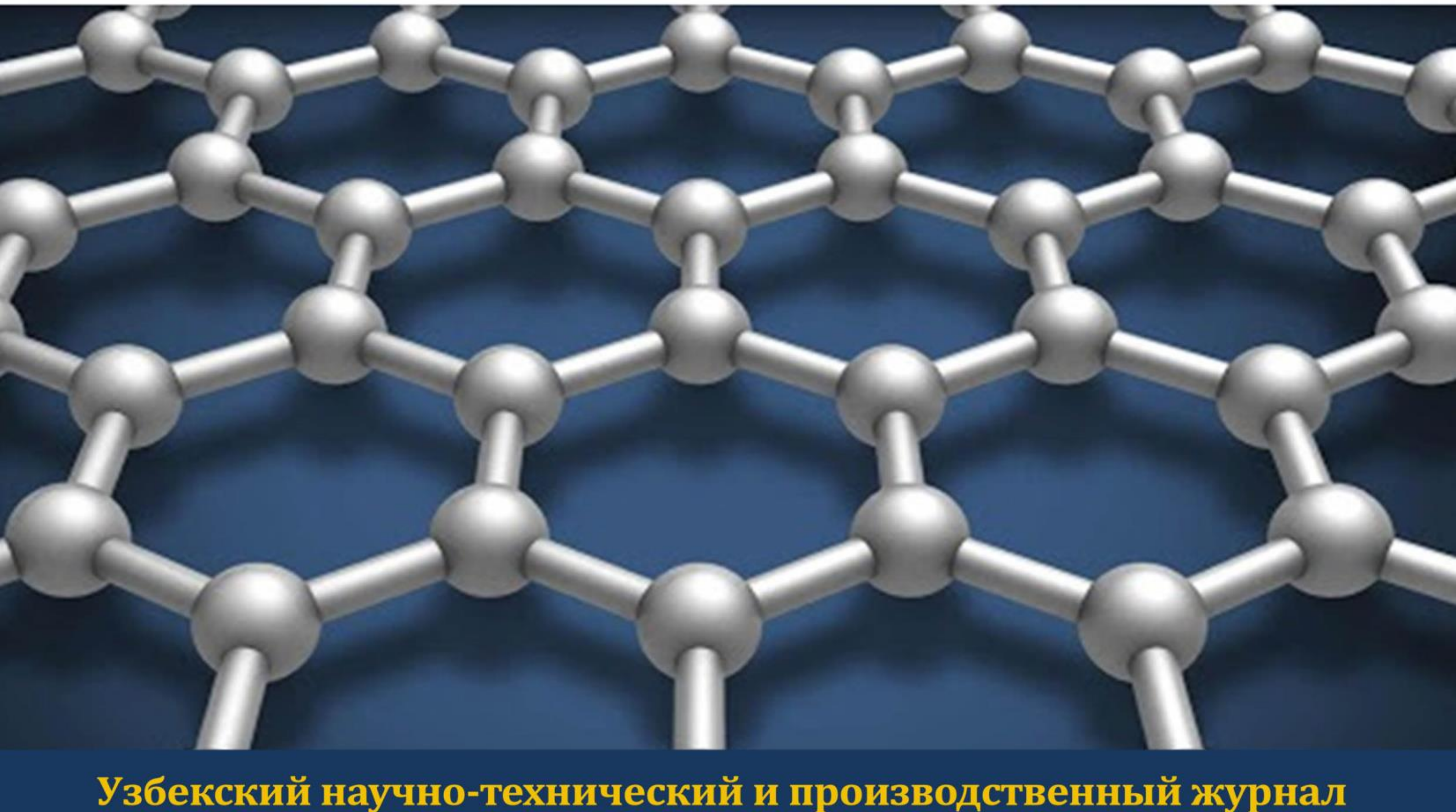
ISSN 2091-5527
№ 1/2025

O‘zbekiston

Kompozitsion Materiallar

Ilmiy-texnikaviy va amaliy jurnali



Узбекский научно-технический и производственный журнал

Композиционные материалы

ЛИТЕРАТУРА

1. Лебедев Н. Н. Химия и технология основного органического и нефтехимического синтеза. - М.: Химия, 1988. – 592 с.
2. Н. А. Петров, В.М. Юрьев, Хисаева А.И. Синтез анионных и катионных ПАВ для применения в нефтяной промышленности / Учеб. пособие/ УГНТУ. – Уфа, 2008. – 54с.
3. Ланге К. Поверхностно-активные вещества: синтез, свойства, анализ, применение / Перевод с англ. – М.:Из-во «Профессия», 2016. – 240 с.
4. Шехтер Ю.Н., Крейн С.Э. Поверхностно-активные вещества из нефтяного сырья. - М.: Химия, 1971. – 488 с.
5. Жидкова М.В., Коновалов В.В., Городнов В.П. Исследование возможности получения анионных поверхностно-активных веществ из низкокачественного углеводородного сырья для повышения нефтеотдачи пластов // Управление техносферой. -2018. -Т.1.- Вып. 1. -С. 34 – 46.
6. Петров Н.А. Научные основы и особенности синтеза ионогенных поверхностно-активных веществ для применения в нефтяной промышленности //Автореф.дисс. док.хим.наук. –М.: 2008. –45 с.
7. Юрьев Ю.К. Практич еские работы по органической химии. - М.: Издат. МГУ, 1964. – 259 с.

UDK: 66.092-977,547.21

STUDY OF THE COMPOSITION OF THE "TAR-PRODUCT" AND THE SEPARATION OF ASPHALTENE HOMOLOGUES

[1]Kurbanbayeva S.A., [2]Ikramov A., [3]Turabdjanov S.M., [4]Qodirov O.Sh., [2]Kadirov X.I.

[1]Navoi Mining Institute Nukus branch, [2]Tashkent Institute of Chemical Technology
[3]Tashkent State Technical University, [4]National University of Uzbekistan

Abstract. The qualitative and quantitative analysis of the by-product "TAR-product" from the production process of lower olefins was carried out, and it was determined that its main components consist of asphaltene and its homologs. A fraction of asphaltene homologs was separated from the "TAR-product" at 230-250 °C and purified by steam distillation.

Keywords: industrial by-products, pyrolysis, olefins, TAR-product, asphaltenes, chromatogram.

Currently, pyrolysis is the primary method used for the production of lower olefins. In the process of hydrocarbon pyrolysis, fractions such as crude gasoline, naphtha, paraffin fractions derived from the initial refining of petroleum, and products from natural gas processing like ethane, propane-butane, and gas condensates are predominantly utilized. The products formed during pyrolysis are divided into two parts: pyro-gas and pyro-condensate fractions. From the pyro-gas, ethylene and propylene are extracted as the main products, while hydrogen, butene-1, butadiene-1,3, and acetylene are obtained as by-products. Pyro-condensate, on the other hand, is processed differently across various industries to produce secondary products. For instance, at gas deep-processing enterprises in our country, pyro-condensate is primarily divided into three parts. At the "Uz-Kor Gas Chemical" JV LLC, natural gas purified from mechanical impurities is first separated into methane, ethane, propane-butane, and gas condensate fractions. The methane fraction is sent for consumption, while the remaining fractions undergo pyrolysis. From the pyrolyzed products, lower olefins such as ethylene, propylene, hydrogen, butenes, etc., are extracted and sent for polymerization. The pyro-condensate is divided into three fractions: the first is the 30-160°C TAR-product fraction, the second is the 160-270°C TAR-product fraction, and the third is the residue above 270°C TAR-product fraction [1].

Pyrolysis condensate is sold as fuel without further processing, despite being a secondary product rich in valuable reagents. Deep processing of such secondary products presents the opportunity to produce essential raw materials for the oil and gas, rubber, household chemicals, and chemical industries. According to the literature, the chemical composition of the TAR-product, one of the secondary products at "Uz-Kor Gas Chemical" JV LLC, primarily consists of bi-nuclear aromatic hydrocarbons. Among these compounds are asphaltene homologs, such as 1-methylasphaltene, 2-methylasphaltene, 1,6-dimethylasphaltene, 2-ethylasphaltene, and others. Based on these raw materials, products like ion-exchange resins, functional additives for concrete mixtures, and essential products for energy, construction, pharmaceuticals, and other industries are being developed. Developing technology for producing various chemical compounds from primary and secondary products of oil and gas processing remains one of the critical tasks.

The rapid development of the oil, gas, and chemical industries worldwide has highlighted the importance of developing theoretical foundations for processing secondary products generated alongside primary products. Creating technologies to produce new products from these secondary materials is a crucial task. Additionally, addressing the scientific aspects of industrial wastewater treatment and reuse is of significant importance. Currently, scientific research is being conducted to achieve these goals, including developing new technologies for producing cation exchangers and identifying raw material sources for their synthesis.

In many countries, deep processing of products derived from pyrolysis has been established, enabling the extraction of various valuable reagents. For instance, in this study, the authors investigated the efficiency of asphaltene extraction through thermal processing of heavy pyrolysis tar. The heavy pyrolysis tar was treated in a stirred reactor using atmospheric-vacuum distillation at temperatures ranging from 250 to 270 ºC for 6-8 hours. This process resulted in distillate and residue fractions. The distillate was further separated into narrow temperature range fractions through redistillation: the initial fraction (up to 200 ºC), the asphaltene fraction (200-230 ºC), the methylasphaltene fraction (230-245 ºC), and the residue (245-340 ºC).

As a result of the thermal processing conducted by the authors, an increase in the asphaltene fraction and its asphaltene content was observed. Simultaneously, a decrease in the amounts of mono- and bicyclic alkenes and dienes, vinylaromatic hydrocarbons, indene and its homologs, as well as dihydroasphaltenes, was noted in the product composition [2]. Under specific thermal processing conditions, heavy pyrolysis tar can be efficiently converted into petroleum-polymer resins with targeted complex properties, which can be used as functional additives in polymer composites. Additionally, high-purity asphaltene of commercial-grade quality can be extracted without the need for further costly processing.

Under such conditions, the thermal processing of heavy pyrolysis tar not only improves the quality of asphaltene but also increases its melting point, reduces its color intensity on the iodine scale, and enhances the degree of asphaltene separation during crystallization. This is achieved by minimizing losses in the distillate fractions during the filtration process [3].

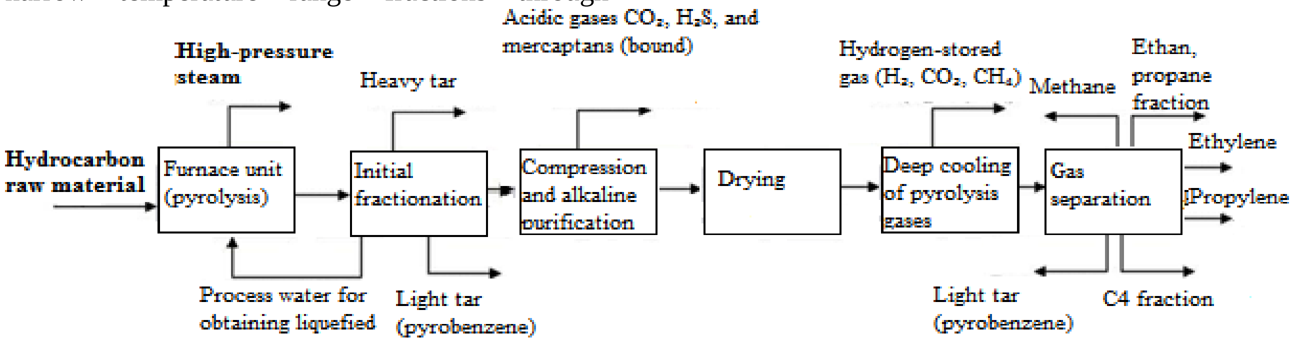


Figure 1. Block diagram of pyrolysis product separation

A wide range of products is formed during hydrocarbon pyrolysis (Table 1), including hydrogen and other by-products such as CO, CO_2, and H_2S. Experimental results related to their step-by-step separation (Figure 1) are presented in the literature [4].

Table 1

The release of certain products from the pyrolysis of various hydrocarbon feedstocks in modern industrial furnaces

Components	Pyrolysis raw materials			
	Ethane	n-Butane	Gasoline	Gasoil
Hydrogen	3,5	1,3	1,0	0,7
Methane	4,3	21,6	16,1	11,5
Acetylene	0,3	0,9	0,8	0,3
Ethylene	48,0	37,8	30,3	25,0
Ethane	39,4	5,1	3,5	3,4
Propylene	1,3	17,3	14,9	14,5
Divinyl	1,1	3,6	5,2	5,1
Butenes	0,3	1,5	3,7	3,9
S_5 hydrocarbons	0,3	0,3	3,2	3,4
Benzene	0,6	2,5	6,7	7,1
Heavy tar	0,1	0,6	5,2	9,1

The deep processing of raw materials and the expansion of the product range are driving forces behind modern oil and chemical industries. According to another source, monomers such as ethylene and propylene, which are raw materials for producing multi-ton polymers like polyethylene and polypropylene, are mainly produced through the pyrolysis of hydrocarbons. Despite improvements in the design of pyrolysis furnaces and optimization of the process, around 20% of additional products-liquid products from the pyrolysis process, or pyro-condensates-are produced. The use of pyro-condensate presents a serious technical and economic challenge, directly affecting the profitability of production.

Currently, the utilization of pyrolysis process liquid products is primarily focused on the extraction of specific fractions for further use, such as technical hydrogenation products and individual compounds (benzene, toluene, xylene, dicyclopentadiene, asphaltene, etc.). Additionally, the liquid products of the pyrolysis process are also utilized for the production of “petroleum-polymer resins,” which are commonly referred to as non-high molecular weight compounds [5].

The quality and quantitative composition of the pyrolysis distillate sample from “Uz-Kor Gas Chemical” LLC were analyzed using the Agilent 7890 GC 5977B MS gas-liquid chromatograph. The TAR-product contains 149 components belonging to various hydrocarbon groups such as alkanes, cycloalkanes, olefins, dienes, and arenes (mono- and bicyclic aromatic hydrocarbons). These components are categorized based on the number of carbon and hydrocarbon groups. The analysis results are shown in Figure 2 and Table 2.

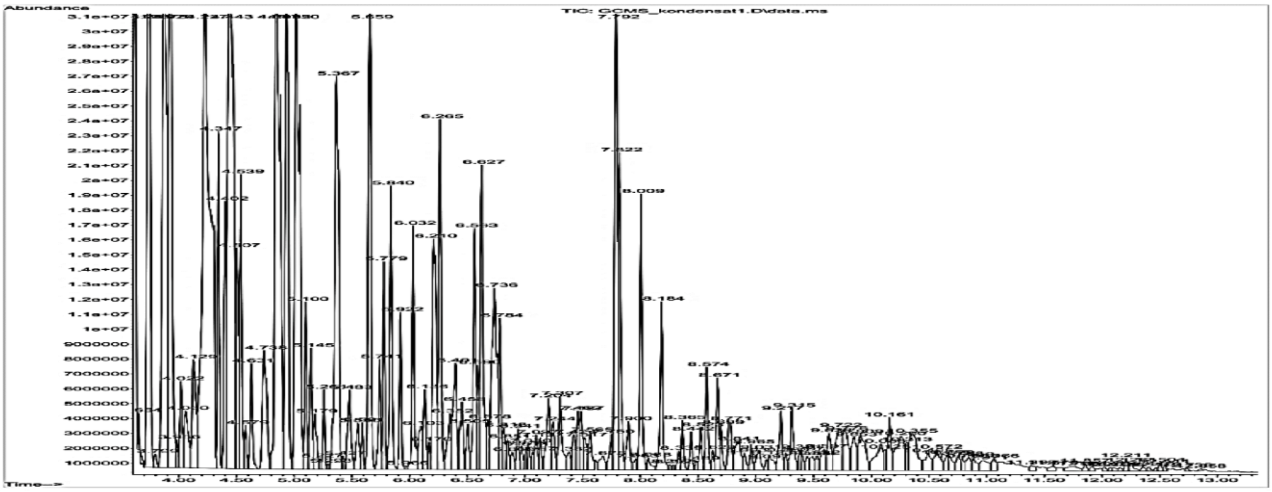


Figure 2. Chromatogram of the light fraction of the TAR product

Table 2

Chemical composition of the light fraction of the TAR product

Number of carbons	Alkanes	Cycloalkanes	Olefins	Dienes	Aromatic hydrocarbons	Total
8	0,15	0,09	0,19	0,46	9,08	9,97
9	0,05	0,11	0,02	0,17	8,41	8,76
10	0,03	0,80	9,12	0,50	5,30	15,75
11	0,80	0,59	2,83	0	0,35	4,57
12	0,02	0,18	1,75	0	0	1,95
Total	**2,48**	**2,98**	**23,41**	**2,24**	**68,89**	**100,0**

The identification of various functional groups in the structure of the TAR-product was carried out using FTIR spectroscopy. The sample was analyzed using a Spectrum 65 IR spectrometer with a KBr pellet. The FTIR spectrum of the TAR-product is shown in Figure 3.

The FTIR spectrum indicates the presence of characteristic bands for aromatic groups (3047.53 cm^{-1}, 1610.56 cm^{-1}), the alkene group -C=C- (1253.73 cm^{-1}; 1440.83 cm^{-1}), vinyl group-specific lines >C=CH_2 (700.16 cm^{-1}), dienes (C=C=C, 1980.89 cm^{-1}), and alkene-specific fragments =C-H (599.66 cm^{-1}).

The characteristic triplet at 725.23 cm^{-1}, 754.17 cm^{-1}, and 802.39 cm^{-1} is clearly observed, which indicates the presence of aromatic structural elements.

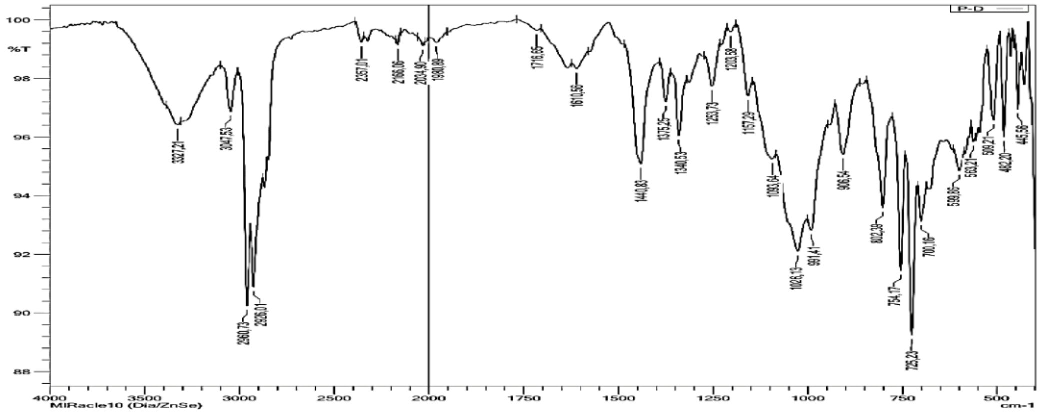


Figure 3. IR spectrogram of the TAR product

The fraction composition is of significant practical importance in the oil and gas refining technology, as it is a determining characteristic for identifying the quality of hydrocarbon raw materials and their processed products. The fraction composition of the TAR-product was determined by laboratory distillation according to the GOST 2177-99 (ISO 3405-88) interstate standard, where fractions with different boiling ranges are distilled from the product at gradually increasing temperatures.

Table 3 presents the results of a series of experiments conducted to determine the fraction composition (% by weight) of the TAR-product through distillation under atmospheric pressure, at distillation temperatures ranging from 40 to 168 ºC.

Table 3

Main results of experiments on fractionation of light fraction of tar product

Indicator name	Experiments			
Density at 20ºC, kg/m³	№1	№2	№3	№4
Kinematic viscosity, mm²/s	842			
Fraction composition	0,779			
Beginning of boiling point, °C				
10 %	40			
20 %	60	62	59	58
30 %	72	73	74	72
40 %	82	84	82	80
50 %	89	90	89	88
60 %	94	93	98	95
70 %	100	105	106	103
80 %	130	129	123	124
90 %	146	150	148	147
93 %	130	159	163	165
End of boiling point, °C	130	160	165	168
Productivity, %	90	93	93	95
Remainder, %	7,8	5	5,5	3,8
Losses, %	2,2	2	1,5	1,2

The data in Table 3 show that the average density of the TAR-product measured at standard temperature (20 ºC) is p20 = 842 kg/m³, and its kinematic viscosity coefficient is v20 = 0.779 mm²/s.

Figure 4 shows the curve of the fraction composition of the TAR-product, based on the data from three experiments, with distillation temperatures ranging from 40 to 165 ºC.

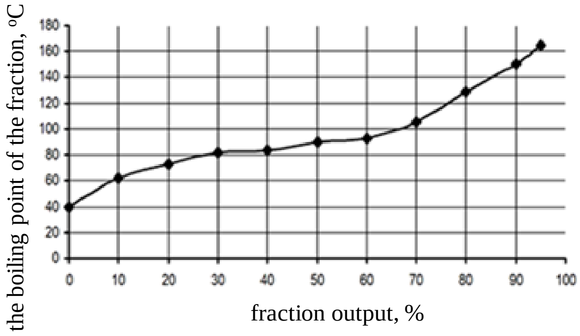


Figure 4. TAR-product fraction composition curve. the boiling point of the fraction, ºC fraction output

As seen, by distilling the TAR-product under atmospheric pressure, it is possible to partially separate more than 80% of the volume of gasoline fractions (40 - 165 ºC) and kerosene fractions (150 - 250 ºC) [6, 7].

The issue of preparing raw materials for hydrocarbon production is of great importance when creating rational compound formulas, considering economic and environmental analysis data. The chemical nature of the TAR-product, along with the scale of production, transforms it into one of the targeted products for producing various types of materials from waste, which, in turn, enhances the production efficiency of the joint venture "Uz-Kor Gas Chemical" LLC through the production of new types of chemical products [8].

Approximately 80% of global butadiene production and 39% of benzene production are achieved through the pyrolysis of hydrocarbons [9]. Different countries use various raw materials for pyrolysis. For example, in the USA and Canada, ethane (49.1% by weight and 69.7%) is the primary raw material, while in Germany, China, France, and Japan, oil (57.4%, 73.3%, and 60.0% respectively) is the main raw material.

In addition, hydrotreated paraffin-gas oil fractions are widely used in Germany and China (32.0% and 26.7%) [10].

TAR product is a viscous liquid ranging from dark brown to dark green with an unpleasant odor. Its composition is unstable and depends on the feedstock used in pyrolysis. The secondary product of production at "Uz-Kor Gas Chemical" LLC, TAR product, was analyzed for its chemical composition in terms of quality and quantity using an Agilent 5977A mass-selective detector gas chromatograph. The prepared sample was analyzed using an "Agilent Technology" GS 6890/MS 5973N chromatograph-mass spectrometer with a 30m×0.25 mm capillary column in a 5% phenylmethylsiloxane/dimethylsiloxane solution, with hydrogen as the carrier gas. The injector temperature was set at 280ºC, MS source temperature at 230ºC, MS quadrupole temperature at 180ºC, and the column thermostat program was set to range from 100ºC to 280ºC, with a temperature ramp of 10ºC/min. The sample volume was 1 µL with no flow separation. The results are presented in Figure 5 and Table 7. The TAR product is a black, odorless solid. Its composition is not constant and varies depending on the feedstock used in the pyrolysis process. The chemical composition of the TAR product, a secondary product of production at "Uz-Kor Gas Chemical" LLC, was analyzed qualitatively using FTIR spectroscopy (Nicolet 6700 Continuum) and Raman-modulated microscope equipment [11]. The obtained results are shown in Figure 6.

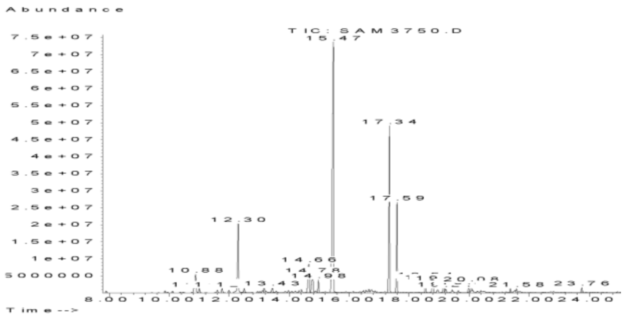


Figure 5. Chromatogram of the TAR product

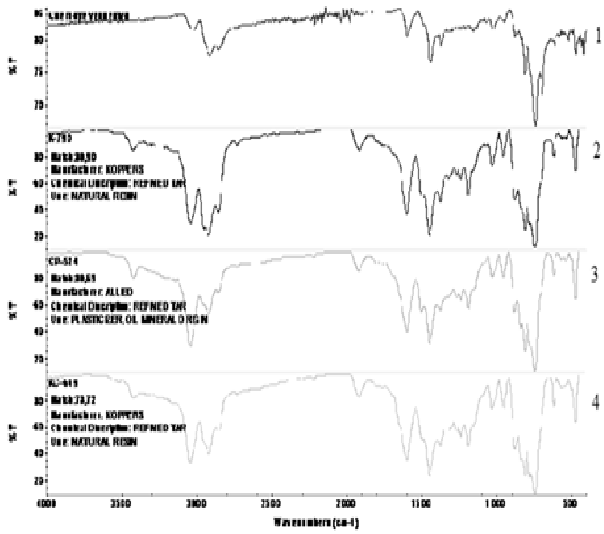


Figure 6. IR spectrogram of the TAR product

4 - table

The chemical composition and qualitative-quantitative analysis results of the secondary product TAR produced by "Uz-Kor Gas Chemical" LLC

Substances	Quantity, %	Database compatibility, %
Inden	9,33	93
1-methylindene	8,96	96
Asphaltene	41,51	90
1-methylasphaltene	8,61	97
2-methylasphaltene	16,25	96
1-ethylasphaltene	1,77	90
1,6-dimethylasphaltene	1,71	95

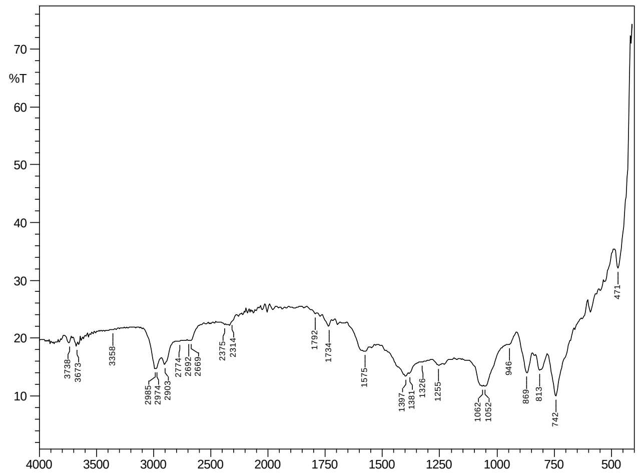


Figure 7. IR spectrogram of asphaltenes.

The issue of preparing raw materials for the production of hydrocarbon materials becomes a key task in creating strong compositional formulas, taking into account economic and environmental analysis data. For example, TAR product and TAR-based products can be used as a binder in the production of "dry anode mass" in metallurgy. The characteristics of the chemical nature of the pyrocondensate produced in pyrolysis, large-scale production, and the transformation of waste into various types of materials, turning pyrocondensate into one of the target products, allows "Uz-Kor Gas Chemical" LLC to increase the efficiency of pyrolysis production and the development of new types of chemical products.

TAR-product was used as a raw material for extracting asphaltene and its homologs from the composition of TAR-product. This secondary product comes from the Ustyurt Gas-Chemical Complex of "Uz-Kor Gas Chemical" LLC.

TAR-product is an odorless liquid ranging from dark brown to dark green. To study its composition, a chromatographic mass spectrometry analysis was conducted (Figure 8).

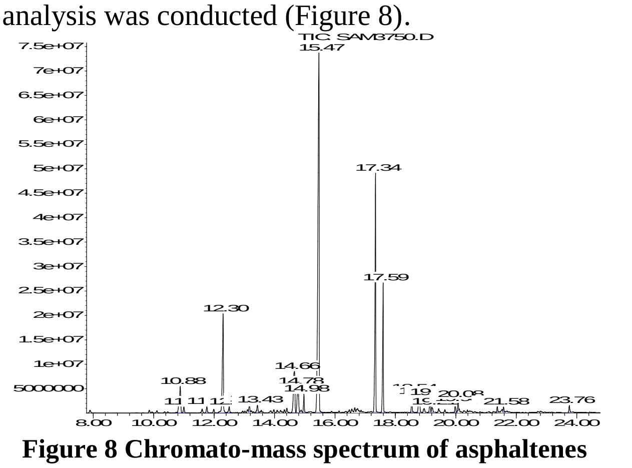


Figure 8 Chromato-mass spectrum of asphaltenes

Chromato-mass spectrum was successfully studied, and the asphaltene composition is presented in Table 5.

Table 5.

Chromato-mass spectrometry results of the TAR product

Substance name	Exit time(min)	Mass fraction (%)
Asphaltene	15,47	41,51
1-methylasphaltene	17,59	8,61
2-methylasphaltene	17,34	16,25
1-ethylasphaltene	18,78	1,77
1,6-dimethylasphaltene	19,15	1,71

The results of chromatography-mass spectrometry showed that naphthalene and its homologs make up the main component in the composition of the TAR product. Among these products, asphaltene homologs constitute a total of 28.34%. A distillation apparatus was installed for fractional distillation of the TAR product (Figure 9). 500 ml of the TAR product was placed in a 700 ml three-necked flask, along with boiling chips, and the setup was connected to a rectification distillation apparatus. The first fraction of the TAR product began distilling at 180-185 ºC. The product was separated into fractions, and their compositions were studied. The first fraction contained asphaltene at 210-220 ºC; the second fraction, at 220-235 ºC, contained asphaltene, 1-methylasphaltene, and 2-methylasphaltene; the third fraction, at 235-250 ºC, contained 1-methylasphaltene and 2-methylasphaltene; and the fourth fraction, at 260-270 ºC, contained 1,6-dimethylasphaltene. The second fraction contained up to 48% asphaltene homologs, while the fourth fraction contained up to 80% asphaltene homologs. The increase in temperature corresponded to the release of higher boiling hydrocarbons.

Figure 9. According to the analysis results, the composition of heavy pyrolysis products includes indene, 1-methylindene, asphaltene, 1-methylasphaltene, 2-methylasphaltene, 1-ethylasphaltene, and 1,6-dimethylasphaltene.

To study the composition of secondary products of the pyrolysis process, the TAR product was first analyzed using chromatography-mass spectrometry (shown in Figure 10).

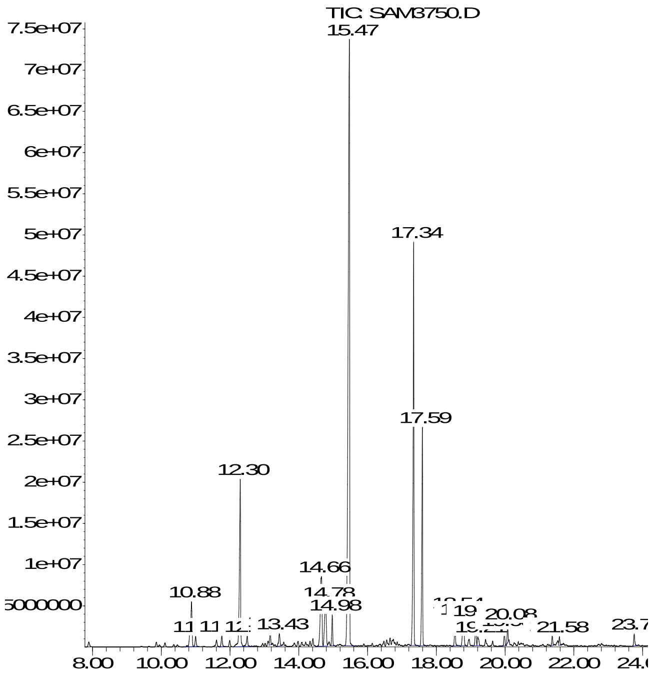


Figure 10. Chromato-mass spectrum of asphaltenes

The results of the chromatographic-mass spectrometry were studied, and the composition of the TAR product is presented in Table 6.

Table 6

Chromato-mass spectrometry results of the TAR product

Substance name	Mass fraction, %
Inden	9,33
1-methylindene	8,96
Asphaltene	41,51
1-methylasphaltene	8,61
2-methylasphaltene	16,25
1-ethylasphaltene	1,77
1,6-dimethylasphaltene	1,71

Table 7

Fractional composition of the TAR product

Fractiont/r	Temperature range, ^oC	The main product in the resulting fraction	Mass fraction of the product (%)	Mass fraction of fractions (%)
1	185-210	Indene, 1-methylindene, Tetraline	70,0	16,85
2	410-420	Asfalten	92,0	32,9
3	420-435	asphaltene, 1-methylasphaltene, 2-methylasphaltene	85,0	22,4
4	435-450	1-methylasphaltene, 2-methylasphaltene	88,0	10,3
5	450-460	Diphenyl	21,0	2,3
6	460-470	1,6-dimethylasphaltene	40,1	1,8
7	470-480	Acenaphthene	50,0	1,2
8	480-490	Trimethylasphalten	75,0	1,95
9	490-500	Fluorene	52,0	1,2
10		Remainder		7,5

To extract asphaltene and its homologs from the TAR product, the secondary product TAR from the Ustyurt Gas Chemical Complex, owned by “Uz-Kor Gas Chemical” JV LLC, was used as raw material. Chromatography-mass spectrometry results showed that asphaltene and its homologs constitute the main component of the TAR product, with asphaltene homologs accounting for 28.34% of the total.

The TAR product was fractionated through rectification distillation, and its composition was studied (Table 7). The fraction obtained in the temperature range of 420-450 ^oC contained up to 80% of 1-methylasphaltene and 2-methylasphaltene, while the fraction obtained in the 460-470 ^oC range contained up to 48% of 1,6-dimethylasphaltene.

Conclusion: Chromatography-mass spectrometry analysis of the TAR product, a secondary product of hydrocarbon pyrolysis, revealed a significant presence of asphaltene and its homologs. As a result, fractional distillation of the TAR product enabled the separation and purification of asphaltene homolog fractions.

List of used literature

1. «Uz-Kor Gas Chemical» QK MChJ rasmiy sayti https://www.uz-kor.com/index.php/ru/deyatelnost.
2. А.И. Юсевич, К.И. Трусов, Е.М. Осипёнок. влияние термической обработки тяжелой смолы пиролиза на выход и качество нафталина., 2022. Т. 95. Вып. 5., С 646-655.
3. Пачин И.М., Павлович О.Н. Усоверш.техн.пол-я дистиллированного нафт-на//Кокс и хим. 2011.№1.с.26-29.
4. В.С. Тимофеев, Л.А. Серафимов, А.В. Тимошенко. Принципы технологии основного органического и нефтехимического синтеза: учебное пособие для вузов /. - М.: Высш. шк., 2010. - 408 с.
5. Ю.В. Думский, Г.М. Бутов. Химия и технология нефтеполимерных смол. – М.: Химия, 1999. – 312 с.

МАРТ	№ 1(103)	2025

С О Д Е Р Ж А Н И Е

1. Химия и физикохимия композиционных материалов и нанокомпозитов

2. Физико-механика и трибология композиционных материалов

3. Разработка и технология получения композиционных материалов