Chemical Technology, Control and Management

Manuscript 1537

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ISSN 1815-4840, E-ISSN 2181-1105
Himičeskaâ tehnologiâ. Kontrol' i upravlenie
CHEMICAL TECHNOLOGY. CONTROL AND MANAGEMENT
2024, №1 (115) pp.28-32
International scientific and technical journal
journal homepage: https://ijctcm.researchcommons.org/journal/
Article history: Received 27 January 2024; Received in revised form 24 February 2024; Accepted 29 February 2024; Available online 19 April 2024
Since 2005

UDC 543

CHROMATOGRAPHIC ANALYSIS OF THE CHEMICAL COMPOSITION OF PYROLYSIS DISTILLATE

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Annotation. *The paper presents the results of a study of the physico-chemical characteristics of the liquid fraction of products of thermal oxidative pyrolysis of worn tires. The mass fraction of the volatile gas compounds, the optimal boiling points of the obtained condensates and the flashpoint of pyrolysis liquids, together with the mass composition of cracking products of rubber products at high-temperature pyrolysis at a temperature of 800-900 °C, were determined. Chromatographic analysis allowed us to determine the composition, mainly the mass composition of pyrolysis products, which consisted of carbon (42.8%), higher aliphatic and aromatic hydrocarbons (17.0%), methane (10.2%), benzene (4.2%) and other components.*
Keywords*: Rubber, pyrolysis, gas composition, ethane, cracking, mass fraction of volatile substances, resin.*

Annotatsiya. *Ishda yaroqsiz avtomobil shinalarini termooksidlovchi pirolizidan olingan mahsulotlarning suyuq fraksiyalari fizik-kimyoviy tavsiflarini tadqiq etish natijalari keltirilgan. 800-900 °C yuqori haroratli pirolizlashda rezinotexnik mahsulotlarning kreking mahsulotlari umumiy tarkibi bilan pirolz suyuqliklarining birgalika yonish harorati, olingan kondensatlarning qaynashini optimal harorati hamda uchuvchan gazli birikmalarning massaviy ulushi aniqlangan. Xromatografik tahlil tarkibi asosan uglerod (42,8 %), yuqori alifatik va aromatik uglevodorodlar (17,0 %), metan (10,2 %), benzol (4,2 %) va boshqa komponentlardan iborat bo'lgan piroliz mahsulotlarining massaviy tarkibini aniqlash imkonini berdi.*
Tayanch so'zlar: *Rezina, piroliz, gaz tarkibi, etan, kreking,uchuvchan moddalarning massa ulushi, smola.*

Аннотация. *В работе приведены результаты исследования физико-химических характеристик жидкой фракции продуктов термоокислительного пиролиза изношенных автомобильных шин. Определены массовая доля летучих газовых соединений, оптимальные температуры кипения, полученных конденсатов и температура вспышки пиролизных жидкостей вместе с массовым составом продуктов крекинга резинотехнических изделий при высокотемпературный пиролиз температуре 800-900 °С. Хроматографический анализ позволил определить в основном массовый состав продуктов пиролиза, который состоял из углерода (42,8 %), высших алифатических и ароматических углеводородов (17,0 %), метана (10,2 %), бензола (4,2 %) и других компонентов.*
Ключевые слово: *Резина, пиролиз, состав газовой, этан, крекинг, массовая доля летучих веществ, смола.*

Introduction. The number of car parks in the world increases every year, which naturally leads to the formation of landfills of used tires. According to statistics from the European Tire Recycling Association, more than 13 million tons are generated in Europe. damped car tires. [1]

According to statistics, only NMMC accumulates about 1.1 thousand tons of used tires annually (2022).

Currently, all existing methods for recycling used tires can be divided into two groups:

1. Physical method of tire recycling
2. Chemical processing method

Among the existing methods for recycling used car tires, the optimal method is thermal decomposition-pyrolysis.

The use of obsolete car tires as a raw material base is relevant both from the economic and environmental side. An automobile tire is a valuable secondary raw material containing rubbers - 65-70%, carbon black-15-25%, metal cord - 10-15% [2-4].

In modern conditions, with the tightening of legislation in the field of solving the problem of waste, the most promising and environmentally friendly method of recycling car tires, with the production of valuable types of chemical product, is pyrolysis. Among the pyrolysis products, carbon black is the most relevant. The scope of application of carbon black depends on the complex of physico-chemical characteristics. However, most processors in the technical documentation indicate their minimum amount, such as the mass fraction of volatile substances, boiling point, humidity, mass fraction of sulfur and pH of the medium.

The central mining department of the Navoi Mining and Metallurgical Combine operates a pyrolysis unit with a capacity of one ton per day. Therefore, to identify and expand possible areas of application of carbon black, a detailed study of the physicochemical characteristics of this product is necessary.

Objects and methods of research. As the object of study, we used pyrolysis liquid obtained from rubber products. The work used modern physico- and colloid-chemical (gas-liquid chromatography) research methods to determine the functional groups and individual hydrocarbon composition of the pyrolysis distillate. Chromatographic analysis was carried out on a Record chromatograph with adsorbent carrier TX-U-1-100 [5-7].

Results of research: The operating temperature range of these processes is determined by the processed product. For example, liquid-phase pyrolysis of rubber products at temperatures above 350 ° C leads to the formation of methane and ethane with high yield. The two-stage method finds universal application. It allows you to obtain high-quality chemical raw materials. At the first stage, a microwave reactor heater is used. Dielectric heating of waste is carried out by adding NaOH to nonpolar polymers (old tires). The second stage of splitting is carried out at temperatures up to 400-450 ° C. The worm reactor has a number of semi-industrial and industrial installations for the disposal of waste rubber products. A two-stage method is mainly used with preliminary melting of rubber products with high-boiling distillate as a reaction medium and pyrolysis (cracking) in the cracking zone. It should be noted that the processing of rubber products is much simpler than polymers, since the composition of rubber waste is more homogeneous.

Table 1

Qualitative and quantitative composition of the gas phase of thermal oxidative pyrolysis of worn car tires

№	Components	Content of components,%	№	Components	Content of components,%
1.	Gas	45,0	8.	Hydrogen	17,5
2.	Ethane	14,9	9.	Carbon monoxide	4,2
3.	Propane	5,0	10.	Carbon dioxide	4,9
4.	Butane	3,5			
5.	Propylene	1,5			
6.	Ethylene	2,2			
7.	Butene	1,3			

Analyzes of the quantitative composition of the gas phase of rubber products based on worn-out car tires occur in the temperature range of 350-550 oC. Therefore, we investigated the thermal-oxidative pyrolysis of worn-out car tires at a temperature of 550 °C. Pyrolysis products mainly consist of gas, liquid and solid phases. The composition of the gas phase was studied using a gas chromatograph, the results of which are given in Table 1.

Analysis of the research results (Table 1) shows that the gas phase mainly consists of 45% methane, 14.9% ethane, and 17.5% hydrogen. Therefore, the gas mixture can be reused for burning car tires in reactors and pyrolysis plants.

The composition of the liquid fraction of the pyrolysis products of worn-out tires was also studied, the results of which are presented in Table 2.

Table 2

Characteristics of the liquid fraction of the products of thermal oxidative pyrolysis of worn car tires in the range at a temperature of 350-550 ° C.

№	Components	Component content,%
1.	Appearance	Dark brown
2.	Mass fraction of volatile substances, % n/a	2
3.	RN	6,5
4.	Boiling point, K	450
5.	Flash point, K	570
6.	Self-ignition temperature, K	725
7.	Pour point, K	243
8.	Molecular mass	1000-1200

High-temperature pyrolysis is carried out at temperatures from 600 to 800 ° C. With direct heating and supply of air or, most often, water vapor, the pyrolysis temperature may be lower. At high pyrolysis temperatures, the yield of aliphatic compounds decreases, and aromatic compounds significantly increases. The main focus is on recycling scrap tires. In order to improve the process, drum reactor installations are being developed. Consider (Table.3) some installations for high-temperature pyrolysis of worn tires. The economic efficiency of pyrolysis is largely determined by the use of its products. The pyrolysis process in the reactor takes place at a temperature from 700 to 750 ° C.

In this case, the composition of pyrolysis products can be adjusted by selecting the appropriate coolant. In this case, it is expected that the resulting pyrolysis oil, containing more aliphatic and aromatic compounds, will be suitable for further chemical processing, mainly as valuable combustible oils and raw materials for the production of motor fuels. Fractions containing unsaturated hydrocarbons can be transformed into thermoplastic polymers by thermal or catalytic polymerization. Aromatic compounds such as naphthalene and its homologues are purified to technically pure products.

Table 3

Mass composition of pyrolysis products of rubber products (at pyrolysis temperature 800-900°C), %

№	Pyrolysis products	Chemical formula	Amount of substance formed, %
1.	Hydrogen	H_2	0,8
2.	Methane	CH_4	10,2
3.	Ethylene	C_2H_4	2,6
4.	Ethane	C_2H_6	1,2
5.	Propane	C_3H_8	0,7
6.	Isobutane	C_4H_{10}	0,2
7.	Butadiene	C_4H_6	0,3
8.	Penten, hexene	C_5H_{10}, C_6H_{12}	0,1
9.	Benzene	C_6H_6	4,2
10.	Toluene	C_7H_8	3,8
11.	Xylene, ethylbenzene	$C_6H_4(CH_3)_2$, $C_6H_5C_2H_5$	1,9
12.	Styrene	C_8H_8	2,3
13.	Naphthalene	$C_{10}H_{10}$	0,9
14.	Higher aliphatic and aromatic hydrocarbons	C_nH_{2n+2}	17,0
15.	Carbon	C	42,8
16.	Hydrogen sulfide	H_2S	1,9
17.	Filler		7,9

The pyrolysis process was studied at various temperatures and various gas carriers (air, oxygen, helium). It has been established that with changes in temperature and the nature of the gas carrier, the qualitative and quantitative composition of the pyrolysis products changes.

Table 4

Composition of the gas obtained from the pyrolysis of tire rubber in an environment of inert gases and nitrogen.

№	Components	Content, % v.		
		He	Ar	N_2
1.	Methane	32,5	31,7	27,1
2.	Ethane	3,8	3,5	2,7
3.	Propane	4,2	3,9	3,4
4.	Butane	2,1	1,8	1,5
5.	Ethylene	10,7	10,1	9,6
6.	Propylene	9,6	9,3	8,7
7.	Butylene	6,4	6,0	5,3
8.	Isoprene	2,3	2,1	1,7
9.	Hydrogen	15,4	15,2	13,6
10.	Carbon monoxide	0,9	1,3	2,8
11.	Carbon dioxide	0,6	1,1	1,9
12.	Helium	11,5	-	-
13.	Argon	-	14,0	-
14.	Nitrogen	-	-	21,7

During pyrolysis carried out in an environment with air, the composition of the pyrolysis gases formed included an increased amount of oxides (Table 3.1.12).

Table 5

The composition of the gas obtained by pyrolysis of tire rubber in an environment with air and oxygen.

№	Components	**Component content**, %.	
		air	oxygen
1.	Methane	18,3	10,2
2.	Ethane	1,9	1,1
3.	Propane	2,4	1,3
4.	Butane	1,1	0,6
5.	Ethylene	7,2	4,8
6.	Propylene	6,5	3,9
7.	Butylene	3,6	2,5
8.	Isoprene	1,3	0,9
9.	Hydrogen	9,5	6,6
10.	Carbon monoxide	4,1	5,8
11.	Carbon dioxide	2,7	3,9
12.	Nitrogen	29,8	-
13.	Oxygen	11,6	58,2

The increased amount of oxides in pyrolysis gases can be explained by the presence of up to 20% free oxygen in the air. Oxidized hydrocarbons saturated with oxygen in the air formed as a result of pyrolysis ignite and carbon oxides are formed.

As a result, we can conclude that the thermal decomposition of tire rubber practically ends at a temperature of 650 - 735 oC, and pyrolysis occurs at different temperatures, but with different ratios of reaction products - with increasing temperature the yield of liquid products increases and it becomes maximum at the highest temperature of 625 oS.

At this temperature value, the yield of the liquid intermediate is the maximum, which is most favorable for obtaining secondary raw materials for the subsequent production of high-quality motor or furnace fuel.

The thermogram of the process indicates the completion of the destruction of raw materials and this gives reason to consider the pyrolysis temperature of tire rubber 625 oC optimal. This value was used on an ongoing basis for the subsequent study of the main parameters of the pyrolysis process - the state of the raw materials and the reaction time.

The experiment showed that the heating time of rubber ranges from 2 minutes to 1530 hours. Moreover, it depends primarily on the thickness of the plate, and not on the final heating temperature. This dependence is well visualized. In Fig. 1, all four curves are practically superimposed on each other, thereby confirming the data of the thermographic analysis.

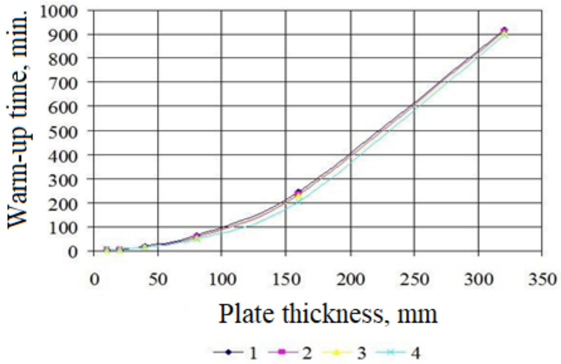

Fig. 1. ***Dependence of the heating time of the central axis of the rubber plate on its thickness at:*** *1 – 525 °C; 2 – 600 °C; 3 – 700 °C; 4 – 800 °C.*

Conclusion. Thus, the determination of the chemical composition of pyrolysis distillate in order to identify promising options for obtaining high-octane hydrocarbon liquids from samples of automobile tires intended for recycling. The mass fraction of the volatile gas compounds, the optimal boiling points of the obtained condensates and the flashpoint of pyrolysis liquids, together with the mass composition of cracking products of rubber products at high-temperature pyrolysis at a temperature of 800-900 °C, were determined. Chromatographic analysis allowed us to determine the composition, mainly the mass composition of pyrolysis products, which consisted of carbon (42.8%), higher aliphatic and aromatic hydrocarbons (17.0%), methane (10.2%), benzene (4.2%) and other components. The main factors for obtaining high-quality hydrocarbon distillate are the selection of optimal heating options for the starting material of 1 hour 45 minutes, pyrolysis time of 2 hours 30 minutes, and the optimal temperature of the pyrolysis reactor of 500-550 ° C.

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