolysis oil and allows for the isolation of alkylbenzenes. It is evident that effective separation of organic compounds differing in polarity and molecular weight can be achieved by sequential liquid-liquid extraction using water, polar organic solvents and reagents. Thus, the information on the chemical composition of pyrolysis oils was analyzed and it was found that the results obtained by different methods are often contradictory. The reliability of the results of the analysis of pyrolysis mixtures is not clear even when using modern GC-MS and multidimensional chromatography methods; to ensure the reliability and accuracy of the analysis, it is proposed to use the preparation of a primary extraction sample of primary pyrolysis oil analysis. Uzbek scientists also studied the chemical composition of pyrolysis oil. Development of natural resources, their rational use, large-scale modernization of industrial production, technical and technological renewal, rapid implementation of modern scientific achievements and advanced innovative technologies, imports that have a stable demand in the world market. Creation of competitive enterprises producing substitute products. The main direction of economic development of our Republic. The purpose of pyrolysis processes, which are extremely common in modern world petrochemistry, is to obtain lower olefins, mainly ethylene, which are valuable raw materials for the synthesis of the most important petrochemical products.

Pyrolysis produces a large number of aromatic hydrocarbons, such as ethylene, propylene, butylene and butadiene, benzene, toluene, xylene, indene, naphthalene, phenanthrene, fluorene, anthracene and its homologues. Ethylene oxide, ethyl alcohol, polymers, styrene, plastic and other products are obtained from ethylene obtained as a result of pyrolysis. The main areas of use of liquid pyrolysis products are the production of benzene and other aromatic hydrocarbons, oil, diesel fuel, carbon, high-quality coke from polymer resins. Pyrolysis oil is an oily liquid from dark brown to dark green in color with an unpleasant odor. Its composition depends on the pyrolysis raw material and is not stable. To determine the quality and quantity of samples of heavy pyrolysis resins obtained from JV OOO Uz-Kor Gas Chemical, they were analyzed on an Agilent 5977A gas chromatograph with a massselective detector [20]. The results of the analysis are presented in Table 1. Pyrolysis oil, as well as heavy fractions of liquid pyrolysis products, are an important secondary raw material for the production of indene, naphthalene and other valuable chemical products, as well as for other purposes in the future.

Table 1. Qualitative and quantitative analysis of heavy pyrolysis tar

№	Substance name	Quantity, %	Compatibility level
1	Inden	24,33	93
2	1- metilinden	13,96	96
3	**Naphthalene**	21,51	90

4	**1, 6-dimethylnaphthalene**	**9,71**	**90**
5	**2-methylnaphthalene**	**6,25**	**96**
6	**1-methylnaphthalen**	**12,61**	**97**
7	**Residual substances**	**-**	**-**

Conclusion. Analysis of oil and its products, separation of individual substances is one of the important tasks of the petrochemical industry. Thanks to the combination of various methods, highly accurate analysis is carried out and products suitable for industrial needs are isolated. These processes are of great importance in the energy, chemical industry and ecology. Aromatic hydrocarbons are not produced in our country due to the lack of optimal technologies for processing pyrolysis waste to obtain indene, naphthalene and their homologues. At the moment, modern technologies allow us to produce expensive and necessary products. Therefore, research aimed at creating a comprehensive technology for processing waste from gas chemical complexes operating in the republic is an urgent task that requires finding a solution.

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