Chem. Chem. Technol., 2026,
Vol. 20, No. 1, pp. 208–222

Chemical Technology

SELECTION OF THERMOOXIDATION TREATMENT CONDITIONS OF GASOLINE FRACTIONS OBTAINED FROM LIQUID PRODUCTS OF WASTE TIRES PYROLYSIS

Serhiy Pyshyev[1], Oleh Kukhar[1], Yurii Lypko[1], Ananiy Kohut[1], Oksana Nahurska[1], Taras Chaikivskyi[1], Bohdan Korchak[1,✉]

[1] Lviv Polytechnic National University, 12, S. Bandery str., Lviv, 79013, Ukraine
✉ *bohdan.o.korchak@lpnu.ua*

https://doi.org/10.23939/chcht20.01.208

Abstract. Waste tires (WT) are the main component of industrial rubber waste. One of the promising methods for rational utilization of WT is the process of their pyrolysis – a thermochemical process during which thermally unstable organic components that make up WT decompose into gaseous, liquid, and solid products at temperatures of 300–900 °C. Pyrolysis combines waste processing with energy and fuel recovery. Liquid pyrolysis products (LPP) can be considered the main products of WT pyrolysis, which are obtained as a result of condensation from volatile fractions of WT pyrolysis. They are a dark, opaque liquid with a characteristic pungent odor and consist mainly of aromatic and unsaturated compounds; therefore, their use as fuels requires extensive processing. This paper describes initial (exploratory) studies on the feasibility and expediency of using the thermal oxidation treatment process to purify the gasoline fraction ≤ 200 °C obtained after atmospheric distillation of LPP. Oxidation was carried out in a batch reactor with air in the presence of water. The composition of the raw material mixture and its phase state during the process were investigated and calculated, and the pressure and raw material: air ratio were justified. These studies will serve as the basis for a future detailed analysis of the thermal oxidation of the gasoline fraction obtained from WT pyrolysis, to reduce its content of undesirable compounds (reactive unsaturated, sulfurous, and high-boiling aromatics).

Keywords: waste tire, tire pyrolysis oil, gasoline fraction, alternative fuel, thermal oxidation.

1. Introduction

Waste tires (WT) are the main component of industrial rubber waste. Excluding metal cord, they consist of rubber (~50 %) and carbon black (~35 %), with admixtures of O_2, N_2, S, Zn, and Si.[1–4] The rubber matrix of tires usually contains natural (polyisoprene) and synthetic rubbers, in PARTICULAR styrene-butadiene and butadiene rubber.[4, 5] Although tires are characterized by high strength and wear resistance, this same stability causes significant environmental problems after the end of their service life, which highlights the need for effective WT recycling technologies.[3–5]

According to ETRMA, nearly 1 billion WT are generated worldwide each year. Some of the waste tires are recycled / disposed of. For example, in the US, about 79 % of tires (~3.8 million tons) are recycled or reused, while in China, due to the rapid growth of the vehicle fleet, the recycling rate remains relatively low.[3–6] In the US and the EU, the main ways of recycling WT are energy recovery and the production of rubber crumbs, while in Japan, WT is mainly used as an alternative fuel in the cement, metallurgical, and chemical industries.[3–6]

Currently, Ukraine does not have a centralized WT collection system. Accordingly, only some regions of the country have private companies engaged in WT disposal and/or recycling.[7] Among the well-known companies engaged in WT recycling processes are Tire Recycling UA (Dnipro),[8] Waste Management Center (Kyiv),[9] and UkrEcoProm (Odesa).[10]

WT management and recycling technologies have developed significantly over the last decade, and high-value products made from recycled rubber are now receiving increasing attention.[11–13] In this paper, the author proposes dividing WT recycling methods into three main areas: 1) shredding and direct use of worn tires by mixing them with polymers, bitumen, asphalt, or concrete; 2) devulcanization, processing, and functionalization of worn tires (recycling);[22, 23] and 3) pyrolysis of WT.[4, 6, 24] Other methods

of recycling waste tires include such environmentally unfriendly processes as incineration and landfilling.[1, 4]

Despite the development of new technologies, their spread is limited by economic and scale factors. Hence, the reuse of WT and rubber crumbs still dominates the global market, but does not solve the problem of disposing of this waste.[1, 4, 25] The accumulation of large volumes of WT causes the loss of carbon resources and increases the risk of fires and toxic emissions, which highlights the need to introduce advanced processing technologies focused on obtaining valuable energy and material products.[1, 4, 24, 25]

One promising method for the rational disposal of WT is pyrolysis, which combines waste processing with energy and fuel recovery and aligns with the principles of waste reduction, resource recovery, and reduced environmental impact.[1, 4, 24, 25] Compared to incineration, retreading, and landfilling, pyrolysis results in lower secondary pollution and higher economic value of the products obtained.[25, 26]

WT pyrolysis is a thermochemical process during which thermally unstable organic components of WT are decomposed into gaseous, liquid, and solid products at temperatures of 300–900 °C in an oxygen-free environment or in the presence of inert gases.[4, 24–26] As a result of the WT pyrolysis process, a solid residue (SR) ~35–50 wt. %, liquid pyrolysis products (LPP) ~30–50 wt. %, and pyrolysis gases ~10–30 wt. % can be obtained.[4, 24–26]

Liquid substances can be considered the main products of WT pyrolysis, which are obtained as a result of condensation from volatile fractions of WT pyrolysis and are a dark, opaque liquid with a characteristic pungent odor.[26, 27] LPP is a complex multicomponent mixture containing more than 100 individual compounds and, after fractionation, can be separated into gasoline (C_5–C_{10}), diesel (C_{14}–C_{18}), and heavy oil fractions (>C_{18}).[26, 27] LPP is characterized by a predominance of aromatic hydrocarbons, in particular benzene, toluene, xylene, styrene, limonene, and their alkylated derivatives, as well as polycyclic aromatic compounds with 2–5 rings, the total share of which reaches about 62.4 %.[26, 27] The proportion of aliphatic hydrocarbons is about 31.6 % and is mainly straight-chain alkanes C_6–C_{37}, with a smaller amount of olefins. The aromatic fraction is dominated by monocyclic compounds (43–58 %), while n-alkanes predominate in heavy aliphatic fractions.[26, 27]

From a practical standpoint, LPPs are considered an alternative motor fuel. For example, mixtures of LPPs with diesel fuel can be used without modifying engines, and increasing the proportion of LPPs can improve thermal efficiency and reduce specific fuel consumption.[27] At the same time, the high LPP content in fuels limits their direct use, as they are characterized by high acidity, sulfur content (1.0–2.0 wt. %), and low thermal stability. Due to the presence of low-boiling components, the flash point is usually below 30 °C, which reduces fire safety. In this regard, LPPs require additional purification and processing to improve their operational properties.[26, 29]

To improve properties, distillation, hydrotreating, catalytic treatment, co-pyrolysis, and adsorption with activated carbon are used.[26, 28, 29] Rectification allows obtaining a light fuel fraction with a density of 0.76 g/cm³ and a viscosity of 0.4 mPa·s, rich in benzene compounds, which indicates its similarity to petroleum-derived gasoline fractions.[30] Hydrodesulfurization using Co-Mo, Ni-Mo, or Al_2O_3 provides up to 87.8 % sulfur removal, and the calorific value of purified LPP reaches 44 MJ/kg, which is close to diesel fuel.[31] However, the use of hydrogenation processes is feasible provided that consistently large volumes of WT are processed and expensive hydrogen and catalysts are available, which is impractical in small or medium-sized plants and creates an additional economic burden. Accordingly, technologies that do not require expensive hydrogen or catalysts and are characterized by compact size and simple hardware design are becoming economically efficient.[24]

In work,[24] it is proposed to fractionate LPP by atmospheric distillation to obtain a gasoline fraction ≤ 200°C, enriched with aromatic and unsaturated compounds. Fr. > 200 °C met modern requirements for modern boiler fuels and commercial fuel oils. To reduce the content of undesirable components, the gasoline fraction was treated with formaldehyde in the presence of HCl (resins were obtained). The unreacted components were further extracted with N-methyl-2-pyrrolidone.[24] The purified raffinate was mixed with low-octane gas condensate in a ratio of 35:65, yielding gasoline with an octane number of about 93, which meets the requirements of the Euro 4 standard.[24]

In work,[32] CaO, $Ca(OH)_2$, and NaOH were used to reduce the sulfur content in LPP. The effect of temperature, catalyst dosage, and N_2 flow rate on product yield was investigated. The maximum yield was achieved at 500 °C and a N_2 flow rate of 200 cm³/min.[32] The use of 5 % $Ca(OH)_2$ reduced the sulfur content by 34.25 % compared to non-catalytic pyrolysis.[33] Further treatment with acid-peroxide systems and H_2SO_4 provided additional desulfurization, with 10 % H_2SO_4 giving the highest effect – up to 75.27 %, and the combined scheme (5 % $Ca(OH)_2$ + 10 % H_2SO_4) – a total reduction in sulfur of 83.75 %.[32]

Despite the progress made, the complex, highly aromatic nature of WT LPP continues to limit its high-value applications. The practical application of this product is complicated by its extremely complex composition, which is enriched with polycyclic aromatic hydrocarbons and sulfur- and nitrogen-containing compounds formed by aromatization and condensation reactions.

One promising method for purifying gasoline fractions may be the process of thermo-oxidative treatment with air, previously developed for desulfurization of straight-run gasoline and diesel fractions with high sulfur content[33–35] in the presence of water, as well as for the regeneration of waste oils.[36, 37] These processes were carried out in a bubbling reactor at temperatures of 180–220 °C and pressures of 2.5–3.0 MPa for 20–30 minutes with an air/raw material ratio of 1.6–2.2 m³/m³, which made it possible to obtain jet and diesel fuel components with acceptable sulfur content and good lubricating properties[33–35] and to obtain regenerated oils, which, compared to waste oils, were characterized by a higher viscosity index, as well as lower ash content, coking tendency, and acid number.[36, 37] During thermal oxidation, relatively selective heterogeneous and condensed aromatic compounds were converted into solid and/or liquid products with a higher boiling point than the initial raw material. Accordingly, these condensation products could be separated from the oxidate by relatively simple methods (filtration, rectification, adsorption).

Given the above, it can be assumed that thermo-oxidative treatment of gasoline fractions will reduce the content of heterogeneous, unsaturated, and aromatic compounds, thereby improving their environmental and operational properties, color, and stability. Therefore, this work aimed to conduct preliminary (exploratory) research on the possibility/feasibility of using the thermo-oxidative treatment process to purify the gasoline fraction ≤ 200 °C obtained after atmospheric distillation of WT LPP.

2. Experimental

2.1. Materials

The starting raw material was a gasoline fraction with a boiling point of ≤ 200 °C, obtained by atmospheric distillation of the liquid products of the WT pyrolysis process. The physicochemical characteristics of the gasoline fraction are presented in Table 1.

Table 1. Physicochemical characteristics of the gasoline fraction ≤ 200 °C

Indicator name	Fr. ≤ 200 °C
Saturated vapor pressure,[38] kPa	53
Density[39] at 15 °C, kg/m³, within range	842
Copper strip corrosion test,[40] class	4
Detection of water-soluble acids and alkalis using indicators[41]	–
Sulfur content,[42] mg/kg	51
Refractive index,[43] n_d^{20}	1.4782
Bromine number[44], g Br_2/100g of product	67.9

2.2. Methods for conducting experiments and calculations

In previous studies,[33–35] which were carried out to desulfurize light oil fractions, a continuous-flow bubble reactor was used, which is the most commonly used in modern processes involving reactions between liquid and gaseous components. Given the work's purpose (the development of relatively simple methods for processing liquid tire pyrolysis products), a batch reactor was used in these experiments, suitable for small-scale enterprises without complex automation and control systems.

The laboratory setup for the thermo-oxidative processing of gasoline fractions with air is shown in Fig. 1.

The above-mentioned previous similar studies were carried out in the presence of water, which improved the selectivity of oxidation. Therefore, 0.2 L (G_{raw} = 0.17 kg) of gasoline fraction and 0.08 L (0.08 kg) of water were loaded into a 0.75 L batch reactor. The conditions of the search experiments, adopted based on 33–35, were as follows: water-to-raw material volume ratio – 0.4 vol., process temperature – 220 °C, duration – 20 min.

The raw liquid mixture (gasoline fraction ≤ 200 °C and water) was heated to a temperature of 100 °C (as a rule, the absolute pressure in the system was about 5000 kPa), after which air was supplied, the start of the experiment was recorded, and the reactor continued to be heated. After the start of air supply, the temperature in the reaction zone reached the required level within 0.5–2 minutes due to the onset of exothermic reactions and external reactor heating. The air supply was carried out to achieve the necessary pressure at the end of the fixed process time (20 minutes), but no later than 90 % of the total oxidation time. The required amount of air was calculated using the formulas below to achieve the target reactor pressure. The amount of air was controlled using a rotameter. At the end of the thermal oxidation process with air, the batch reactor was cooled, the exhaust air was vented into a collector for further purification, and the liquid and solid products obtained were sequentially sent for further separation processes:

– solid oxidation products were separated by filtration;

– after settling in a separating funnel, water was separated;

– using atmospheric distillation, the distillate (≤ 200 °C – target product, purified gasoline fraction) was separated from the still bottom residue.

The analysis of the target product, gasoline distillate, was conducted in accordance with standardized methods.[39, 43, 44]

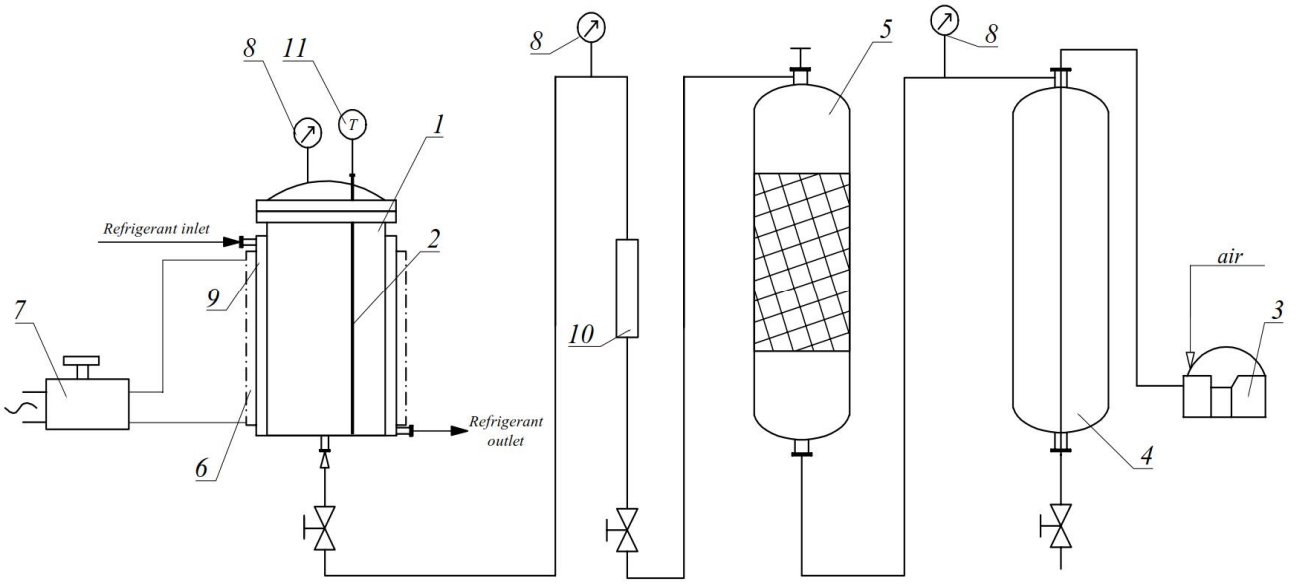

Fig. 1. The laboratory setup for the thermo-oxidative processing of gasoline fractions with air: 1 – reactor; 2 – thermometer casing; 3 – compressor; 4 – receiver; 5 – adsorber; 6 – removable electric heater; 7 – autotransformer; 8 – pressure gauge; 9 – reactor cooling jacket; 10 – rotameter; 11 – thermometer

Chromatographic analysis to determine the composition of the gasoline fraction ≤ 200 °C was performed using a Shimadzu GC-MS-QP2020 chromatograph with an Rtx-5MS capillary column (5 % diphenyl – 95 % dimethylpolysiloxane, Restek; 30 m × 0.25 mm × 0.25 μm).[45] This method allows you to estimate the composition of the vapor phase that is formed during chromatographic analysis on a Shimadzu GC-MS-QP2020 instrument. Gas chromatographic analysis does not accurately reflect the actual composition of liquid pyrolysis products, but it is considered representative.[46] Carrier gas – helium with a flow rate of 1.27 mL/min; purge flow – 3.0 mL/min. The vapor phase was injected above the liquid sample using a 1 μl syringe in a 1:30 split mode at 250 °C. 45 Data processing was performed using LabSolutions Insight™.[45] The column temperature program was set as follows: 32 °C (5 min), heating to 60 °C at a rate of 2 °C/min, then to 270 °C at a rate of 30 °C/min with a hold time of 8 min. The analysis lasted 30 min.[45]

To characterize the amount of air required for the thermal oxidation of raw materials, the raw material: air ratio (kg/kg) was used.

The calculation of the amount of air, kg, supplied to the reactor was based on the assumption that the pressure in the reactor was created by ai, minus the pressure of the raw material mixture vapors at the start of air supply, according to the formula:

$$G_{air} = (V_r/1000) \times (P_{work\ pres} - P_{init}^{raw\ mat}) \times \rho_{init}, (1)$$

Where V_r is the free reactor volume (reactor volume excluding liquid raw material mixture), V_r = 0,47 l; $P_{work\ pres}$ is the working pressure in the reactor at the end of the experiment, kPa; $P_{init}^{raw\ mat}$ is the initial pressure of the raw material mixture in the reactor at 100 °C; ρ_{air} is the air density, ρ_{air} = 1,29 kg/m^3.

A calibrated rotameter was used to control the amount of air. The relative error between the calculated air volume and the rotameter-determined volume in all experiments did not exceed 3 %.

To determine the phase state of the steam-water mixture at different temperatures in the reactor, the fraction that converted to steam was calculated. Of course, it is practically impossible to calculate the phase state of a three-component system of air: water: hydrocarbon raw materials, which is in a state of constant equilibrium change, both as a result of reactions and possible changes in partial pressures, for example, due to the formation / use of water during reactions, the conversion of the lightest hydrocarbons, *etc.* Therefore, during the phase-state calculation, it was assumed that the air partial pressure is constant and that the partial pressure of the water-hydrocarbon mixture depends only on temperature and does not change during the process. The amount of raw material and water vapor, kg, that will be in the reactor in a vapor state was found using the following formula:

$$G_{mixture} = (G_{air} \times P_{mixture} \times M_{mixture}) / (P_{air} \times 29), (2)$$

where $M_{mixture}$ is the molecular weight of the mixture of the steam-water mixture; $P_{mixture}$ is the total pressure of saturated vapor of a mixture of the steam-water mixture, Pa; $P_{air} = P_{work\ pres} - P_{init}^{raw\ mat}$ is the total air pressure in the reactor, Pa; 29 is the molecular weight of air.

$$P_{mixture} = P_{HC}^{sat} + P_{water\ vapor}^{sat}, \quad (3)$$

where P_{HC}^{sat} *and* $P_{water\ vapor}^{sat}$ are partial pressures of hydrocarbons and water.

The partial pressures of saturated hydrocarbon vapors at different temperatures (50–250 °C) were determined based on the results of chromatographic analysis of raw materials in accordance with Raoult's law:[47–50]

$$P_{HC}^{sat}(T) = \sum Y_i \cdot P_i^{sat}(T), \quad (4)$$

where $P_i^{sat}(T)$ is the pressure of saturated vapors of raw material components at process temperature, kPa; Y_i is the component content in fraction, mole fractions.

To determine the pressure of saturated water vapor in the temperature range of 50–250 °C, Antoine's equation was used:[48]

$$log_{10}(P_{water\ vapor}^{sat}) = A - \frac{B}{T+C}, \quad (5)$$

T is a temperature, °C; *A*, *B*, and *C* are empirical constants for water.

The formula determines the proportion of the mixture $e_{mixture}$ that will turn into vapor:

$$e_{mixture} = \left(\frac{G_{mixture}}{m_{mixture}}\right) \times 100\ \%, \quad (6)$$

$m_{mixture}$ = 0.25 kg is the amount of raw materials and water loaded into the oxidation reactor, kg.

3. Results and Discussion

3.1. Analysis of raw materials and calculation of raw material mixture parameters

According to the physical and chemical characteristics of the fraction ≤ 200 °C presented in Table 1, it has been established that the fraction ≤ 200 °C does not meet the regulatory requirements for gasoline fuels in terms of several indicators, primarily density. In addition, it is characterized by an elevated bromine number, indicating a significant content of unsaturated compounds. The results obtained are consistent with the analysis of its component composition, presented in Table 2, which confirms the high content of aromatic hydrocarbons, in particular benzene (2.96 wt. %), as well as other aromatic and unsaturated components, the presence of which is limited in commercial gasoline.

As noted above, to increase the selectivity of oxidation processes, it is advisable to use water, since its introduction into the reaction medium can inhibit the oxidation of certain classes of organic compounds, directing the process in the desired direction (if this occurs in a liquid-liquid medium).

Table 2. Analysis and calculation of the component composition of raw materials

No.	Formula	Component name	Molecular weight of comp., M_i	B. p., °C	Content of comp. in fr., X_i, wt. %.	X_i / M_i	Content of comp. in fr., Y_i, mole %	$(M_i / Y_i) / 100$
1	2	3	4	5	6	7	8	9
1	C_4H_{10}	n-Butane	58	–0.5	1.7354	0.0299	2.6146	1.5
2	C_4H_8	2-Butene	56	0,9	8.9417	0.1597	13.9529	7.8
3	C_5H_{10}	Cyclopropane, 1,1-dimethyl-	70	21	0.9598	0.0137	1.1982	0.8
4	C_5H_{12}	Butane, 2-methyl	72	28	1.4518	0.0202	1.7620	1.3
5	C_5H_{10}	2-Butene, 2-methyl-	70	37	5.4922	0.0785	6.8562	4.8
6	C_5H_{10}	trans-2-Pentene	70	36	4.0770	0.0582	5.0895	3.6
7	C_5H_8	1,3-Pentadiene	68	42	9.8423	0.1447	12.6480	8.6
8	C_6H_{12}	1-Hexene	84	63	1.7726	0.0211	1.8440	1.5
9	C_6H_{14}	Pentane, 2-methyl-	86	60	2.1411	0.0249	2.1756	1.9
10	C_6H_{14}	Pentane, 3-methyl-	86	63	0.3924	0.0046	0.3987	0.3
11	C_6H_{12}	Pentane, 3-methylene-	84	64	1.2646	0.0151	1.3156	1.1
12	C_6H_{14}	n-Hexane	86	69	0.6737	0.0078	0.6845	0.6
13	C_6H_{12}	2-Pentene, 3-methyl-, (E)-	84	69	1.2128	0.0144	1.2617	1.1
14	C_6H_{12}	2-butene, 2,3-dimethyl-	84	73	1.3056	0.0155	1.3582	1.1
15	C_6H_{10}	Cyclopentane, methylene-	82	77	1.1250	0.0137	1.1989	1.0
16	C_7H_{16}	Pentane, 2,4-dimethyl-	98	80	1.0577	0.0108	0.9431	0.9
17	C_7H_{14}	1-Pentene, 2,4-dimethyl-	98	82	0.9281	0.0095	0.8276	0.8
18	C_6H_{10}	Cyclopentene, 1-methyl-	82	72	1.9934	0.0243	2.1243	1.7
19	C_7H_{14}	2-Pentene, 2,4-dimethyl-	98	83	0.7536	0.0077	0.6720	0.7

Continuation of Table 2

1	2	3	4	5	6	7	8	9
20	C_6H_6	Benzene	78	80	2.9639	0.0380	3.3205	2.6
21	C_7H_{16}	Hexane, 3-methyl-	100	91	0.4742	0.0047	0.4144	0.4
22	C_8H_{18}	Pentane, 2,2,4-trimethyl-, Isooctane	114	99	0.2502	0.0022	0.1918	0.2
23	C_7H_{16}	Heptane	100	98	0.4377	0.0044	0.3825	0.4
24	C_7H_{12}	Cyclopentene, 3,5-dimethyl-	96	100	0.3083	0.0032	0.2806	0.3
25	C_7H_{12}	Cyclopentene, 1,5-dimethyl-	96	102	0.2212	0.0023	0.2013	0.2
26	C_8H_{16}	1-Pentene, 2,4,4-trimethyl-	102	101	0.2634	0.0026	0.2257	0.2
27	C_8H_{16}	1-Hexene, 2,3-dimethyl-	112	112	0.2715	0.0024	0.2118	0.2
28	C_8H_{16}	2-Pentene, 3,4,4-trimethyl-	112	112	0.4860	0.0043	0.3792	0.4
29	C_7H_{12}	Cyclobutane, (1-methylethylidene)-	96	83	0.4575	0.0048	0.4164	0.4
30	C_7H_{12}	Cyclohexene, 4-methyl-	96	102	0.4583	0.0048	0.4172	0.4
31	C_7H_{12}	2,4-Heptadiene	96	108	0.3009	0.0031	0.2739	0.3
32	C_7H_{10}	1-Methyl-1,4-cyclohexadiene	94	115	0.3319	0.0035	0.3085	0.3
33	C_7H_{10}	1,3-Cyclopentadiene, 1,2-dimethyl-	94	106	1.2082	0.0129	1.1232	1.1
34	C_7H_8	Toluene	92	111	5.9041	0.0642	5.6079	5.2
35	C_8H_{16}	2-Pentene, 2,3,4-trimethyl-	112	116	0.9735	0.0087	0.7595	0.9
36	C_8H_{16}	Cyclopentane, 1-ethyl-2-methyl-	112	124	0.2260	0.0020	0.1763	0.2
37	C_8H_{16}	1-Heptene, 2-methyl-	112	120	0.1953	0.0017	0.1524	0.2
38	C_8H_{14}	Cyclopentene, 1,2,3-trimethyl-	110	122	0.1654	0.0015	0.1314	0.1
39	C_8H_{18}	Octane	114	126	0.1512	0.0013	0.1159	0.1
40	C_8H_{14}	Cyclohexene, 3,5-dimethyl-	110	120	0.1129	0.0010	0.0897	0.1
41	C_8H_{14}	Cyclopentene, 1-Ethyl-2-methyl-	110	127	0.2171	0.0020	0.1725	0.2
42	C_8H_{12}	Cyclopentene, 3-ethylidene-1-methyl-	108	140	0.6563	0.0061	0.5310	0.6
43	C_8H_{14}	1-Ethylcyclohexene	110	137	0.1296	0.0012	0.1030	0.1
44	C_8H_{10}	Ethylbenzene	106	136	1.2554	0.0118	1.0349	1.1
45	C_8H_{10}	m-Xylene	106	139	4.5767	0.0432	3.7729	4.0
46	C_9H_{20}	Octane, 3-methyl-	128	142	0.2635	0.0021	0.1799	0.2
47	C_8H_{10}	o-Xylene	106	145	0.8445	0.0080	0.6962	0.7
48	$C_{10}H_{22}$	Hexane, 2,2,3,3-tetramethyl-	142	160	0.1240	0.0009	0.0763	0.1
49	$C_{14}H_{28}$	3-Heptene, 2,2,3,5,5,6,6-heptamethyl-	196	225	0.3029	0.0015	0.1350	0.3
50	C_9H_{12}	Benzene, 1-Ethyl-3-methyl	120	159	0.6734	0.0056	0.4904	0.6
51	$C_{10}H_{16}$	Bicyclo(2.2.1)heptane, 7,7-dimethyl-2-methylene-	136	160	1.2785	0.0094	0.8215	1.1
52	$C_{10}H_{18}$	Bicyclo(4.1.0)heptane, 3,7,7-trimethyl- = Carane	138	168	0.2526	0.0018	0.1600	0.2
53	C_9H_{12}	Mesitylene	120	166	0.8236	0.0069	0.5997	0.7
54	$C_{10}H_{22}$	Decane	142	175	0.1342	0.0009	0.0826	0.1
55	$C_{10}H_{16}$	2,5,6-Trimethyl-1,3,6-heptatriene	136	140	0.1667	0.0012	0.1071	0.1
56	$C_{10}H_{18}$	Cyclohexene, 1-methyl-4-(1-methylethyl)-	138	173	1.0043	0.0073	0.6359	0.9
57	$C_{10}H_{14}$	o-Cymene	134	178	2.9578	0.0221	1.9288	2.6
58	$C_{10}H_{16}$	Cyclohexene, 1-methyl-4-(1-methylethenyl)	136	197	1.7237	0.0127	1.1075	1.5
59	$C_{10}H_{14}$	m-Cymene	134	175	0.3296	0.0025	0.2149	0.3
60	$C_{10}H_{14}$	Benzene, 1-methyl-4-(1-methylethyl)	134	178	0.1904	0.0014	0.1242	0.2
61	$C_{10}H_{14}$	Benzene, 1-methyl-3-propyl-	134	184	0.3431	0.0026	0.2237	0.3
62	$C_{10}H_{16}$	Cyclohexene, 1-methyl-4-(1-methylethylidene)-	136	185	0.3384	0.0025	0.2174	0.3

Continuation of Table 2

1	2	3	4	5	6	7	8	9
63	$C_{14}H_{30}$	Heptane, 2,2,3,3,5,6,6-heptamethyl-	198	177	0.1502	0.0008	0.0663	0.1
64	$C_{12}H_{16}$	1,2,4a,4b,7,8,8a,8b-Octahydrobiphenylene	160	180	0.2448	0.0015	0.1337	0.2
65	$C_{10}H_{10}$	1H-Indene, 3-methyl-	130	205	0.2044	0.0016	0.1374	0.2
66	$C_{11}H_{14}$	1-Methyl-4-[1-methyl-2-propenyl]benzene	146	198	0.0826	0.0006	0.0494	0.1
67	$C_{12}H_{16}$	3a,4,7,7a-tetrahydrodimethyl-4,7-methano-1H-Indene	160	200	0.0646	0.0004	0.0353	0.1
Unidentified compounds*			126	140	17.3851	0.1380	12.0567	15.2
Total			–	–	100.0000	1.1444	100.0000	87.4

* Accepted as the average molecular weight of the fraction.

To simplify calculations, in accordance with Table 2, the components of the gasoline fraction ≤ 200 °C are divided into five groups, indicating the type of hydrocarbons and a representative hydrocarbon for each type, and are presented in Table 3.

Table 3. Component composition of gasoline fraction ≤ 200 °C for determining partial pressures

Group	Type of hydrocarbons	Representative component	Molecular weights of representative components, M_i	Content of comp. in fr., X_i, mass fractions	Content of comp. in fr., Y_i, mole fractions	$M_i \times Y_i$
I	$C_4 – C_5$ olefins, dienes	2-methyl-2-butene	70	0.28353	0.3855	27.0
II	$C_4 – C_{10}$ paraffins and isoparaffins	n-hexane	86	0.12462	0.1279	11.0
III	$C_6 – C_7$ olefins, cycloolefins, dienes	methylcyclopentene	82	0.13185	0.1321	10.8
IV	Aromatic $C_6 – C_8$	toluene	92	0.16661	0.1533	14.1
V	$C_8 – C_{12}$, C_{14} + unidentified	o-cymene	134	0.29340	0.2012	27.0
Total			–	1.0000	1.0000	89.9

The average molecular weight calculated for representative components of hydrocarbon groups in Table 3 is 89.9, which corresponds to the molecular weight of gasoline fraction ≤ 200 °C, indicated in Table 2 (87.4 – molecular weight determined by component composition). Therefore, it can be concluded that modeling the composition of raw materials based on representative components is sufficiently accurate.

To determine the optimal pressure values for the thermo-oxidative processing of gasoline fractions ≤ 200 °C with air in the presence of water in a batch reactor, it is necessary to establish the proportions of raw material and the mixture (raw material + water) that vaporize. Accordingly, an essential stage of the study is to determine the partial pressures of saturated raw material vapors and water vapor at different process temperatures (50–250 °C) and pressures (0.5–5 MPa).

The partial pressures of saturated vapors of raw materials and water vapor at different temperatures were determined in accordance with Raoult's law and Antoine's equation.[47–50] The results are presented in Table 4 below.

According to Table 4, with an increase in temperature from 50 to 250 °C, there is a sharp, exponential increase in both the total partial pressure of hydrocarbons and the saturated water vapor pressure. This behavior corresponds to the Antoine equation and indicates a significant increase in the volatility of the mixture components. A particularly intense increase in pressure is observed in the range of 200–250 °C, where the contribution of water vapor to the total pressure becomes decisive; for example, at 50 °C, the vapor phase is almost entirely hydrocarbons.

Table 4. Determination of partial pressures of saturated vapors of raw materials and water vapor at different temperatures

Group	Representative component	Content of comp. in fr., Y_i, mole fractions	Partial and reduced pressures of components $P_i^{sat}(T)$, kPa									
			50°C		100°C		150°C		200°C		250°C	
			P_i^{sat}	$Y_i \cdot P_i^{sat}$	P_i^{sat}	$Y_i \cdot P_i^{sat}$	P_i^{sat}	$Y_i \cdot P_i^{sat}$	P_i^{sat}	$Y_i \cdot P_i^{sat}$	P_i^{sat}	$Y_i \cdot P_i^{sat}$
I	2-methyl-2-butene	0.3855	238	92	839	323	2123	818	4334	1671	7630	2941
II	n-hexane	0.1279	53	7	243	31	739	95	1731	221	3386	433
III	methylcyclopentene	0.1321	22	3	119	16	413	55	1065	141	2247	297
IV	toluene	0.1533	12	2	74	11	275	42	748	115	1641	252
V	o-cymene	0.2012	3	1	22	4	99	20	309	62	757	152
Total partial pressure of saturated hydrocarbon vapors, P_{HC}^{sat}, kPa			–	104	–	386	–	1030	–	2210	–	4075
Partial pressure of saturated water vapor, $P_{water\ vapor}^{sat}$, kPa			–	12	–	101	–	476	–	1554	–	5170
Partial pressure of the mixture, $P_{mixture}$, kPa			–	116	–	487	–	1506	–	3764	–	9245
Mole fraction of hydrocarbon vapors, $P_{HC}^{sat}/P_{mixture}$			–	0.8964	–	0.7926	–	0.6838	–	0.5871	–	0.4408
Mole fraction of water vapor, $P_{water\ vapor}^{sat}/P_{mixture}$			–	0.1036	–	0.2074	–	0.3162	–	0.4129	–	0.5592
Molecular weight of the vapors of the mixture			–	82.5	–	75.0	–	67.2	–	60.2	–	49.7
Mass fraction of hydrocarbon vapors			–	0.9774	–	0.9502	–	0.9153	–	0.8766	–	0.7974
Mass fraction of water vapor			–	0.0226	–	0.0498	–	0.0847	–	0.1234	–	0.2026

In contrast, at 250 °C, water vapor accounts for more than half of the gas-phase composition, indicating a fundamental change in the gas-phase composition at high temperatures. At the beginning of the experiment (100 °C, at the start of air supply), the calculated partial pressure of the mixture is 4.9 atm, which agrees with the absolute pressure observed in the reactor at that time (about 5 atm). This, in turn, once again confirms the validity of modeling the composition of raw materials based on representative components.

3.2. Pressure selection and raw material : air ratio

The amount of air G_{air}, kg, supplied to the reactor at different pressure values is given in Table 5.

Based on the amount of raw material loaded into the reactor (0.17 kg), the dependence of the change in the mass ratio of raw material to air flow on the operating pressure of the thermal oxidation process was constructed and is presented in Fig. 2.

Let us conventionally show the oxidation process of the most reactive hydrocarbons by the equation, in which products with a higher molecular weight are formed (mainly alcohols, as well as aldehydes and ketones):

$$2\ C_nH_m + O_2 \rightarrow C_nH_{m-1}–OH + C_nH_{m-2}=O,$$

which at relatively high temperatures can react with each other and/or with unsaturated compounds, forming solid oxidation products and high-boiling components (cubic residue). In this case, the amount of oxygen used per one molecule of raw material can be reduced by at least half (*i. e.*, 1 mole of oxygen will be required for 4 moles of raw material). For the complete oxidation of 1 kg of a raw material with a molecular weight of 90, 0.09 kg of oxygen is required. With an average oxygen content in the air of 23 % by weight, the amount of air required to oxidize the entire *fr.* < 200 °C will be 0.39 kg per 1 kg of raw material. According to work,[24] to obtain a product that can be used as a gasoline component, it is necessary to extract/process about 56 wt. % of the feedstock, which is equivalent to the oxidetion / removal of the most reactive components (unsaturated, group I, III) and 50 % of the heaviest hydrocarbons (group V). Thus, the mass ratio of feedstock / air can be:

$$1 / (0.39 \times 0.56) \approx 4.6.$$

If we assume that, under the influence of high temperatures, unsaturated hydrocarbons will undergo thermal polymerization, and about 50 % of the heaviest hydrocarbons (group V) need to be oxidized, then the mass ratio of raw material / air can be:

$$1 / (0.39 \times 0.15) \approx 17.3.$$

Table 5. Mass of air in the reactor at different pressures

Indicator	Pressure, kPa					
	507	1013	2027	3040	4053	5066
The amount of air G_{air}, kg	0.00061	0.00364	0.00970	0.01576	0.02183	0.02789

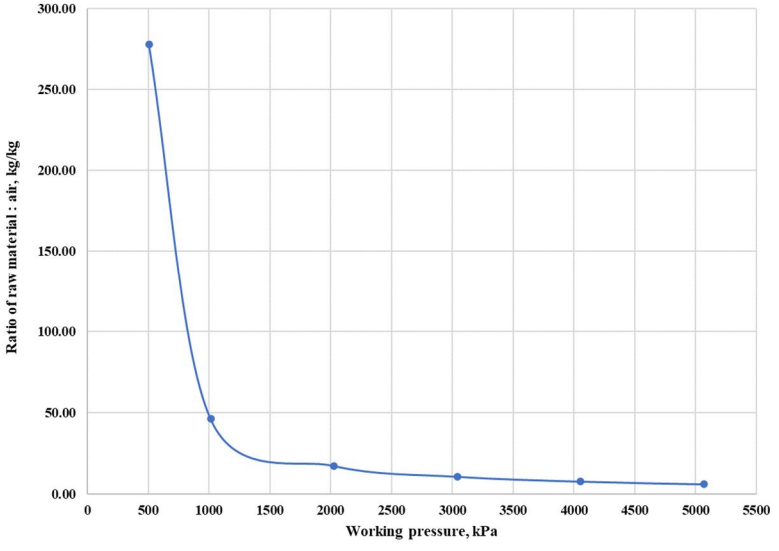

Fig. 2. Dependence of the change in the mass ratio of raw materials: air, kg/kg, on the working pressure of the process

Therefore, according to Fig. 2, such ratios of raw material to air flow will be provided at pressures of about 5000–2000 kPa (6.1–17.5 kg/kg). Taking the above into account, a study was conducted at operating pressures for the thermal oxidation process with air of 2026–5066 kPa (20–50 atm), as described in Section 3.3.

Based on the data in Tables 4 and 5 and the formulas given in Section 2.2, the proportions of water and raw materials in the vapor state at different process temperatures were calculated (see Fig. 3).

As shown in Fig. 3, with increasing temperature, the mass fractions of the raw material and the mixture that pass into the vapor phase increase nonlinearly. At temperatures up to 100 °C, the system remains predominantly liquid, with evaporation insignificant. According to the calculations, the changes in the mass fractions of the raw material and the mixture that will pass into vapor at 50 °C are 0.8 and 1.14 wt. %, respectively, which, in turn, correlates with the experimental data on losses given in Table 6, and are 1.1 and 1.65 wt. %, respectively. In view of the above, the thermal oxidation of the raw material mixture with air on an industrial scale should be carried out with additional equipment for extracting hydrocarbon vapors from the exhaust air, thereby minimizing these losses and environmental pollution. Absorbers or adsorbers can serve as such equipment.

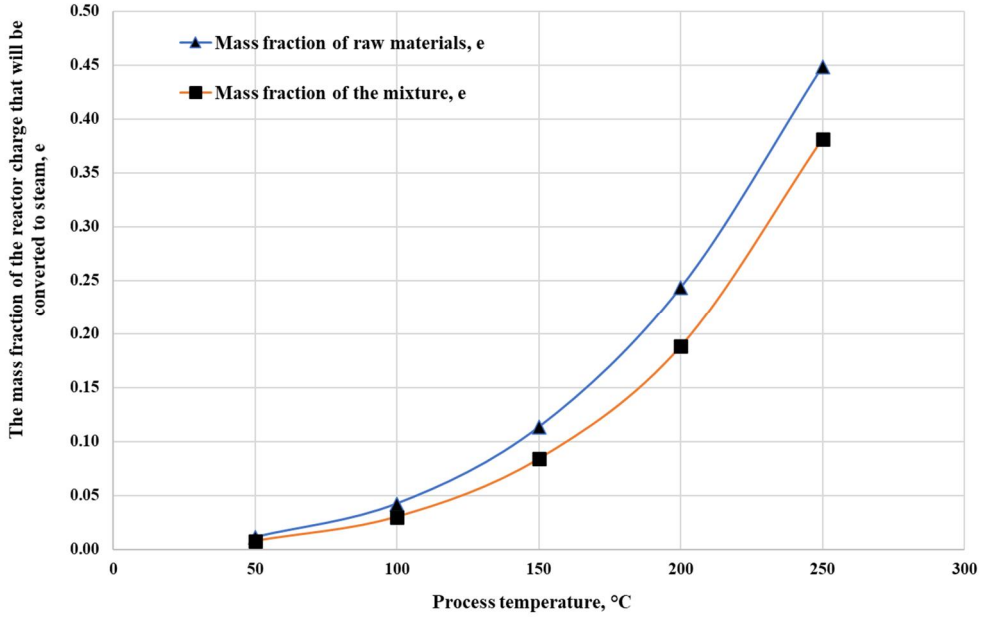

Fig. 3. Dependence of the change in the mass fraction of the raw material and the mixture that will turn into vapor on temperature

The most intensive growth of the distillation fraction is observed in the temperature range of 150–200 °C, corresponding to the transition of the system to a two-phase regime. Hydrocarbon components evaporate earlier than water; therefore, at the initial stages, the gas phase is enriched with hydrocarbons of the gasoline fraction. ≤ 200 °C. At temperatures above 200 °C, the contribution of water vapor increases, significantly affecting the gas-phase composition and pressure, respectively, and liquid-vapor phase oxidation occurs.

3.3. Exploratory studies of thermal oxidation processing of gasoline fraction

The influence of operating pressure on the thermal oxidation of raw materials in the presence of water was established for the fixed process parameters given in section 2.2. The results of the influence of operating pressures on the thermal oxidation of an air mixture are presented in Table 6 below.

As shown in Table 6–8, increasing operating pressure by increasing the air supply (reducing the raw material / air ratio from 17.5 to 6.1 kg/kg) significantly affects the course of thermal oxidation processing. With increasing oxidation intensity, the distillate yield decreases, while the amounts of bottom and solid residues increase (the process shifts towards the formation of heavier, high-molecular compounds with an excess of oxygen). In parallel, a decrease in the bromine number of the distillate is observed, indicating a decrease in the content of unsaturated compounds and an increase in the degree of oxidative transformation of these components. A slight

increase in density and refractive index indicates a shift in the product's composition toward higher aromatic content when oxidation is carried out at higher pressures.

In work,[24] the authors investigated the two-stage purification process for the gasoline fr. ≤ 200 °C, resulting in a component for the production of commercial fuels, which is characterized by a lower content of aromatic compounds (lower values of density and refractive index), but the bromine number is significantly higher than the bromine number values of the purified product of the thermal oxidation process with air, which indicates a higher content of unsaturated compounds.

Table 6. Study of the influence of operating pressures on the process of thermal oxidation with air*

Component	$P_{work.pres.} = 2027\,kPa$ (17.5 kg of raw material/kg of air)	$P_{work.pres.} = 5066\,kPa$ (6.1 kg of raw material/kg of air)
	wt. % on raw material	wt. % on raw material
Stage – thermal oxidation		
Received		
Fr. ≤ 200 °C	100.00	100.00
Water	47.50	47.50
Total	147.50	147.50
Obtained		
Thermal oxidation products	146.40	145.85
Losses	1.10	1.65
Total	147.50	147.50
Stage – vacuum filtration		
Received		
Thermal oxidation products	146.40	145.85
Total	146.40	145.85
Obtained		
Liquid thermal oxidation products + water	144.41	143.41
Solid residue	0.98	1.23
Losses	1.01	1.21
Total	146.40	145.85
Stage – settling		
Received		
Liquid thermal oxidation products + water	144.41	143.41
Total	144.41	143.41
Obtained		
Liquid thermal oxidation products	97.47	96.71
Water	46.34	46.05
Losses	0.60	0.65
Total	144.41	143.41
Stage – atmospheric distillation		
Received		
Liquid thermal oxidation products	97.47	96.71
Total	97.47	96.71
Obtained		
Distillate (purified product)	87.57	82.31
Liquid (cubic) residue	9.00	13.50
Losses	0.90	0.90
Total	97.47	96.71

* Volume ratio water : raw material – 0.4 vol., process temperature – 220 °C, duration – 20 min.

Table 7. Consolidated material balance study of the influence of operating pressures on the process of thermal oxidation with air*

Component	$P_{work.pres.} = 2027\ kPa$ (17.5 kg of raw material/kg of air)	$P_{work.pres.} = 5066\ kPa$ (6.1 kg of raw material/kg of air)
	wt. % on raw material	wt. % on raw material
Received		
Fr. ≤ 200 °C	100.00	100.00
Water	47.50	47.50
Total	147.50	147.50
Obtained		
Distillate (purified product)	87.57	82.31
Liquid (cubic) residue	9.00	13.50
Solid residue	0.98	1.23
Total losses	3.61	4.41
Water	46.34	46.05
Total	147.50	147.50

* Volume ratio water : raw material – 0.4 vol., process temperature – 220 °C, duration – 20 min.

Table 8. Physico-chemical properties of the obtained distillate (purified product)

Indicator name	Fr. < 200 °C	Distillate (purified product)		Gasoline fraction after two-stage* purification[24]
		$P_{work.pres.} = 2027\ kPa$ (17.5 kg of raw material / kg of air)	$P_{work.pres.} = 5066\ kPa$ (6.1 kg of raw material / kg of air)	
Density at 15 °C, kg/m^3, within range	842	826	829	792
Refractive index, n_d^{20}	1.4782	1.4685	1.4691	1.4587
Bromine number, g Br_2/100 g of product	67.90	44.92	40.03	54.26

* The 1st stage of purification is treatment with formalin and hydrochloric acid; the 2nd stage is extraction purification with N-methylpyrrolidone.

4. Conclusions

The work first substantiates the feasibility of using thermal oxidation treatment with air in the presence of water to purify the gasoline fraction ≤ 200 °C obtained from liquid pyrolysis products of worn tires. It was established that the initial fraction is characterized by high density, a high bromine number, and a significant content of aromatic and unsaturated compounds, which limit its direct use as a gasoline component. Modeling the fraction composition using representative components showed good agreement between the calculated average molecular weight and the saturated vapor pressure and the experimentally determined values, confirming the correctness of the adopted approach.

Calculation of the partial pressures of saturated hydrocarbons and water vapors in the range of 50–250 °C showed an exponential increase in total pressure and a change in the vapor-phase composition with increasing temperature. It was established that, within the range of 150–200 °C and 2.0–5.0 MPa, generated by air supply, the system enters a two-phase mode. At temperatures above 200 °C, water vapor begins to dominate the gas medium.

The choice of working pressures of 2.0–5.0 MPa as possible for the implementation of the process is justified. It was experimentally established that an increase in the working pressure from 2.0 MPa to 5.0 MPa, which is realized through an increase in air supply (a decrease in the raw material/air ratio from 17.5 to 6.1 kg/kg), leads to a

decrease in the yield of purified distillate and an increase in the amount of bottoms and solid residues, which indicates an intensification of oxidative condensation reactions and the formation of high-molecular products at an excess concentration of oxygen. There is a slight decrease in the bromine number (from 44.9 to 40.0 g Br_2/100 g), confirming a decrease in the content of unsaturated compounds and an increase in product stability. At the same time, with a decrease in the raw material / air ratio, there is a slight increase in the density and refractive index, which indicates an increase in the content of aromatic structures due to the removal of unsaturated and, possibly, oxidation of cycloalkanes and paraffins. Given the above, it is advisable to carry out the process at 2.0 MPa, which provides a raw material / air ratio of 17.5 kg/kg.

The results obtained allow us to state that thermal oxidation processing with air of gasoline fractions obtained from the pyrolysis of waste tires provides a sufficiently effective reduction of the most reactive unsaturated compounds, with a relatively simple hardware design and without the need for expensive reagents or hydrogen. The purified product – distillate – can serve as a component of gasoline, similar to that previously obtained in studies of the two-stage purification process of the gasoline fraction ≤ 200 °C (1st purification stage – formalin treatment in the presence of hydrochloric acid, 2nd – extraction purification with N-methylpyrrolidone).[24] After mixing the aforementioned obtained gasoline component[24] with gas condensate, it was possible to obtain commercial gasoline. As a result of the process of thermal oxidation treatment of gasoline fractions with air, a similar (in terms of the content of unsaturated and aromatic compounds) product was obtained, but by a different (more straightforward) method, therefore, it can be predicted that it can be used as a component of gasoline, which will be the topic for further research. Therefore, the process is promising for small-scale enterprises processing liquid products of pyrolysis of high-pressure steam. These studies provide a scientifically sound basis for further studies of the influence of factors and the phase state of the raw material, the reaction chemistry, *etc.*, and for scaling up the thermal oxidation process with air for gasoline fractions obtained from liquid products of pyrolysis of high-pressure steam.

Acknowledgements

Bohdan Korchak is grateful to the Committee of the Borys Paton National Prize of Ukraine for awarding a scholarship to the Cabinet of Ministers of Ukraine for young scientists.

Conflict of Interest

The authors declare that they have no conflicts of interest.

References

[1] Du, Z.; Li, P.; Yang, L.; Xue, Z.; Zhou, Y.; Chen, T. Pyrolysis Treatment of Waste Tires and Resource Utilization of Products: A Review. *J. Anal. Appl. Pyrolysis.* **2026**, *195*, 107605. https://doi.org/10.1016/j.jaap.2026.107605

[2] Alzahrani, N.; Nahil, M. A.; Williams, P. T. Co-Pyrolysis of Waste Plastics and Tires: Influence of Interaction on Product Oil and Gas Composition. *J. Energy Inst.* **2025**, *118*, 101908. https://doi.org/10.1016/j.joei.2024.101908

[3] Zerin, N. H.; Rasul, M. G.; Jahirul, M. I.; Sayem, A. S. M. End-of-Life Tyre Conversion to Energy: A Review on Pyrolysis and Activated Carbon Production Processes and Their Challenges. *Sci. Total Environ.* **2023**, *905*, 166981. https://doi.org/10.1016/j.scitotenv.2023.166981

[4] Pyshyev, S.; Lypko, Y.; Demchuk, Y.; Kukhar, O.; Korchak, B.; Pochapska, I.; Zhytnetskyi, I. Characteristics and Applications of Waste Tire Pyrolysis Products: A Review. *Chem. Chem. Technol.* **2024**, *18*, 244–257. https://doi.org/10.23939/chcht18.02.244

[5] Ferdous, W.; Manalo, A.; Siddique, R.; Mendis, P.; Zhuge, Y.; Wong, H. S.; Lokuge, W.; Aravinthan, T.; Schubel, P. Recycling of Landfill Wastes (Tyres, Plastics and Glass) in Construction – A Review on Global Waste Generation, Performance, Application and Future Opportunities. *Resour. Conserv. Recycl.* **2021**, *173,* 105745. https://doi.org/10.1016/j.resconrec.2021.105745

[6] Pyshyev, S.; Lypko, Y.; Korchak, B.; Poliuzhyn, I.; Hubrii, Z.; Pochapska, I.; Rudnieva, K. Study on the Composition of Gasoline Fractions Obtained as a Result of Waste Tires Pyrolysis and Production Bitumen Modifiers from It. *J. Energy Inst.* **2024**, *114*, 101598. https://doi.org/10.1016/j.joei.2024.101598

[7] Where to recycle old tires: recycling waste tires. https://ascania-shina.com/ua/articles/kuda-sdat-starye-shiny-na-pererabotku (accessed 2022-07-24).

[8] Tire Recycling UA. https://www.tirerecycling.com.ua/uk (accessed 2026-01-01).

[9] Waste Management Center. https://recycle.com.ua/ (accessed 2025-11-05).

[10] Scientific and Production Company “UkrEkoprom”. https://ueco.com.ua/tires (accessed 2025-08-15).

[11] Doja, S.; Pillari, L. K.; Bichler, L. Processing and Activation of Tire-Derived Char: A Review. *Renew. Sustain. Energy Rev.* **2022**, *155*, 111860. https://doi.org/10.1016/j.rser.2021.111860

[12] Wang, B.; Fu, Y.; Zheng, H.; Zeng, D.; Xiao, R. Catalytic and Noncatalytic Fast Pyrolysis of Waste Tires to Produce High-Value Monocyclic Aromatic Hydrocarbons. *J. Anal. Appl. Pyrolysis* **2021**, *156*, 105131. https://doi.org/10.1016/j.jaap.2021.105131

[13] Wu, Q.; Leng, S.; Zhang, Q.; Xiao, J. Resource and Environmental Assessment of Pyrolysis-Based High-Value

Utilization of Waste Passenger Tires. *Waste Manage.* **2021**, *126*, 201–208. https://doi.org/10.1016/j.wasman.2021.03.008
[14] Formela, K. Waste Tire Rubber-Based Materials: Processing, Performance Properties and Development Strategies. *Adv. Ind. Eng. Polym. Res.* **2022**, *5*, 234–247. https://doi.org/10.1016/j.aiepr.2022.06.003
[15] Hoyer, S.; Kroll, L.; Sykutera, D. Technology Comparison for the Production of Fine Rubber Powder from End of Life Tyres. *Procedia Manuf.* **2020**, *43*, 193–200. https://doi.org/10.1016/j.promfg.2020.02.135
[16] Bowles, A. J.; Fowler, G. D.; O'Sullivan, C.; Parker, K. Sustainable Rubber Recycling from Waste Tyres by Waterjet: A Novel Mechanistic and Practical Analysis. *Sustainable Mater. Technol*. **2020**, *25*, e00173. https://doi.org/10.1016/j.susmat.2020.e00173
[17] Li, J.; Xiao, X.; Chen, Z.; Xiao, F.; Amirkhanian, S. N. Internal De-Crosslinking of Scrap Tire Crumb Rubber to Improve Compatibility of Rubberized Asphalt. *Sustainable Mater. Technol.* **2022**, *32*, e00417. https://doi.org/10.1016/j.susmat.2022.e00417
[18] Mohajerani, A.; Burnett, L.; Smith, J. V.; Markovski, S.; Rodwell, G.; Rahman, M. T.; Kurmus, H.; Mirzababaei, M.; Arulrajah, A.; Horpibulsuk, S.; *et al*. Recycling Waste Rubber Tyres in Construction Materials and Associated Environmental Considerations: A Review. *Resour. Conserv. Recycl.* **2020**, *155*, 104679. https://doi.org/10.1016/j.resconrec.2020.104679
[19] Sienkiewicz, M.; Janik, H.; Borzędowska-Labuda, K.; Kucińska-Lipka, J. Environmentally Friendly Polymer-Rubber Composites Obtained from Waste Tyres: A Review. *J. Clean. Prod.* **2017**, *147*, 560–571. https://doi.org/10.1016/j.jclepro.2017.01.121
[20] Nagurskyy, A.; Grynyshyn, O.; Khlibyshyn, Yu.; Korchak, B. Use of Rubber Crumb Obtained from Waste Car Tires for the Production of Road Bitumen and Roofing Materials from Residues of Ukrainian Oil Processing. *Chem. Chem. Technol.* **2023**, *17*, 674–680. https://doi.org/10.23939/chcht17.03.674
[21] Pyshyev, S.; Kukhar, O.; Korchak, B.; Donchenko, M.; Yavorskyi, O. Temperature Effect on the Process of Road Bitumen Modification with Carbonized Residue from the Waste Tires Pyrolysis. *Chem. Chem. Technol.* **2025**, *19*, 590–600. https://doi.org/10.23939/chcht19.03.590
[22] Kazemi, M.; Fini, E. H. State of the Art in the Application of Functionalized Waste Polymers in the Built Environment. *Resour. Conserv. Recycl.* **2022**, *177*, 105967. https://doi.org/10.1016/j.resconrec.2021.105967
[23] Zhang, G.; Guo, B.; Zhang, L. Significant Trends in Rubber Research Driven by Environment, Resource, and Sustainability. *Macromolecules* **2025**, *58*, 5883–5903. https://doi.org/10.1021/acs.macromol.5c00494
[24] Pyshyev, S.; Korchak, B.; Miroshnichenko, D.; Lebedev, V.; Yasinska, A.; Lypko, Y. Obtaining New Materials from Liquid Pyrolysis Products of Waste tires for Waste Valorization. *Sustainability* **2025**, *17*, 3919. https://doi.org/10.3390/su17093919
[25] Dewangan, A.; Ahmad, A.; Yadav, A. K. Innovative Research on Waste Tire Recycling for Sustainable Biofuel Production: Assessment of Its Usability on Multi-Cylinder Diesel Engine Employing Constant Injection of Oxyhydrogen and Biogas through a Premixing Device. *Int. J. Hydrogen Energy* **2024**, *84*, 155–163. https://doi.org/10.1016/j.ijhydene.2024.08.131
[26] Han, W.; Han, D.; Chen, H. Pyrolysis of Waste Tires: A Review. *Polymers* **2023**, *15*, 1604. https://doi.org/10.3390/polym15071604
[27] Liu, J.; Zhou, J.; Ren, J. Recent Advances of Energetic Valorization Technologies for Waste Tires: A Systematic Review of Thermochemical and Integrated Processes, Challenges, and Future Directions. *Renew. Sustain. Energy Rev*. **2025**, *218*, 115800. https://doi.org/10.1016/j.rser.2025.115800
[28] Grioui, N.; Halouani, K.; Agblevor, F. A. Assessment of Upgrading Ability and Limitations of Slow Co-Pyrolysis: Case of Olive Mill Wastewater Sludge/Waste Tires Slow Co-Pyrolysis. *Waste Manage.* **2019**, *92*, 75–88. https://doi.org/10.1016/j.wasman.2019.05.016
[29] Alvarez, J.; Amutio, M.; Lopez, G.; Santamaria, L.; Bilbao, J.; Olazar, M. Improving Bio-Oil Properties through the Fast Co-Pyrolysis of Lignocellulosic Biomass and Waste Tyres. *Waste Manage.* **2019**, *85*, 385–395. https://doi.org/10.1016/j.wasman.2019.01.003
[30] Costa, G. A.; Santos, R. G. D. Fractionation of Tire Pyrolysis Oil into a Light Fuel Fraction by Steam Distillation. *Fuel* **2019**, *241*, 558–563. https://doi.org/10.1016/j.fuel.2018.12.075
[31] Jantaraksa, N.; Prasassarakich, P.; Reubroycharoen, P.; Hinchiranan, N. Cleaner Alternative Liquid Fuels Derived from the Hydrodesulfurization of Waste Tire Pyrolysis Oil. *Energy Convers. Manag.* **2015**, *95*, 424–434. https://doi.org/10.1016/j.enconman.2015.02.003
[32] Aydın, H.; İlkılıç, C. Optimization of Fuel Production from Waste Vehicle Tires by Pyrolysis and Resembling to Diesel Fuel by Various Desulfurization Methods. *Fuel* **2012**, *102*, 605–612. https://doi.org/10.1016/j.fuel.2012.06.067
[33] Pyshyev, S.; Korchak, B.; Miroshnichenko, D.; Vytrykush, N. Influence of Water on Noncatalytic Oxidative Desulfurization of High-Sulfur Straight-Run Oil Fractions. *ACS Omega.* **2022**, *7*, 26495–26503. https://doi.org/10.1021/acsomega.2c02527
[34] Pysh'yev, S.; Lazorko, O.; Bratychak, M. Temperature and Water Effect on the Oxidative Desulphurization of Straight-Run Diesel Fraction with a High Sulphur Content. *Chem. Chem. Technol.* **2009**, *3*, 163–168. https://doi.org/10.23939/chcht03.02.163
[35] Pysh'yev, S.; Lazorko, O.; Bratychak, M. Oxidative Processing of Light Oil Fractions. A Review. *Chem. Chem. Technol.* **2009**, *3*, 77–81. https://doi.org/10.23939/chcht03.01.077
[36] Korchak, B.; Grynyshyn, O.; Chervinskyy, T.; Shapoval, P.; Nagurskyy, A. Thermooxidative Regeneration of Used Mineral Motor Oils. *Chem. Chem. Technol.* **2020**, *14*, 129–134. https://doi.org/10.23939/chcht14.01.129
[37] Korchak, B.; Grynyshyn, O.; Chervinskyy, T.; Nagurskyy, A.; Stadnik, V. Integrated Regeneration Method for Used Mineral Motor Oils. *Chem. Chem. Technol.* **2021**, *15*, 239–246. https://doi.org/10.23939/chcht15.02.239
[38] DSTU EN 13016-1:2012 https://online.budstandart.com/ua/catalog/doc-page.html?id_doc=29250 (Accesed 2012-09-01).
[39] DSTU 7261:2012 https://online.budstandart.com/ua/catalog/doc-page.html?id_doc=54397 (Accesed 2013-03-01).
[40] DSTU EN ISO 2160:2012 https://online.budstandart.com/ua/catalog/doc-page.html?id_doc=29253 (Accesed 2012-09-01).

[41] GOST 6307-75
https://online.budstandart.com/ua/catalog/doc-page.html?id_doc=97246 (Accesed 2024-02-11).
[42] DSTU EN ISO 20884:2022
https://online.budstandart.com/ua/catalog/doc-page.html?id_doc=110466 (Accesed 2023-12-31).
[43] DSTU GOST 18995.2:2009
https://online.budstandart.com/ua/catalog/doc-page.html?id_doc=59182 (Accesed 2022-07-15).
[44] DSTU GOST 33550:2019
https://online.budstandart.com/ua/catalog/doc-page.html?id_doc=82870 (Accesed 2019-06-10).
[45] Ultrafast gas chromatography-mass spectrometer Shimadzu GCMS-QP2020. https://www.shimadzu.com.ua/chromatographic-equipment/gcms-qp2020-nx?lang=en (Accesed 2018-09-01).
[46] Vir Singh, M. Deformation of Waste Tube-Tyres into Liquid Green Hydrocarbons (LGHs) through Pyrolysis Using the $FeCO_3$. *Materials Today: Proceedings*, **2022**, *51*, 1669–1674. https://doi.org/10.1016/j.matpr.2020.08.689
[47] Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001.
[48] Yaws, C. L. *Thermophysical Properties of Chemicals and Hydrocarbons*; Elsevier: Amsterdam, 2008.
[49] Speight, J. G. *The Chemistry and Technology of Petroleum*, 5th ed.; CRC Press: Boca Raton, FL, 2014.
[50] Williams, P. T. Pyrolysis of Waste Tyres: A Review. *Waste Manage.* **2013**, *33*, 1714–1728. https://doi.org/10.1016/j.wasman.2013.05.003

Received: February 13, 2026 / Revised: February 21, 2026 / Accepted: February 23, 2026

ВИБІР УМОВ ТЕРМООКСИДАЦІЙНОЇ ОБРОБКИ БЕНЗИНОВИХ ФРАКЦІЙ, ОТРИМАНИХ З РІДКИХ ПРОДУКТІВ ПІРОЛІЗУ ВЖИВАНИХ ШИН

Анотація. *Вживані шини (ВШ) є основною складовою промислових гумових відходів. Одним із перспективних методів раціональної утилізації ВШ є піроліз – термохімічний процес, під час якого термічно нестабільні органічні компоненти, що входять до складу ВШ, розкладаються на газоподібні, рідкі та тверді продукти за температур 300–900 °C. Використання піролізу поєднує перероблення відходів із рекуперацією енергії та палива. Рідкі продукти піролізу (РПП) можна вважати основними продуктами піролізу ВШ, які одержують у результаті конденсації з летких фракцій піролізу ВШ. Це темна непрозора рідина із характерним різким запахом, що складається, значною мірою, з ароматичних і ненасичених сполук, тому для використання цих продуктів як палив необхідне глибоке перероблення. У цій роботі описано первинні (пошукові) дослідження стосовно можливості / доцільності застосування процесу термооксидаційної обробки для очищення бензинової фракції ≤ 200 °C, одержаної після атмосферної перегонки РПП ВШ. Окиснення здійснювали в реакторі періодичної дії повітрям за наявності води. Досліджено і розраховано склади сировинної суміші, її фазовий стан під час процесу та обґрунтовано тиск і співвідношення сировина : повітря. Ці дослідження в майбутньому стануть базовими для детального вивчення термооксидації бензинової фракції, отримуваної в ході піролізу ВШ, щоб зменшити в ній вміст небажаних сполук (реакційноздатних ненасичених, сірчистих, висококиплячих ароматичних сполук).*

Ключові слова: *вживані шини, рідкі продукти піролізу шин, альтернативне паливо, термоокиснення.*