

CHARACTERISTICS AND APPLICATIONS OF WASTE TIRE PYROLYSIS PRODUCTS: A REVIEW

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Abstract. The review considers the environmental problem of generation, accumulation and utilization of waste tires in Ukraine and the world. It is established that waste tires can serve as a valuable raw material for obtaining fuel components and technical/individual chemicals for further industrial processing. One of the promising methods for the rational utilization of waste tires may be their pyrolysis. The pyrolysis process of waste tires produces gaseous, liquid and solid carbonized residue. At the same time, there is no ideal universal technology for the use of waste tire pyrolysis products without preliminary treatment/purification methods. The main characteristics, processing methods and applications of products obtained from the pyrolysis of waste tires are briefly considered.

Keywords: waste tires; alternative fuel; tire pyrolysis; carbon black; pyrolysis oil; pyrolysis gas.

1. Introduction

Given the depletion of global oil reserves, the use of alternative energy sources is becoming a pressing issue. The oil refining industry is gradually adapting to cheaper and heavier raw materials due to the depletion of expensive and light oil, which prompts a gradual transition to unconventional types of raw materials, such as spent hydrocarbon materials (waste) and biomass¹.

Industrial waste has become one of the most significant environmental problems, seriously undermining the stability of the environment. In particular, the vast volumes of industrial and household waste pose a real environmental threat to society and nature. The problem of rational utilization of industrial waste is extremely

relevant and requires immediate and effective resolution, as it has a serious impact on the environment and human health. It is worth noting that the reuse of industrial waste (used tires, oils, plastic, *etc.*) for the production of energy resources can reduce the negative impact on the environment^{1–10}.

Among the different categories of waste that cause environmental pollution, waste tires (WAT) occupy a special place, which is a serious threat to the diversity of ecosystems and human health. Their huge volume and features of utilization make them a key factor in environmental anxiety.

Tires are one of the main consumables of any motor transport¹¹. According to the European Tyre & Rubber Manufacturers Association (ETRMA), 289 million tires are sold in the European Union every year, which is equivalent to only 20 % of the world market (approximately 1.5 billion tires worldwide per year)^{12,13}. The average number of passenger cars in the European Union per 1000 population is 560, according to the EU Statistical Office¹⁴. According to the Law of Ukraine “On Waste”, used car tires are used materials that belong to the fourth class of danger and require disposal at special enterprises¹⁵. In Ukraine, the number of cars as of 2020 was 245 units per 1000 inhabitants, excluding freight and specialized transport, and it is growing annually¹¹. Fig. 1 shows data on the formation of WAT in different countries of the world¹⁶ as of 2021.

Waste tires are not biodegradable and at the same time, they are difficult to reuse or recycle without any prior mechanical or thermal treatment due to their thermomechanical properties¹². The growing number of used tires is a serious threat to the natural environment and human health. Illegally dumped or accumulated used tires pose a potential risk of uncontrolled combustion.¹⁷ Accordingly, millions of WAT are subject to disposal annually. At the same time, there is no centralized system of WAT collection in Ukraine and only in some regions of the country there are private enterprises for the disposal and/or recycling of WAT¹⁸.

To perform their initial function and achieve a long service life, tires are made from materials that do not

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biodegrade^{19–21}. Typically, the main component of tires is rubber (~45–47 %), due to its good elasticity and damping properties²². Rubber consists of a mixture of various natural rubbers, such as polyisoprene, or synthetic rubbers, such as polybutadiene, styrene-butadiene rubber (SBR), and (halo)butyl rubber, the proportions of which depend on the purpose of the product. These rubbers are most often found in treads (32.5 wt. %) and sidewalls (22 wt. %)²². If technical carbon and silica (~21–22.5 %) are not added to the tire composition, the mechanical strength and wear resistance of the tires will be very low²². The main effect of technical carbon is to improve the wear resistance of tires and also helps to remove heat from the tread to avoid thermal damage to the tires. The role of steel is to provide support and strength to the tires²³. Sulfur as a vulcanizing agent increases the elasticity of tires and increases their strength and hardness²⁴, and zinc oxide acts as an activator that accelerates the vulcanization of rubber²². However, the amounts of these components in the tire recipe vary depending on the requirements of tire production and their properties.

Due to the above composition and structure, when a tire reaches the end of its life cycle, it cannot be restored and directly reused, accordingly, it becomes a used tire. The presence of different components creates a problem of choosing a method for their rational utilization.

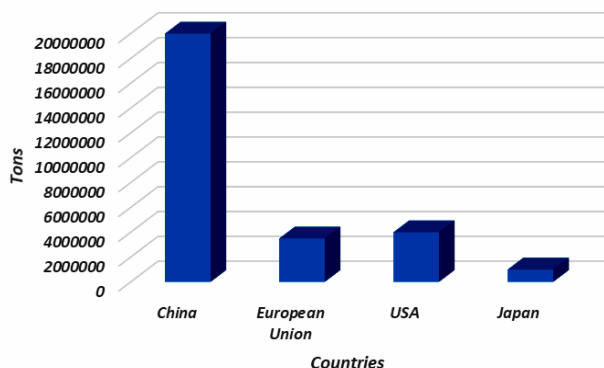


Fig. 1. The annual production of waste tires in some countries¹³

The main methods of disposal/recycling of WAT can be attributed to burial in landfills, reuse, incineration, use of raw materials of the pyrolysis process, and carbon black production²⁵. Part of the WAT is used for the production of modified bitumens^{26,27}. On the other hand, the high energy intensity of WAT has prompted their reuse in various industries. Pyrolysis^{28,29}, gasification³⁰, and combustion³¹ of WAT can maximize resource utilizations and reduce dependence on fossil fuels.

The methods of disposal of WAT and their common areas of application are presented in Fig. 2.

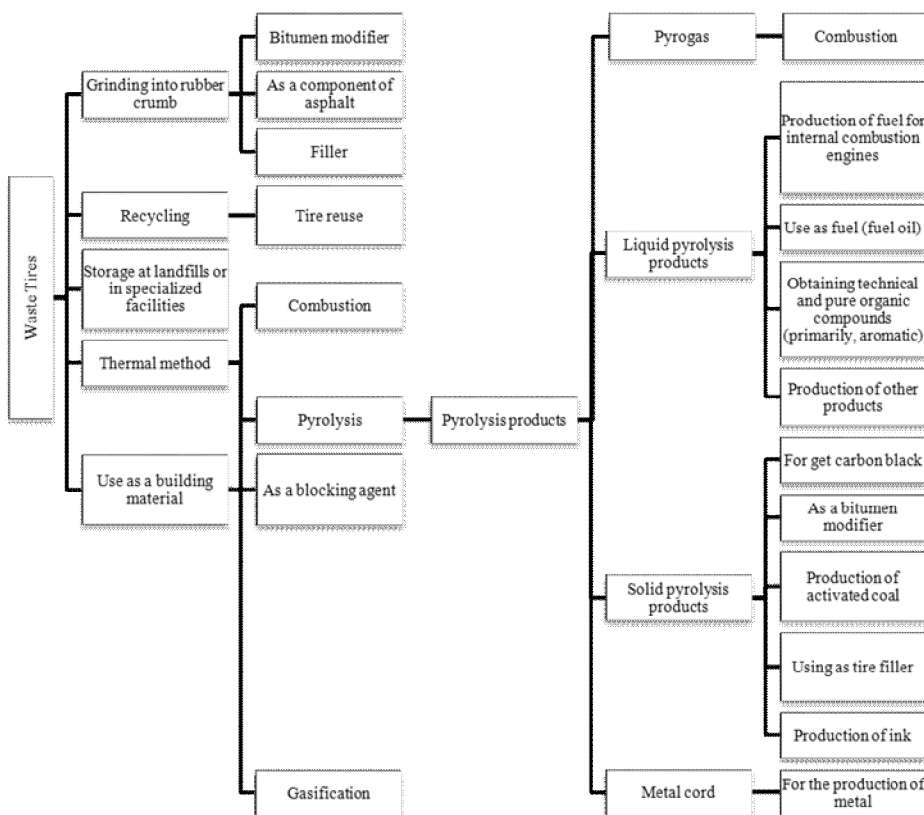


Fig. 2. Methods of WAT disposal and their general areas of application

As can be seen from Fig. 2, the methods of WAT disposal can be divided into 5 groups:

- shredding into crumb rubber and use as a component of road coverings^{32,33};
- recycling – restoration of the operational characteristics of car tires by physicochemical methods for a certain time³²;
- thermal methods – incineration (the simplest but the most non-ecological method), gasification (for the production of gases) and pyrolysis (one of the most promising methods)²⁴;
- use as a building material³⁴;
- storage in landfills or on specialized sites^{35,36}.

Therefore, in view of the above, considering the significant amount of WAT formation in the world, they are a valuable secondary raw material for the production of products of various purposes and new energy resources. At the same time, due to their complex structure and qualitative composition, there is a problem of choosing a method for their rational utilization. Among the various methods of WAT disposal, with the receipt of products of various purposes, a special place is occupied by the processes of pyrolysis of used tires, with the receipt of fuel and chemical raw materials. Accordingly, below is a brief review of the process of WAT pyrolysis, characteristics and ways of application of the products obtained in this process.

2. Processes of Pyrolysis of WAT

The pyrolysis process is a promising method of processing, as well as energy and fuel recovery in the field of used tire recycling, which can meet three principles of solid waste recycling: reduction, resource recovery, and reduction of pollutant emissions. Compared to other disposal methods (for example, incineration³⁷, tread restoration, waste burial³⁸) the use of pyrolysis, as a method of disposal, has been widely studied, as it leads to a reduction in secondary environmental pollution and an increase in the economic value of the products. In the pyrolysis process, the organic components of WAT decompose to form gases, liquid pyrolysis products³⁹ and solid residue²⁸. Accordingly, the conversion of WAT into alternative fuel allows reducing the use of conventional fossil fuel, and the pyrolysis of WAT is a real way of indirect reduction of greenhouse gas emissions⁴⁰. In addition, the steel reinforcement of the tire can be removed from the residual carbon and sent back to the metallurgical industry⁴¹.

The pyrolysis process (a thermal process that is carried out at high temperatures without access to oxygen or with its minimal amount) is one of the common methods of used tire recycling, with the aim of obtaining

fuel and chemical raw materials^{3,16,42}. Typically, its raw material is crumb rubber, which is obtained as a result of shredding WAT and removing metal parts (metalcord).

The quality and yield of pyrolysis products strongly depend on the initial composition of the tires and the conditions of the pyrolysis process, and also play a significant role from the point of view of the economic feasibility of the pyrolysis process of WAT⁴³. In general, the quality and quantity of pyrolysis products are determined by the following factors:

- type of pyrolysis reactor (with a stationary layer, fluidized layer, conical spouting layer, and reactor with a rotary furnace)⁴⁴;
- type of pyrolysis process (vacuum pyrolysis, microwave pyrolysis, hydrolysis, co-pyrolysis, and catalytic pyrolysis)⁴⁵;
- factors of the process implementation⁴⁶ (temperature, pressure, residence time, carrier gas (N₂, CO₂), particle size, catalyst);
- initial composition of the tires.

In order to change the distribution of products, improve the quality of pyrolysis products or obtain products with better operational properties, various processes alternative to conventional thermal pyrolysis were proposed in⁴⁵. These can include vacuum pyrolysis, pressure pyrolysis, microwave pyrolysis, plasma pyrolysis, hydrogenating pyrolysis, co-pyrolysis, and catalytic pyrolysis⁴⁵. However, they are characterized by high energy consumption, capital investments, and needs for reagents (hydrogen), which is feasible under the conditions of large-scale processing of WAT and economically unfeasible under the conditions of processing at small-scale mini-plants, as it happens in Ukraine.

During this process, approximately 33–39 wt. % of solid residue, 34–45 wt. % of liquid products, and the rest – gases are predominantly formed (data are given in terms of 100 % crumb rubber, which, on average, makes up 85 % of WAT; the rest – steel cord). Depending on the type of process, its factors, the composition of the raw material, the yields of products can vary significantly. Possible limits of the yield of pyrolysis products of crumb rubber are present in Table 1^{3,21,24,28,29,34,37}.

Table 1. Yield limits of crumb rubber pyrolysis products

Raw materials and products	wt. %
Loaded: Crumb rubber	100.0
Products: Gas	1.7–77.0
Liquid products	14.9–63.7
Solid residue	21.6–69.0
Total	100.0

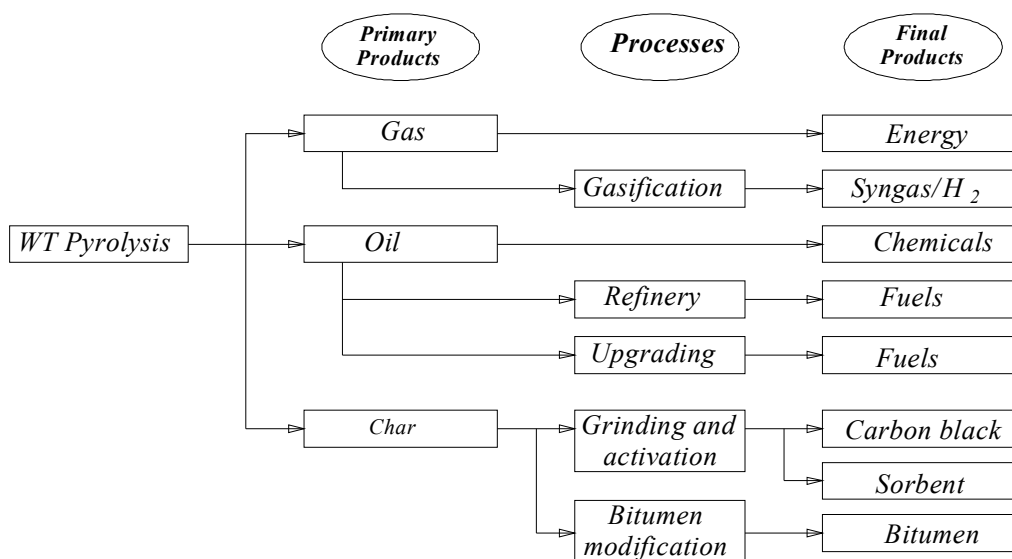


Fig. 3. Products obtained as a result of WAT pyrolysis and their areas of application

The characteristics and areas of application of the WAT pyrolysis products are presented in Figs. 2, 3 and considered below.

3. Characteristics and Application of WAT Pyrolysis Gases

During WAT pyrolysis, a significant amount of tire pyrolysis gases (pyrogas) is obtained, which mainly consists of alkanes, hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and unsaturated compounds (primarily, alkenes, dienes). The average composition and characteristics of pyrogas are given in Table 2³. Alkene, butadiene, and similar secondary unsaturated compounds are formed throughout the duration of the pyrolysis process⁴⁷. In addition to the fact that pyrogas contains a highly desirable petrochemical substance and has a high potential energy capacity to support the pyrolysis process itself (combustion of pyrogas in reactors).

Before using pyrogas from WAT, depending on the conditions of its receipt, it must be subjected to purification processes. For example, in the literature^{48,49}, the need to clean pyrolysis gas before combustion due to the presence of hydrogen sulfide is emphasized. Also, Aylón *et al.*⁵⁰ noted that to avoid emissions of acidic gases, a pyrogas cleaning unit should be included in the WAT pyrolysis unit. Removal of H_2S from pyrogas is important to prevent corrosion of equipment and pipelines, as well as to meet the needs of fuel gas. In addition, reducing the content of H_2S to a very low level is mandatory for environmental reasons⁵¹.

Table 2. The results of the gas composition study

Component	wt. %
H_2	12.78
CH_4	24.66
C_2H_6	8.49
C_2H_4	7.29
C_3H_8	3.69
C_3H_6	5.69
2-methylpropane	1.00
C_4H_{10}	0.60
C_4H_8	6.99
Cyclopentane	0.10
2-methylbutane	0.10
1,3-Butadiene	0.40
Sum of C_5^+ hydrocarbons	1.30
Sum of C_6^+ hydrocarbons	0.40
CO_2	4.89
O_2	0.50
N_2	18.07
CO	3.00
H_2S	0.05
Total	100.00
Heating value, J/mol	942.80
Wobbe Index, MJ/m ³	44.28

Desulfurization of pyrolysis gas obtained from the WAT pyrolysis process is an important process, as according to the Directive on Industrial Emissions⁵², a pyrolysis unit in which further combustion of produced gases takes place is considered the same as a waste incineration plant. Thus, it must comply with very strict emission limits, which is a serious limitation for the development of the WAT pyrolysis process. However,

there is an exception to the above rule, namely, the pyrolysis unit should not comply with emission limits if the produced pyrogas is cleaned before combustion and cannot cause pollution worse than the combustion of natural gas. In view of the above, researchers are looking for an appropriate method of desulfurization of pyrolysis gas, with the aim of ensuring the quality of the obtained gas close to the quality of natural gas.

Another direction of pyrogas application could be its use as raw materials for polymerization processes or as a liquefied gas (LPG). The main condition for the application of these methods is a close location to oil refineries, which will allow separating pyrogas into separate components at GFP (gas fractional plants).

4. Characteristics and Application of Liquid Products of WAT Pyrolysis

Depending on the type of tires used for pyrolysis and the process parameters, the yield of liquid pyrolysis products from WAT is about 35–50 wt. %^{28,29}. It is also known that the composition of liquid pyrolysis products can significantly depend on the quality of tires and the conditions of pyrolysis^{43,45,53–56}. Therefore, in each specific case, it is necessary to study the pyrolysis products and their application.

Liquid pyrolysis products have a dark brown color with a characteristic smell. The density of the liquid phase is 0.85–0.88 g/cm³. Liquid products of WAT pyrolysis are a mixture of aliphatic, aromatic, and hybrid polar compounds with a boiling temperature of approximately 343 to 673 K.

Liquid pyrolysis products mainly consist of a mixture of C₆–C₂₄ hydrocarbons of aliphatic structure (pri-

marily, unsaturated), aromatic structure, and also contain some oxygen-containing, nitrogenous, and sulfur compounds^{45,53,57}. The formation of sulfur compounds in liquid pyrolysis products occurs as a result of the thermal decomposition of vulcanizing (cross-linking) agents, which are added during⁵⁸.

Given the above diverse composition, it can be predicted that it is difficult to find possible applications, for example, as a component of gasoline or diesel fuel without the stage of purification or separation, except for their direct combustion⁵⁹.

The C₆–C₂₄ fraction can be an important source for obtaining individual aromatic hydrocarbons (a mixture of benzene, toluene, xylene, ethylbenzene, and limonene)^{57,60–62}. In addition, thanks to the high calorific value of 41–44 MJ/kg⁶³, the C₆–C₂₄ hydrocarbon fraction can be used as heating oils. Such a fraction has a higher heat of combustion than a fuel oil of oil origin. But the possible high sulfur content (sometimes 1–1.4 %) limits its use without additional preparation. Also, the C₆–C₂₄ fraction can be used as the raw material for obtaining fuels for internal combustion engines. To improve its operational properties and reduce emissions of pollutants, some authors have studied the behavior of mixtures with diesel fuel^{64–68}.

Liquid pyrolysis products also contain a small amount of oxygen-containing compounds and a high H/C ratio (close to 1.5), which may indicate a high content of aromatic and aliphatic unsaturated compounds. The increase in the amount of aromatic compounds occurs with an increase in the temperature of the process, at the same time a decrease in the amount of aliphatic compounds is observed⁶⁹.

Table 3. Dependence of properties and elemental composition of WAT pyrolysis liquid products on their production temperature

The content of light fractions, wt. %	Elemental composition, wt. %						Caloric content, MJ/kg	Temperature of the pyrolysis process, K	Link/Source
	C	H	N	S	O	H/C			
53.10	87.90	10.10	0.50	1.30	0.10	–	41.20	873	according to ⁷⁵
45.00	86.50	10.80	0.50	0.80	2.20	1.50	43.70	793	according to ⁷⁶
43.00	87.90	11.20	0.70	1.00	0.20	1.53	44.80	758	according to ⁷⁶
38.00	85.60	10.10	0.40	1.40	2.10	1.42	42.10	773	according to ⁶⁹
44.60	84.55	9.59	0.64	1.26	3.96	1.36	41.00	823	according to ⁷⁷
38.00	84.90	9.60	0.40	1.60	3.50	1.36	40.77	823	according to ⁷⁸
48.40	87.57	10.35	<1.00	1.35	–	1.42	41.60	923	according to ⁷⁹
43.20	85.27	10.35	1.01	0.99	–	1.46	–	873	according to ⁸⁰
46.10	85.40	11.40	0.40	0.60	–	1.60	43.27	823	according to ⁸¹

Given the high content of unsaturated and aromatic compounds, liquid pyrolysis products can be used as primary raw materials for the production of plastics, resins, surfactants, and pharmaceutical compounds^{70–72}. Also, these products can be used as raw materials for hydrocracking processes at an oil refinery to obtain both aromatic substances and olefins⁷³. Research⁷⁴ has established the possibility of using liquid pyrolysis products as raw materials for obtaining coke. Coking of these liquid pyrolysis products of tires allows obtaining a liquid fraction and high-calorific combustible gas. The liquid fraction obtained during the coking process can be divided into a highly aromatic part of gasoline (b. p. –478 K), medium distillate (the boiling temperatures 478–623 K), and heavy gas oil fraction (the boiling temperatures >623 K), which contains a large amount of asphaltenes. In Table 3 we can see the average elemental compositions and caloric value of liquid pyrolysis products from WAT.

The main directions of the use of WAT pyrolysis liquid products are briefly characterized below.

4.1. Fractional composition of liquid pyrolysis products of WAT

In the study⁵⁷, the distillation was carried out at atmospheric pressure on liquid pyrolysis products from WAT obtained at a temperature of 773 K. It was found that about 20 wt. % of the liquid pyrolysis products can be classified as a light oil fraction (<433 K), while about 10 wt. % as heavy gasoline (433–477 K). Researchers⁸² have established that about 20 % by mass of the liquid pyrolysis products (pyrolysis temperature 783 K, pressure 2–20 kPa) can be classified as a light gasoline fraction (<433 K), 6.8 wt. % as heavy gasoline (433–477 K), 30.7 wt. % as medium distillate (477–623 K), and 42.5 wt. % as residue (>623 K).

4.2. Limonene in Liquid Pyrolysis Products of WAT

One of the most valuable individual liquid pyrolysis products of tires, which are advisable to isolate in the form of pure/technical compounds, is limonene.

It is used in the production of industrial solvents, resins, adhesives, cosmetics, and as a pigment dispersant⁸³.

Limonene exists in the form of D,L-limonene (dipentene) and D- and L-limonene, a racemic form of dipentene^{58,75}. According to the authors^{58,75,82,84}, the gasoline fraction of liquid pyrolysis products from WAT contains up to 25 wt. % of limonene.

The formation of D,L-limonene depends on the conditions of pyrolysis of WAT (pyrolysis pressure,

temperature, and residence time of vapors in the reactor), as well as the size and composition of the raw material^{58,75}. The yield of D,L-limonene decreases with increasing temperature due to secondary reactions. D,L-limonene can be converted into aromatic compounds such as trimethylbenzene, *m*-cymene, and indane⁵⁸. However, at lower pyrolysis pressure and residence time of volatile substances, the occurrence of secondary reactions is minimized, and therefore, the yield of D,L-limonene increases. For this reason, the concentration of limonene in vacuum pyrolysis is higher than in pyrolysis at atmospheric or elevated pressure^{58,82,84}. The content of limonene also depends on the temperature. In the literature⁸⁵, it is reported that at a pressure of 3.5–4.0 kPa, the content of limonene in the liquid fraction decreased from 11.97 to 4.72 wt. % with an increase in pyrolysis temperature from 723 to 823 K. At a pyrolysis temperature of 773 K, the content of limonene decreased from 11.73 to 7.8 wt. % with an increase in pyrolysis pressure from 3.5 to 10 kPa. In studies⁷⁵, it was found that the yield of limonene was 3.1 wt. % at 723 K and decreased to 2.5 wt. % of the total amount of liquid at 873 K. In the work⁷⁷, it was observed that the yield of limonene in liquid pyrolysis products from WAT was 5.4 wt. % at 723 K. At a process temperature of 923 K, the yield decreased to 0.07 wt. %.

4.3. Aromatic Hydrocarbons in Liquid Products of WAT Pyrolysis

Liquid products of WAT pyrolysis contain a large amount of polycyclic aromatic hydrocarbons^{57,75,77,86–88}. For example, in the study⁸⁶, it was found that liquid pyrolysis products from WAT contain in their composition alkanes, alkenes, and aromatic compounds such as benzene, toluene, xylene, styrene, polycyclic hydrocarbons containing 2–6 rings, their alkyl derivatives.

Also, studies were conducted related to the influence of the temperature regime on the yield of polycyclic aromatic hydrocarbons. Thus, Cypres and Bettens⁸⁹ found that in the temperature range of 873–1073 K (post-cracking), the yield of naphthalene and phenanthrene increases with increasing temperature. Similarly, in the work⁸⁷, experiments were conducted with the pyrolysis of WAT in two stages to study secondary reactions that occur during the formation of polycyclic aromatic hydrocarbons in the temperature range from 773 to 993 K. Thus, with an increase in temperature, especially in the range of 913–973 K, the total content of polycyclic aromatic hydrocarbons increases from 1.4 to 10.1 wt. %. The authors claim that the increase in the content of aromatic hydrocarbons occurs due to the aromatization of olefinic hydrocarbons by the Diels-Alder reaction⁸⁷.

According to the above, it can be concluded that the content of aromatic hydrocarbons increases with an increase

in the WAT pyrolysis temperature. However, in the work⁸⁰, the content of polycyclic aromatic hydrocarbons was not found. The authors explain this fact by the short residence time of volatile substances in the pyrolysis reactor. Similarly, scientists⁵⁷ noted a low yield of polycyclic aromatic hydrocarbons obtained at 773 K, which may be explained by the short residence time of volatile substances in the reactor and the efficient operation of this type of reactor in the context of heat and mass transfer.

It should be noted that the composition of the raw material (tires) also has a significant effect on the yield of polycyclic aromatics. Kwon and Castaldi⁹⁰ found that the increase in the content of aromatic hydrocarbons in liquid pyrolysis products from WAT depends on the content of SBR (styrene-butadiene rubber) in the raw material. They also stated that cyclization by the Diels-Alder reaction is not the dominant reaction during the decomposition of SBR.

4.4 Use of Liquid Products of WAT Pyrolysis as Fuel for Internal/External Combustion Engines

Liquid products of WAT pyrolysis can be an alternative to fuels obtained from traditional oil raw materials. Primarily, they can have some advantages in terms of storage and transportation, as well as in view of the current consequences of using fossil fuels and the increase in their prices. In addition, as mentioned above, liquid products of WAT pyrolysis possess a high thermal

efficiency and heat capacity. Therefore, they can be used as a fuel component, especially for diesel internal combustion engines (which possess a higher thermal efficiency)⁹¹.

However, as noted in subsection 4.1, liquid products of WAT pyrolysis are a mixture of hydrocarbons, primarily aromatic and olefinic hydrocarbons, with wide temperature ranges, which limit their direct use in ICE. Along with other problems, such as sulfur content and viscosity, this raw material has a lower flash point and cetane number compared with diesel fuel obtained from traditional raw materials. Despite this, there are some works in the literature showing the impact of pyrolysis liquid products with diesel fuel on the performance and emissions of diesel engines^{91–96}. Table 4 lists the properties of liquid pyrolysis products.

The analysis of the petrol fraction established that its octane number is higher than the octane number of the petrol fraction of petroleum origin⁸². According to several authors^{3,88,99}, the gasoline fraction was analyzed using the method of IR-spectroscopy and chromatography. It was established that the obtained gasoline fraction has a high content of aromatic and unsaturated compounds. The authors also proposed methods of processing these fractions without using the hydrogenation processes, namely, polycondensation⁸⁸ and extraction⁹⁹. Polycondensation of gasoline fractions with formalin in the presence of hydrochloric acid enables an adhesive additive for road bitumen. Extraction can reduce the content of aromatic and partially unsaturated structures and use the raffinate as a high-octane component of gasoline.

Table 4. Properties of WAT pyrolysis liquid products according to literature sources

Density at 288 K, kg/m ³	Kinematic viscosity at 313 K (cSt)	Caloric content, MJ/kg	Cetane number	H/C ratio	Flash temperature, K	Temperature of the pyrolysis process, K	Link/Source
–	–	42.10	–	1.44	288	773	according to ⁷⁵
910	6.30	42.10	–	1.28	293	–	according to ⁹⁷
950	9.70	43.70	–	1.50	301	793	according to ⁷⁶
941	2.87	41.90	–	1.55	300	723	according to ⁷⁷
943	4.62	41.60	–	1.42	<303	923	according to ⁷⁹
957	4.75	42.00	40	1.27	<305	748	according to ⁹⁸
871	1.70	45.78	–	–	309	723	according to ⁹³
900	2.81	43.27	–	1.60	293	823	according to ⁸¹
945	3.80	43.34	44	–	323	773	according to ⁹²
904	2.16	40.90	<40	–	333	–	according to ⁹¹

Diesel fuel obtained from traditional raw materials has a cetane number from 40 to 55¹⁰⁰, while liquid products of pyrolysis of used car tires from 40 to 44^{92,96}. A low cetane number (<40) means that the fuel will have a large ignition delay, and therefore, more fuel than desired will enter the cylinder before the first particles of fuel ignite. Thus, a rapid and significant increase in pressure at the beginning of fuel ignition is achieved. This

phenomenon leads to a low thermal efficiency and uneven engine operation, as well as increased exhaust gas emissions and harmful emissions¹⁰¹.

It was established by Ilkilic and Aydin⁹² that the use of WAT pyrolysis liquid products as fuel for diesel engines results in larger emissions of CO, HC and SO₂ than traditional diesel fuel. The authors explained such behavior by a poor atomisation and a low cetane

number⁹⁰. In addition, high density led to the injection of a larger amount of fuel, causing the formation of the so-called “rich” mixture. Also, the authors concluded that liquid products of pyrolysis of used car tires in a mixture with diesel fuel up to 75 wt. % can be effectively used in diesel engines without any engine modification. Similarly, in the work⁹⁵, an increase in emissions of NO_x, HC and CO was observed when studying the effect of the ratio of liquid products of pyrolysis of used car tires to diesel fuel (up to 70 vol. % liquid products of pyrolysis of used car tires). The authors explained such behavior by an increased content of aromatics, higher viscosity, and lower volatility of the fuel. According to Heywood¹⁰⁰, aromatic compounds have low flammability. Cycloalkanes and aromatic compounds generally lower the cetane number unless they have a long unbranched alkane chain attached to the ring.

In addition, the high viscosity of liquid products of pyrolysis of used car tires can lead to problems in the long term, which may include carbon deposition⁹³, which will affect the pumpability of the fuel and, accordingly, the performance and accelerated wear of the fuel pump⁷⁷. In addition, high viscosity is associated with a large molecular weight and the chemical structure of the components of liquid products of pyrolysis of used car tires⁹³. Also, in addition to high sulfur content, liquid products of pyrolysis of used car tires may contain solid particles of sand or alkaline metals¹⁰², which can cause problems with the engine part wear and also affect the environment.

The work⁹³ also indicates the presence of some polymers and resinous compounds in the liquid products of pyrolysis of used car tires, suggesting a possible effect of carbon formation in the combustion chamber, exhaust valves, and also in the grooves of piston rings. For this reason, before using such fuel, it is recommended to carry out an additional process of re-cleaning^{93,96,103,104}. To solve such problems, scientists⁹³ recycled the liquid products of pyrolysis of WAT to reduce viscosity and sulfur content. The recycling process included three stages: removal of moisture, desulfurization, and vacuum distillation. As a result, the recycled fuel had approximately 7 % higher calorific value than the original one. The authors noted that the engine was able to operate up to 90 vol. % of recycled fuel and 10 vol. % of diesel fuel, while a decrease in thermal efficiency of approximately 1–2 % compared to diesel fuel was detected. However, HC and CO emissions were higher than those of regular diesel fuel (due to the presence of unsaturated hydrocarbons), NO_x emissions were lower by approximately 18 % compared to diesel fuel. Usually, the use of purified liquid products of pyrolysis of used car tires without the application of traditional fuel in the mixture does not allow its use in an internal combustion engine. Similarly, the effect of mixtures of liquid products of waste tires pyrolysis with diesel fuel on engine

performance and exhaust gas emissions of an unmodified direct injection diesel engine at full load and four different crankshaft rotation speeds (1400, 2000, 2600 and 3200 min⁻¹) was studied. The pyrolysis process was carried out under vacuum, and the liquid products of pyrolysis of used car tires were pre-treated before use in the engine. The treatment consisted of a cleaning and desulfurization process as follows: treatment with sulfuric acid, treatment with activated bentonite (calcium oxide), vacuum distillation, oxidative desulfurization, and drying. The authors did not find a significant effect on the initial engine torque, engine power, specific energy consumption, and thermal efficiency compared to the original diesel fuel (the content of recycled fuel was 90 vol. %). When using 100 vol. % of liquid products of pyrolysis of used car tires, failures in operation at higher engine speeds were observed.

The main conclusion on the use of liquid products of waste tires pyrolysis as fuel for diesel engines is that they can be used in a mixture with traditional diesel fuel (up to 70 % of liquid products).

It was shown by us previously³ that after separating from the liquid products of pyrolysis of used car tires light petrol fractions (b. p. – 473 K), the obtained residue (fraction > 473 K) fully complies with the requirements of regulatory documents for high-viscosity commercial oil fuels (for example, fuel oil grades 100, RMG 180)^{105,106}.

4.5 Other Directions of Use of WAT Pyrolysis Liquid Products

In the work⁷⁶, the fraction with a boiling point up to 477 K is proposed to be used as a plasticizer for rubbers. Its use as a plasticizer contributes to the reduction of the curing time, which, in turn, will accelerate the vulcanization time of the rubber. The residue (fraction > 623 K) is proposed to be used as a raw material for the production of coke or for the production of bitumen.

Another promising method of using liquid pyrolysis products of WAT is the production of modifiers based on them. The method of polycondensation of formalin with liquid pyrolysis products in the presence of hydrochloric acid was used to obtain an adhesive additive for bitumen.⁸⁸

5. Characteristics and Application of Solid (Carbonized) Residue of WAT Pyrolysis

The pyrolysis process allows the production of a solid substance rich in carbon. In the case of tires, this solid carbon fraction, also referred to as a solid residue (SR), pyrolytic charcoal, or carbonized residue, is similar

to technical carbon used in tire production^{107,108}. The composition of the solid residue depends on the pyrolysis conditions and the composition of the tire^{58,85}. It is known that the part of the organic gaseous products released during pyrolysis is converted into the residue as a result of dealkylation and dehydrogenation reactions or is absorbed on the surface of the solid residue^{85,109,110}. For this reason, it is expected that the SR has much larger particle sizes than stated in the work¹¹¹. The authors believe that these results indicate that carbon particles are likely to act as germinal nuclei from which coherent solid carbon structures grow (by cyclization and/or crosslinking). This additional carbon also appears upon further activation of the SR by steam or CO₂^{112–114}.

At first glance, the most relevant use of the SR is rubber production. However, such waste cannot be used in part due to the significant content of inorganic impurities^{80,115}. Also, the production of rubber for tires from solid products of WAT pyrolysis requires an appropriate chemical composition and surface activity, as these properties determine the strength of the soot interaction with rubber^{76,107}. Despite this, the content of the inorganic part is the most important characteristic, as mentioned above. These compounds can be removed by the demineralization process¹¹⁶. To reduce the ash content, a sequential acid-alkaline treatment is used.

Despite the above, almost 93 % of the SR produced worldwide is used as an elastomeric reinforcing agent in rubber¹¹⁷. The remaining 7 % of the product is used for other applications, including inks, coatings, dyes, as a conductivity agent in batteries, as an ultraviolet (UV) stabilizer¹¹⁸, and also as nanomaterials for the removal of heavy metals.

In general, to improve the quality of the pyrolysis solid residue and its reuse as technical carbon, various alternative approaches have been proposed, which are briefly considered below.

Gas activation of the solid residue of pyrolysis for the production of activated carbon is usually carried out by steam or CO₂ at temperatures above 1073 K. It is worth noting that for CO₂ activation, higher temperatures are required than for steam (H₂O), due to the lower reaction rate achieved with the previous activating agent; in addition, steam also has a better ability to develop micropores¹¹⁹. Different behavior of CO₂ and H₂O lies in the smaller molecular size of water, which facilitates diffusion inside the porous structure of the solid residue of pyrolysis¹²⁰. However, air used as an activating agent is limited due to the high reaction rate and difficulties in the process control.

Physical activation of the SR by steam allows to obtain not only high-quality activated carbon but also hydrogen-enriched synthetic gas¹²¹. In addition, the use of steam as an activating agent also contributes to the reduction of sulfur content in the obtained solid residue of pyrolysis¹²², which is of great interest for the end-use as activated carbon.

Impregnation of the solid residue of pyrolysis with a chemical reagent has the potential to remove the inorganic substance of the solid residue of pyrolysis, increase the diameter of pores, improve the relative carbon content, and increase the specific surface of the solid residue of pyrolysis¹²³. A wide range of chemical activators, such as alkali metal hydroxides (NaOH/KOH), inorganic acids (H₃PO₄, HCl and H₂SO₄) or ZnCl₂ has been proposed by Antoniou *et al.*¹²⁴.

It is known that the solid residue (SR) can have a calorific value ranging from 25 to 34 MJ/kg (Table 5), which allows it to be used as the solid fuel. Depending on the pyrolysis conditions, the composition of the tire, and the technology used in the process, the SR can have a carbon and sulfur content higher than 80 and 3 wt. %, respectively. Table 5 presents data on the yield, calorific value, and sulfur content for various results described in the literature.

Table 5. Dependence of the properties and elemental composition of the carbonized residue of WAT pyrolysis on the production temperature

Yield of solid residue, wt. %	Elemental composition, wt. %				Caloric content, MJ/kg	Temperature of the pyrolysis process, K	Link/Source
	C	H	N	S			
39.90	80.82	1.46	0.53	2.41	30.00	823	according to ⁷⁷
38.00	90.27	0.26	0.26	1.22	—	873	according to ¹²⁵
53.00	80.08	0.42	0.17	2.84	28.57	873	according to ⁷⁸
49.09	85.31	1.77	0.34	2.13	30.71	873	according to ¹²⁶
35.00	89.40	0.30	1.80	0.90	30.90	873	according to ¹²⁷

6. Conclusions

It is established that significant volumes of WAT (approximately 1.5 billion tons) are generated annually

worldwide, which in turn creates an environmental problem of their accumulation and rational disposal. This is associated with the fact that WAT are practically not biodegradable and are characterized by the complexity of

reuse or recycling, due to their specific thermomechanical properties.

Part of the WAT can be used in the technologies of modified bitumen production. On the other hand, the high energy intensity of WAT has prompted their reuse in various industries. For example, pyrolysis, gasification, and combustion processes of WAT allow to maximize the use of resources and reduce the dependence on fossil fuels.

The pyrolysis process of WAT is a promising method of recycling, as well as the energy and fuel recovery in the field of recycling used organic materials, which can meet the three principles of solid waste recycling: circular economy, resource recovery, and reduction of pollutant emissions. In the process of pyrolysis, organic components of WAT decompose to form a solid carbonized residue (approximately 33–39 wt. %), liquid (approximately 34–45 wt. %), and gaseous pyrolysis products (approximately 1.7–16 wt. %). The yield of these components depends on the process conditions, raw materials, type of reactor, *etc.* Thus, the conversion of WAT to alternative fuel allows for reducing the use of conventional fossil fuels. In addition, the steel reinforcement of WAT can be removed from the residual coal and sent back for recycling in the metallurgical industry.

Gases obtained as a result of the pyrolysis process of WAT are characterized by the presence of saturated and unsaturated hydrocarbons, as well as a fairly high content of hydrogen and admixtures of carbon oxide and dioxide, nitrogen, *etc.* The pyrolysis gas of WAT can be used for the production of synthesis gas or for re-providing heat in pyrolysis processes. At the same time, it should be noted that before using the pyrolysis gas of WAT, regardless of the conditions of its receipt, it is necessary to subject it to additional purification processes. Another direction of gas pyrolysis recycling can be its use as raw materials in the processes of producing liquefied fuel (LPG), provided that the pyrolysis installation of WAT is located close to oil refineries, where there will be an opportunity to further separate it on gas fractionation units.

Liquid products of WAT pyrolysis (LPWTP) mainly consist of aromatic and aliphatic hydrocarbons. Some of their properties are similar to the characteristics of diesel fuel; others, for example, viscosity, are similar to the requirements for boiler fuels and fuel oils. Based on various literary sources, it can be asserted that the main direction of LPWTP application is as components of various fuels or raw materials for obtaining organic compounds (especially aromatic). At the same time, LPWTP are characterized by a high content of low-boiling and a number of unsaturated, condensed aromatic,

and heteroatomic compounds, which makes their use without preliminary processing as fuels for existing internal and external combustion engines practically impossible.

To bring the characteristics of LPWTP up to the standards set for petrol, diesel, and boiler fuels, traditional oil and oil fraction processing methods can be used: rectification, hydrotreating, isomerization, and reforming. However, pyrolysis processes are often implemented in places of mass tire storage in the form of small-scale productions. In this case, the construction of the aforementioned “traditional” oil refining technologies is economically and technologically impossible (primarily due to the lack of deficit hydrogen). In addition, considering the possible high content in LPWTP of heteroatomic (primarily, sulfurous) and unsaturated compounds, the production of light petroleum products using hydrotreating may prove to be economically disadvantageous. Therefore, several alternative and relatively simple methods of processing liquid products of WAT pyrolysis are being introduced (extraction, acid cleaning, *etc.*).

The solid carbonized residue of the WAT pyrolysis process is often considered a by-product. Its composition includes carbon black (80–90 %) and inorganic substances (10–20 %), which are always present in the rubber mixtures used in tire production. The solid carbonized residue of WAT pyrolysis can be directed to further processes for the production of technical carbon, activated carbon, *etc.* Also, the spheres of application of the solid carbonized residue can include its use as an oil-absorbing material, insulator, and concrete component, as well as an adhesive and/or stabilizing additive in bitumen modification processes.

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ХАРАКТЕРИСТИКА ТА ЗАСТОСУВАННЯ ПРОДУКТІВ ПІРОЛІЗУ ВІДПРАЦЬОВАНИХ АВТОМОБІЛЬНИХ ШИН: ОГЛЯД

Анотація. Розглянуто екологічну проблему утворення, накопичення й утилізації відпрацьованих автомобільних шин (ВАШ) в Україні та світі. Встановлено, що ВАШ можуть слугувати цінною сировиною для одержання компонентів палив і технічних/індивідуальних хімічних речовин для подальших промислових процесів переробки. Одним із перспективних методів раціональної утилізації ВАШ може бути процес їхнього піролізу. У результаті процесу піролізу ВАШ одержуються наступні продукти: газоподібні, рідкі та твердий карбонізований залишок. Водночас, не існує ідеальної універсальної технології застосування продуктів піролізу ВАШ без попередніх методів обробки/очищення. Коротко розглянуто основні характеристики, методи переробки та сфери застосування продуктів, одержаних у результаті процесу піролізу ВАШ.

Ключові слова: відпрацьовані автомобільні шини, альтернативні палива, піроліз шин, карбонізований залишок, рідкі продукти піролізу, піролізний газ.