PIROLIZ USULI YORDAMIDA AVTOMOBIL SHINALARI CHIQINDISIDAN OLINGAN DISTILLATNING KIMYOVIY VA FRAKSION TARKIBINI O‘RGANISH.

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Annotatsiya: Bu tadqiqot ishida eskirgan avtomobil shinalarini piroliz qilish natijasida olingan distillatning fizik-kimyoviy xususiyatlari tahlil qilingan va natijalari keltirilgan. Bunda piroliz distillatining fraksion tarkibi, uning zichligi, umumiy oltingugurt miqdori va oktan soni aniqlandi. NKMK AJ ning avtoparklarida ishlatilgan avtomobil shinalari chiqindisidan piroliz distillati namunalaridan tahlillar o‘tkazilib bunda piroliz distillatining tarkibini sifat va miqdoriy tahlil qilish, fraksion tarkibini aniqlash bilan bir qatorda mass-xromatografik spektrometriya yo'li bilan miqdor tarkibi aniqlandi. Piroliz distillatining tarkibiga uglerod soni 6 dan 12 gacha bo'lgan arenlar va olefinlar kiradi. Olefinlarning tarkibi 22,81% ni, arenlar 67,19% ni tashkil etadi. Bundan tashqari tarkibida alkanlar, dienlar va sikloalkanlar ham mavjud.

Piroliz distillatidan 50% dan ortiq hajmdagi benzin fraktsiyalari (40-165°C) va kerosin fraktsiyasining qisman (150-350 °C)da ajralib chiqadi.

Kalit so‘zlar. Piroliz, piroliz distilyati, kauchuk, fraksiya tarkibi, umumiy oltingugurt miqdori, oktan soni, massa-xromatografik spektrometriyasi, zichlik.

ИССЛЕДОВАНИЕ ХИМИЧЕСКОГО И ФРАКЦИОННОГО СОСТАВА ДИСТИЛЛЯТА, ПОЛУЧЕННОГО ПРИ ПИРОЛИЗЕ ИЗНОШЕННЫХ АВТОМОБИЛЬНЫХ ШИН

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В исследовательской работе приводены результаты анализа физико-химических характеристик дистиллята, полученного пиролизом изношенных автомобильных шин. Определен фракционный состав пиролизного дистиллята, его плотность, общее содержание серы и октановое число. Выполнен анализ образцов пиролизного дистиллята из отходов автомобильных шин АО НГМК, вышедших из употребления. Качественный и количественный анализ состава пиролизного дистиллята выполнен методом хромато-масс-спектрометрии вместе с определением фракционного состава. В состав пиролизного дистиллята входили арены и олефины с углеродным числом от 6 до 12. Содержание олефинов составляло 22,81%, аренов 67,19 %. Присутствовали также алканы, диены и циклоалканы. Путем атмосферной перегонки пиролизного дистиллята были получены фракции бензина (40-165°С) в объеме более 50 % и частичный отбор керосиновой фракции (150-350°С)

Ключевые слова: *Пиролиз, пиролизный дистиллят, резина, фракционной состав, общее содержание серы, октановое число, хромато-масс-спектрометрия, плотность.*

ANALYSIS OF THE CHEMICAL AND FRACTIONAL COMPOSITION OF DISTILLATE OBTAINED THROUGH THE PYROLYSIS OF USED AUTOMOBILE TIRES.

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Annotation. The research paper presents the results of an analysis of the physicochemical characteristics of distillate obtained by pyrolysis of worn automobile tires. The fractional composition of pyrolysis distillate, its density, total sulfur content, and octanee number were determined. The analysis of samples of pyrolysis distillate from waste automobile tires of JSC NMMC, which are out of use, was performed. Qualitative and quantitative analysis of pyrolysis distillate composition was performed by chromatography-mass spectrometry together with determination of fractional composition. The composition of hydrolyzed distillate included arenas and olefins with a carbon number from 6 to 12. The content of

olefins was 22,8 %, and 67,19 % of arenas. Alkanes, dienes and cycloalkanes were also present. By atmospheric distillation of pyrolysis distillate, gasoline fractions (40-165ºC) in a volume of more than 50% and partial selection of the kerosene fraction (150-3503ºC) were obtained

Key words: *Pyrolysis, pyrolysis distillate, rubber, fractional composition, totale sulfur content, octanee numbero, chromatography-mass spectrometry, density.*

Introduction.

In our work we used cracking, the high-temperature processing of rubber waste at elevated pressure, opens up the possibility of obtaining liquid hydrocarbon products and a gas mixture. By using high pressure in a hydrogen environment, high-quality liquid fuels with low sulfur content can be obtained. Despite the value of these products, thermal liquefaction and cracking methods are not widely used due to the complexity of the technical equipment. Currently, the method of pyrolysis of waste rubber and other organic waste, which is a process of physical and chemical decomposition of the material at high temperatures without oxygen, is attracting much attention from specialists. The composition of pyrolysis products depends on the type of starting material and process conditions. During the pyrolysis of rubber products, gaseous, solid and liquid products are formed, the proportions of which depend on the reaction conditions. The gas phase usually contains a mixture of hydrogen, methane, carbon monoxide and carbon dioxide, and the liquid phase contains mainly unsaturated aliphatic and aromatic compounds. Two methods of rubber pyrolysis are used in industry: low-temperature liquid-phase with temperatures up to 600°C and high-temperature with temperatures mainly 600 – 900°C. Our work used high-temperature pyrolysis, which produces gas and solid residue with minimal or even no resin.In the face of growing environmental concerns and the urgent need for sustainable solutions, the recycling and repurposing of waste materials have become paramount. Among these materials, worn automobile tires pose a significant challenge due to their non-biodegradable nature and the sheer volume in which they are discarded globally. Pyrolysis, a thermal decomposition process in the absence of oxygen, has emerged as a promising technology for converting waste tires into valuable resources, including pyrolysis distillate.

For comparison, in the United States in 2022, the number of worn tires was about 1.5 million tons [1].

In the United Kingdom, approximately 500,000 tons of worn tires are generated annually. Among these, about 34% undergo recycling, 2.6% are recovered, 15% are repurposed, and 6% are disposed of in landfills. NMMC JSC, a joint venture renowned as one of the world's largest producers of rare and precious metals, reportedly accumulates around 1.33 thousand tons of worn tires annually as of 2023. Existing methods for recycling worn automobile tires can generally be categorized into two main groups: physical processing methods and chemical processing methods. Among these methods, thermal decomposition, specifically pyrolysis, stands out as the optimal approach. Utilizing discarded automobile tires as a raw material base holds significant economic and environmental relevance. These tires constitute valuable secondary raw materials, consisting of approximately 65-70% rubber, 15-25% carbon black, and 10-15% metal cord. Although pyrolysis distillate production is currently exclusive to NMMC JSC in Uzbekistan, the management of pyrolysis waste remains unaddressed. Pyrolysis distillate emerges as the most pertinent product among the outputs of the pyrolysis process. Its potential applications hinge upon a complex array of physical and chemical characteristics. However, technical documentation predominantly emphasizes parameters such as density, fractional composition, total sulfur content, and octane number [2,3]. A pyrolysis plant with a daily capacity of one ton operates within the central mining department of the Navoi Mining and Metallurgical Combine. Consequently, there exists a pressing need to comprehensively examine the physicochemical attributes of hydrolyzed distillate to identify and broaden its potential applications.

Objects and methods of the research

Distillate obtained by pyrolysis of worn-out automobile tires was chosen as the objects of research. Some physical and chemical characteristics were determined, such as density (Ph)-GOST 3900-2022; octanee number according to the GOST 511_2015 method, total sulfur content (St)-GOST 32139-2019. [4-5].

In our experiments, we used modern physical and colloidal-chemical (IR spectroscopy and gas-liquid chromatography) research methods that allow us to determine the presence of functional groups and individual hydrocarbon composition of pyrolysis distillate, as well as the method for determining the fractional composition according to the interstate standard GOST 2177-99 (ISO 3405-88). IR spectra were obtained on a Shimadzu IRTracer-100 spectrophotometer with potassium bromide. [6].

Results obtained and their discussion

During the pyrolysis process, aside from the primary products, additional products characterized by significantly higher molecular weights (ranging from 19% to 38%) are generated. The resultant pyro condensate can be classified into three distinct groups based on their boiling points: pyrolysis distillate (with a boiling point range from 33°C to 150°C), heavy pyrolysis resin (boiling point range from 173°C to 305°C), and product (with a boiling point beginning at 288°C). The proportion of pyro condensate produced typically ranges between 3% to 2.7% of the total mass of pyrolysis products, varying depending on the composition of the raw material utilized. Pyrolysis distillate, characterized by its light yellow to light brown color and unpleasant odor, is a variable liquid whose composition is contingent upon the specific raw material subjected to pyrolysis. To assess both the quality and quantity of the pyrolysis distillate samples obtained from these processes, preliminary testing was conducted utilizing a chromatography-mass spectrometer, specifically the Chromatek Kristall model. The results of the analyses are shown in Figure 1 and Table 1.

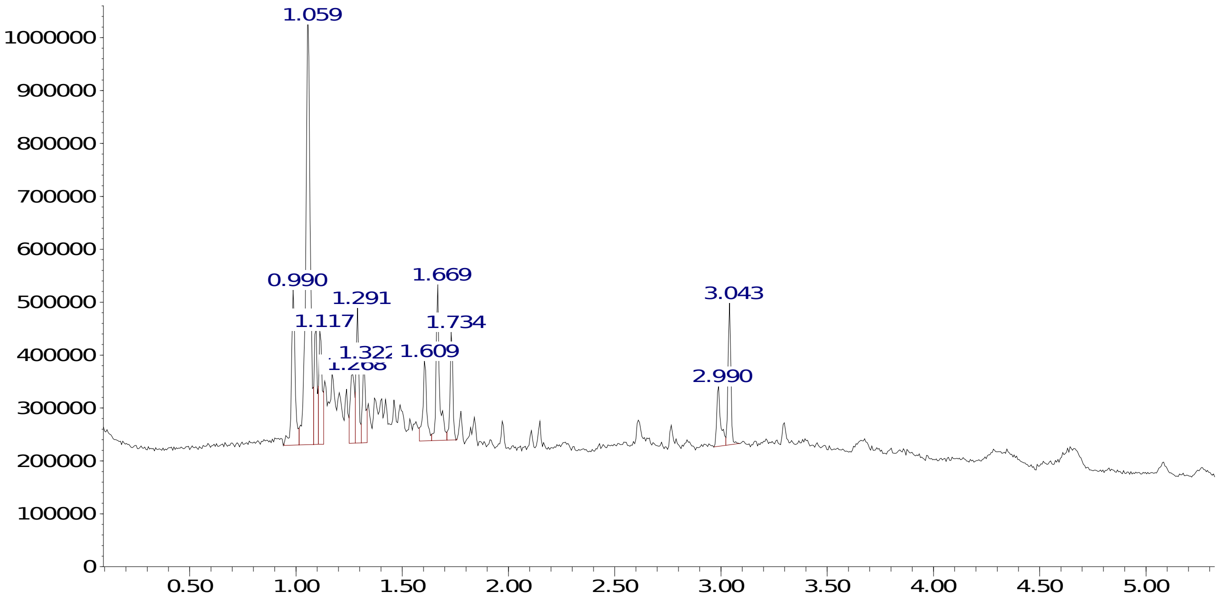

Figure 1. Mass spectrogram of pyrolysis distillate

Table 1.

Quantitative and qualitative composition of heavy pyrolysis resin of worn tires

№	Substance	Quantity, %	Base match
1	Ethylbenzene	9.7	93
2	Benzene, 1,3-	dimethyl-13.2	94
3	Cyclopentanone, 2-ethyl-	44.1,1	90
4	Benzenemethanol, 2,5-dimethyl-	9.5	91
5	Benzene, 1,2,4-trimethyl-	7,6	95
6	1,6-Dimethylnaphthalene	8,4	94
7	Pyridine, 2,4-	dimethyl-	7.5 96

IR spectroscopic analysis of pyrolysis distillate to determine various functional groups in its structure showed that (Figure 2) it has bands, characteristic of aromatic groups of hydrocarbons at wavelengths from 3053.11,11 cm^{-1} to 1,543. 56cm^{-1}, for the alkene group –C=C– (1,377. 12,12 $cm\text{-}1^{1}$).1; 1440.83 $cm\text{-}^{1}$), for the vinyl group >$C=CH_2$ (725.16cm^{-1}), for dienes C=C=C (1980.89 cm^{-1}) and bands characteristic of alkyne ≡C–H (621.66$cm\text{-}^{1}$).

Here, a characteristic triplet of wavelengths in the 725.23, 754.17, and 802.39 cm^{-1} ranges is clearly visible, which indicates the presence of aromatic structures.

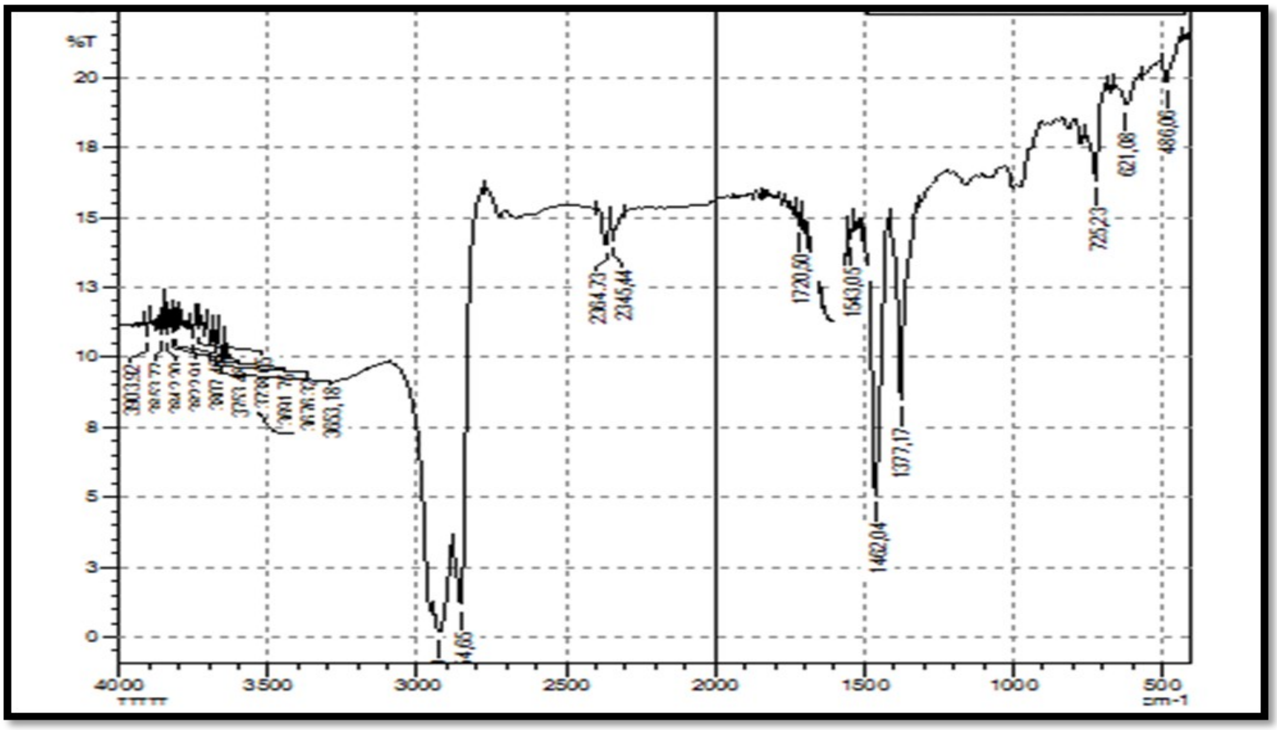

Figure 2. IR spectrum of pyrolysis distillate

The analysis of fraction composition plays a pivotal role in assessing the quality of hydrocarbon raw materials and their processed products, serving as a crucial determinant. Determining the fractional composition of pyrolysis distillate is carried out through laboratory distillation, following the guidelines outlined in the interstate standard GOST 2177-99 (ISO 3405-88). This method involves distilling fractions with distinct boiling limits from the pyrolysis distillate at incrementally increasing temperatures. Each fraction within the distillate exhibits specific boiling temperature ranges, denoted by the initial boiling temperature (Tnk) and the end boiling temperature (Tcc), which are influenced by their respective chemical compositions. By employing this methodology, it becomes feasible to ascertain the fractional composition of the hydrocarbon raw materials under investigation and their processed products based on their true boiling points. Furthermore, this approach facilitates the determination of the potential presence of individual fractions within the distillate, allowing for the acquisition of distillate samples for further analysis of their composition and properties. Table 2 shows the results of a series of experiments to determine the fractional composition of pyrolysis distillate (wt %). by distillation under atmospheric pressure at acceleration temperatures from 40 to 350 °C

Table 2.

Main results of experiments on distillation of pyrolysis distillate

№	. Name of indicators	Experiments		
		1	2	3
1	Density at 20 °C, kg / m3	882.3		
2	Determination of e octane numbers UIT octane, cm^3/ kg	96		
3	Fractional composition			
	Boiling point, °C	38		
	10 %	82	81	83
	20 %	109	110	111
	30 %	131	129	130
	40 %	154	159	162
	50 %	181	179	180
	60 %	201	208	205
	70 %	254	251	248
	80 %	303	305	309
	90 %	312	319	321
	End-of-boiling point, °C	344	350	349
4	Yield, %	90	93	91
5	Residue, %	7.4	5.5	7.4,4
6	Loss, %	2.6	1.5	1.6

As can be seen from the data in Table 2, the average value of the measured density of pyrolysis distillate at a standard temperature (20°C) is p20 = 882.3 kg /m^3. The initial boiling point, or the temperature at which the first drop of liquid, pyro distillate condenses and breaks off, is the same in all experiments and amounts to 38°C. The results of distillation of distillate samples (60-350°C) show that the distillate fractions formed during the experiments respond to the gasoline fraction in terms of the boiling point temperature limit (n. c.-180°C). Based on the results of each experiment, the yield of fractions was calculated, which is 90÷93 %, and the loss value ranged from 1.6 to 2.6 %. Figure 3 shows the curve of the fractional composition of pyrolysis distillate at acceleration temperatures from 40 to 350 °C, constructed according to experiment № 3.

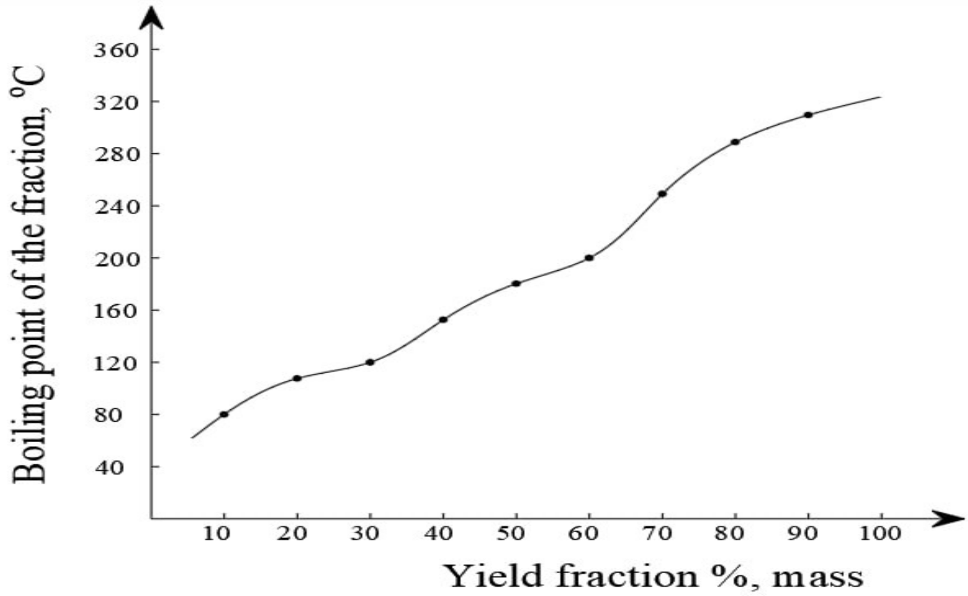

Figure 3. Fractional composition curve of pyrolysis distillate

Thus, by atmospheric distillation of pyrolysis distillate, it is possible to obtain gasoline fractions at temperature parameters from 40 to 165°C in a volume of more than 80 % and partially isolate kerosene fractions in the range from 150 to 310°C.

Conclusion

The aim of this study was to investigate the physicochemical properties of pyrolysis distillate derived from samples of worn automobile tires, with the objective of addressing the challenge of rational utilization and assessing the efficacy of chemical processing methods in diesel fuel production. The findings from the analysis of the fractional composition of pyrolysis distillate demonstrated its potential as a valuable raw material for the generation of light oil products through atmospheric distillation. Experimental results confirmed that, within the temperature range of 40 to 350°C, the yield of light fractions from pyrolysis distillate ranged between 90% and 93.3%. Notably, the gasoline fraction (C40-165°C) accounted for over 50% of the total yield, with minimal losses not exceeding 1.6-2.6%. Addressing the preparation of raw materials for hydrocarbon material production is crucial in formulating economically and environmentally sound composite formulas. Given the chemical nature of pyrolysis distillate and its substantial production volume, it emerges as a key target product for various material productions from waste. This underscores its significance in waste management strategies and highlights its potential as a valuable resource for the production of diverse material types.

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