

Production of low-sulfur fuel distillates from waste tyres via pyrolysis and their application in petroleum refining

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ABSTRACT

This study investigates the conversion of end-of-life tyre rubber into liquid fuel distillates and the subsequent upgrading of the products to meet key motor-fuel quality requirements. Thermal behavior of tyre rubber was assessed by thermogravimetric analysis to justify process conditions, and pyrolysis parameters (temperature, residence time, and crumb size) were systematically evaluated to maximize distillate yield. Under the established optimum conditions (400 °C, 60 min, 0.5–6 mm), the liquid distillate yield reached up to 50%. The tyre-derived distillate exhibited a density of ~870 kg/m³ at 20 °C and a boiling range of approximately 65–360 °C. GC–MS analysis revealed a complex mixture dominated by naphthenic and aromatic hydrocarbons with minor sulfur-containing species (notably benzothiazole and benzo[b]thiophene derivatives). The total sulfur content of the untreated distillate was ~0.798 wt.%. A practical low-temperature upgrading route based on sulfonation with concentrated H₂SO₄, followed by neutralization and isolation of sulfonates as salts, was developed, reducing sulfur to ~0.07 wt.% under severe treatment. Co-processing feasibility was demonstrated by blending 5% (v/v) of the tyre-derived distillate into an atmospheric-distillation feed (crude oil/gas condensate mixture), which increased gasoline and gasoil fractions while decreasing the kerosene cut without deteriorating key properties. The proposed approach provides a resource-efficient pathway for tyre-waste valorization and supports refinery integration of upgraded tyre-derived distillates.

Keywords: petroleum, end-of-life tyres, fuel distillate, GC–MS, desulfurization, sulfonation, refinery co-processing, recycling, fractional composition, pyrolysis.

INTRODUCTION

Most hydrocarbon-containing household wastes, including rubber and plastic wastes, are poorly biodegradable and belong to the class of persistent materials whose chemical structure remains largely unchanged in the environment. Consequently, they pose a serious environmental hazard: their accumulation inevitably leads to the formation and expansion of dumpsites. Once discarded, rubber and plastic wastes gradually fragment under climatic factors into fine dispersed particles that can be transported over long distances by wind and become embedded in the soil

layer. Disposal sites for rubber and plastic wastes also turn into habitats for rodents and other living organisms. To address these problems, it is necessary to develop new, efficient methods for the utilization and elimination of rubber and plastic wastes, thereby supporting environmental protection while simultaneously creating additional energy resources.

Worldwide demand for motor fuels is high and continues to grow rapidly (on the order of ~4.0 billion tons annually), which in turn sharply increases the demand for crude oil and other fuel-producing feedstocks. Considering that global production of gasoline and diesel fuel alone was

around 2.8 billion tons in 2023, the depletion of crude-oil and gas-condensate reserves remains a pressing issue. Therefore, due to the rapid decline of natural hydrocarbon reserves, meeting motor-fuel demand through alternative resources and processing routes is of great importance (Abedin et al., 2023; Akhmedova et al., 2023).

Worldwide, scientific research is being conducted on the recycling and utilization of end-of-life tyres used in all types of road vehicles, aimed at obtaining products suitable for the national economy, expanding the raw-material resource base through regeneration, producing high-quality fuel products, and developing efficient methods for processing or utilizing plastic wastes. In this context, particular attention is being paid to the recycling of waste vehicle tyres and plastic materials to produce fuel distillates, the development of effective purification methods to upgrade these fuel distillates to the quality requirements for motor fuels, and the investigation of the feasibility of using the carbonaceous char (soot) formed during waste-tyre processing as an adsorbent (Ma'rif et al., 2025; Derakhshan et al., 2017; Abdul-Raouf et al., 2010). Currently, there are many approaches to the management of end-of-life tyres, including warehouse storage, landfilling, decorative reuse, incineration, retreading/restoration, thermal and thermocatalytic conversion, use as an alternative energy source, and others (Figure 1) (Williams and Brindle 2002; de Marco Rodriguez et al. 2001).

Another approach is to use end-of-life tyres as a fuel by incineration. Direct combustion of tyre waste in furnaces has several advantages: lower costs of electricity generation, high energy-recovery efficiency, and reduced environmental impact compared with landfilling. However, the method has notable drawbacks: no material recovery,

high capital investments, the need for flue-gas treatment, increased CO₂ emissions, and higher operating costs. Therefore, additional research is required to reduce the impacts of tyre combustion on the environment—especially the emission of polycyclic aromatic hydrocarbons (PAHs) (Machin, Pedroso, and de Carvalho 2017).

A further application of tyre waste as fuel is the generation of electricity. When tyre waste is burned in boilers, high-pressure steam is produced, which is fed to a steam turbine coupled to a generator. Combustion can be carried out in stationary or fluidized-bed conditions. Combustion of tyre waste in fluidized-bed reactors has been successfully demonstrated by several authors. Nevertheless, fluidized-bed combustion of tyre waste is relatively expensive due to high operating costs and the complexity of feed preparation (Shah et al., 2007; Mastral et al., 2000).

A rotary kiln furnace enables the combustion of tyre wastes of various sizes at relatively low operating costs, although such systems require technologies for filtering particulate matter in flue gases and for controlling the emissions. Because PAH emissions may be significant, this route still requires additional investigation (Mentes et al., 2022).

In comparison with coal combustion, burning end-of-life tyres results in 3–4 times lower NO_x emissions than coal, while CO₂ emissions are comparable. However, CO (carbon monoxide) and PAH emissions are generally higher for tyres than for coal (Carmo-Calado et al., 2020).

Mechanical and thermomechanical recycling of tyres (Adhikari et al., 2000) is currently the most widespread approach. Dozens of equipment manufacturers operate worldwide. Typical processing includes cutting off bead rings, shredding tyres into large pieces, separating steel wires, and

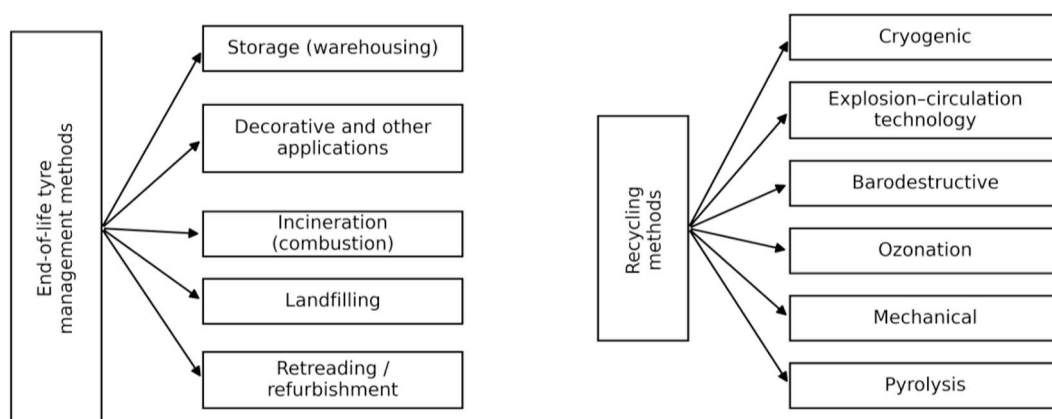


Figure 1. Methods for recycling end-of-life vehicle tyres

milling rubber into smaller fragments. The technology is based on mechanically grinding tyres to small pieces and then, by exploiting the ‘brittleness increase’ of rubber at high impact speeds, mechanically separating metal and textile cords. The resulting rubber chips are further ground (e.g., by extrusion milling) to obtain rubber powders with particle sizes down to ~0.2 mm (Vukanti et al., 2009).

Pyrolysis (thermal distillation, thermolysis) of end-of-life tyres is a thermochemical decomposition of organic matter by cleavage of chemical bonds. It is typically carried out at 600–800 °C in an oxygen-free medium (inert atmosphere or vacuum) (Williams, 2013). In practice, however, thermal processing of tyre waste often proceeds with small amounts of air present, which ultimately leads to partial gasification.

As a result of such reactions, products in the form of gas, vapour, liquid and solid residue are formed (Table 1).

Gasification of waste tyres is the conversion of hydrocarbon feedstocks into combustible gases by heating under pressure at high temperature in the presence of oxidizing agents (oxygen, air, steam, CO₂, or their mixtures). The produced gas mainly consists of carbon monoxide and hydrogen. Gasification of tyre waste is typically

performed at 1200–1500 °C and at 15–18 bar in a steam environment (1 bar = 10⁵ Pa). In the gasification process, tyre-rubber components are first converted to methane, which subsequently reacts with steam to form a CO/H₂ mixture known as synthesis gas. The product distribution depends on the oxygen availability in the system (Figure 2).

The main advantages of converting waste tires into synthesis gas using the gasification process are as follows: (Khojjeva and Khaitov 2021):

- high conversion rate;
- the products can be used as fuels or as feedstocks for organic synthesis;
- gasification is more efficient for energy recovery than direct combustion;
- compounds such as H₂S and NH₃ contaminate synthesis gas and can be removed using appropriate gas-cleaning technologies.

Gasification is a highly efficient method for processing carbonaceous wastes, enabling 60–70% gas yield and 98–99% carbon conversion. Therefore, gasification can be considered a viable route for processing end-of-life tyres (Khojjeva et al., 2023). The main disadvantages of gasification for large-scale tyre-waste treatment include the need for careful size reduction of tyre fragments,

Table 1. Pyrolysis products of end-of-life vehicle tyres

№	Primary products	Yield, %	Composition	Products made from primary products
	Gas	10–30	Hydrogen, CO ₂ , CO, methane, ethane, propane, butane, propene, other hydrocarbons and sulfur.	–
	Distillate	38–55	Alkanes, alkenes, aldehydes, ketones, aromatic hydrocarbons containing high amounts of sulfur (0.3–1%)	carbon
	Solid residue	33–38	>15% ash (ZnO), 3–5% sulfur	Activated carbon

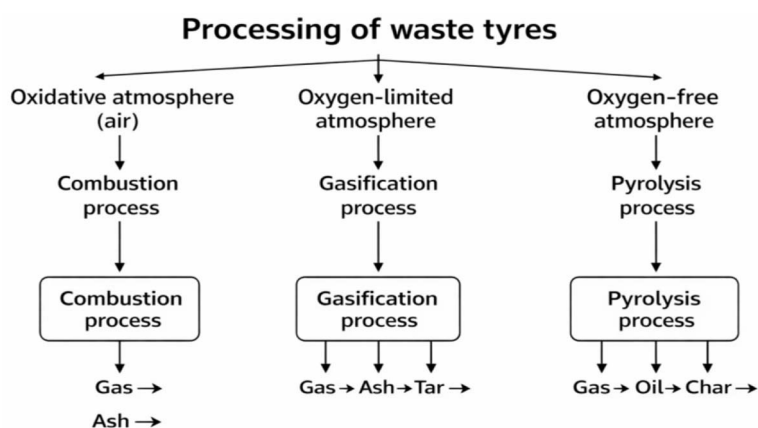


Figure 2. Different thermal conversion routes for waste tyres

complex reactor and gas-cleaning systems, and stringent requirements for controlling tar and particulate formation.

Selecting thermocatalytic processing of end-of-life tyres offers several advantages compared with non-catalytic processing, such as a narrower molecular-weight distribution of products and the possibility of obtaining higher-quality fractions (Khojiev and Azimova, 2024; Hojiyeva et al., 2024). A characteristic feature of catalysts for thermodestructive conversion of tyres and other rubber wastes is their ability to promote cracking, dehydrogenation and aromatization, thereby improving the distillate quality and yield. However, analyses show that in Uzbekistan the production of fuel distillates from rubber and plastic wastes, as well as systematic studies of their composition, properties and optimal technological parameters, have not yet been sufficiently explored.

Thus, an important task is to recycle locally available rubber wastes to obtain fuel distillates, implement industrial-scale technologies, and substantiate the optimal operating regimes theoretically and experimentally.

The aim of this study is to investigate the thermochemical conversion of end-of-life tyre rubber into valuable liquid fuel distillates through pyrolysis, to develop an efficient desulfurization method for improving fuel quality, and to assess the feasibility of co-processing tyre-derived distillates within conventional petroleum refining streams.

The novelty of this study lies in the integrated approach for converting end-of-life tyre rubber into low-sulfur fuel distillates by combining

pyrolysis, compositional analysis, targeted desulfurization, and refinery co-processing assessment. Unlike previous studies focused mainly on tyre pyrolysis, this work also demonstrates the practical upgrading of tyre-derived distillates and evaluates their suitability for incorporation into conventional petroleum-refining streams.

MATERIAL AND METHODS

The most abundant rubber waste is end-of-life vehicle tyres. The main component of tyre rubber is elastomer (rubber), a chemically cross-linked polymer with high strength and elasticity. Tyres also contain fillers (e.g., carbon black), plasticizers, antioxidants, vulcanization agents and reinforcing cords (steel and textile), whose proportions depend on tyre type and manufacturer.

To perform pyrolysis of rubber-based wastes, the experimental setup shown in Figure 4 was assembled. The main unit is a stainless-steel reactor (1) with a length of 100 cm, a capacity of 2 kg, and a maximum operating temperature of 1200 °C under atmospheric pressure. Reactor heating is provided by an electrical heater controlled through a laboratory autotransformer (LATR). The volatilized products are cooled in a condenser (2) and collected in a condensate receiver (3), while the non-condensable gases pass through a gas meter (4). The reactor temperature is monitored by a thermocouple (6).

Each experiment was performed three times under identical conditions. The deviation between replicate results did not exceed 1%.

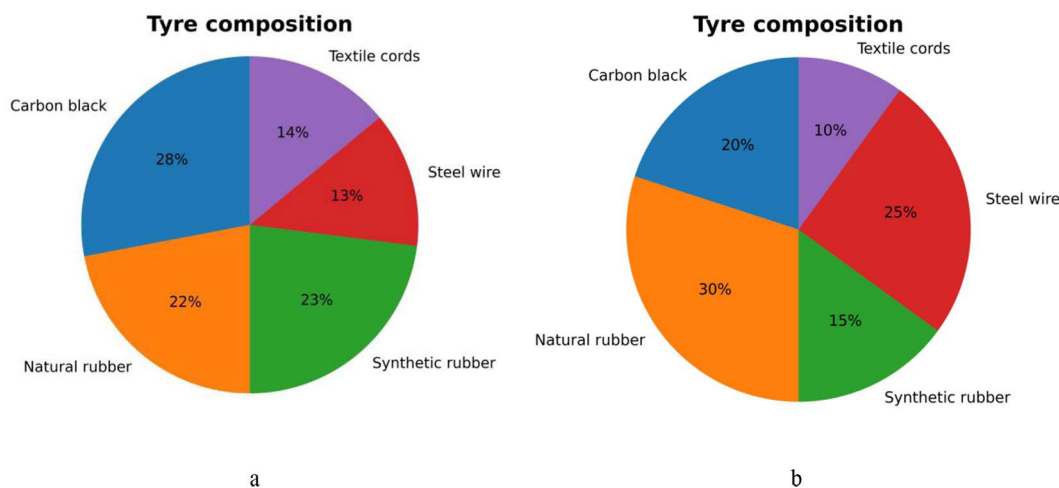


Figure 3. Constituent parts of passenger (a) and truck (b) tyres

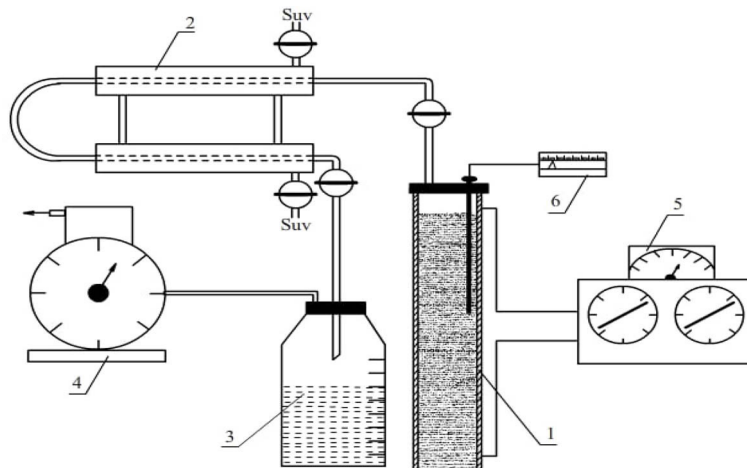


Figure 4. Experimental setup for pyrolysis of waste-tyre rubber under oxygen-free conditions: 1 – reactor; 2 – condenser; 3 – condensate receiver; 4 – gas meter; 5 – autotransformer; 6 – thermocouple

RESULTS

First, the rubber fraction of the end-of-life tyres selected as the research object was analyzed by thermogravimetric analysis (TGA). The purpose of TGA was to determine the content of volatile components in the waste and to provide a basis for selecting and preparing the pyrolysis conditions. The tyre-rubber sample was heated from 30 °C to 700 °C, and the mass-loss profile was recorded (Figure 5).

As can be seen from Figure 5, the sample mass began to decrease at ~215 °C and showed a sharp mass loss around 340 °C, which continued until the thermal decomposition essentially ended at about 550 °C. Above 550 °C, the additional mass loss was approximately 1%. In the temperature interval

300–500 °C, the rubber sample experienced the main degradation stage, corresponding to the volatilization and cracking of organic components.

According to the TGA results, the main mass losses for the tyre waste occurred in the range 340–500 °C. Based on these data, the effect of process temperature (t) on distillate yield was studied.

Figure 6 shows that the optimal temperature for thermal conversion of tyre-rubber waste is 400 °C, at which the distillate yield reached about 50%. Experiments at 250 and 300 °C did not produce a noticeable yield of fuel distillate. TGA indicates that at 250 and 300 °C the tyre rubber undergoes only limited mass loss (about 3% and 15%, respectively), which is insufficient for intensive distillate formation.

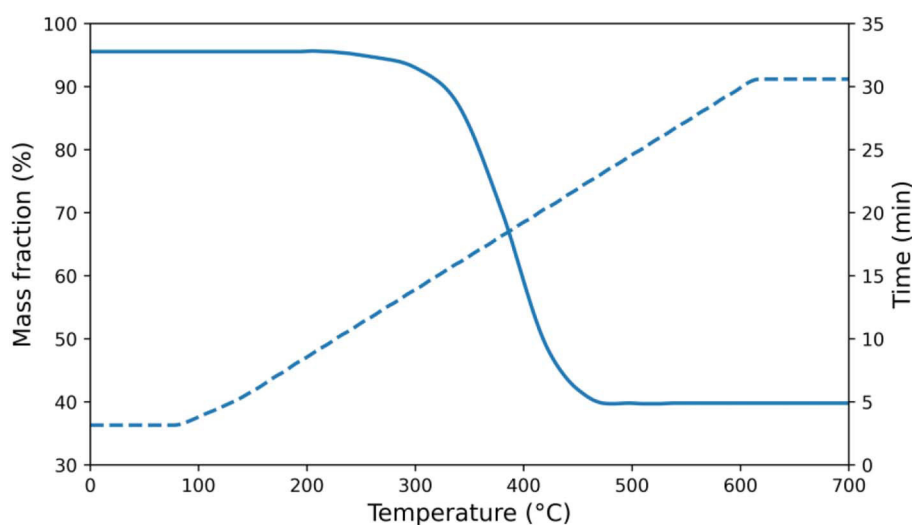


Figure 5. Thermogravimetric analysis (TGA) of tyre samples in the range 30–700 °C

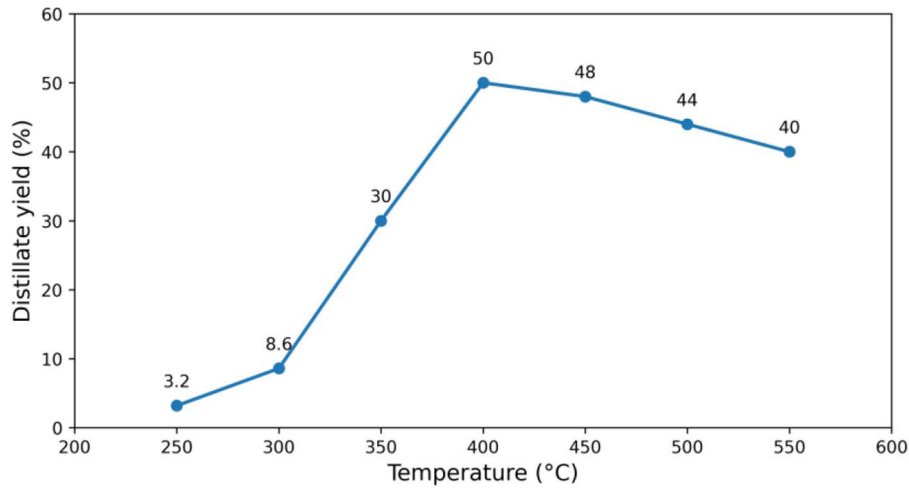


Figure 6. Effect of temperature on distillate yield

As shown in Figure 7, the optimal residence time for thermal processing of tyre-rubber waste is 60 min, at which the fuel-distillate yield reached up to 50%. Longer processing times promote greater formation of gaseous products, which reduces the distillate yield and increases the formation of semicoke/solid residue.

Particle size is one of the key factors in the thermal treatment of tyre-rubber waste. Therefore, the influence of rubber-crumb size on distillate yield was studied. As seen in Figure 8, when the crumb size was 0.5–6 mm, the distillate yield was maximized. When the rubber fragments were larger than this range, heat transfer limitations reduced the conversion rate and distillate formation.

Thus, the optimal conditions for thermal processing of waste tyre rubber are: $t = 400\text{ °C}$, $\tau = 60\text{ min}$, and particle size 0.5–6 mm, yielding approximately 50% fuel distillate.

A material balance for thermal processing of waste tyres under the optimal conditions was calculated (Table 2).

Thus, under the optimal conditions, thermal processing of waste-tyre rubber produced 50% fuel distillate, 20% gas and 28% solid residue, with losses of 2%.

According to the results, thermal processing of waste-tyre rubber tends to generate a larger fraction of high-boiling liquids.

The results of thermal processing of waste-tyre samples (Table 3) show that the distillate yield from a HOWO truck tyre (Roadone 315/80 R22.5 156/153L) rubber waste was about 25% higher than the distillate yield from a passenger/medium-truck tyre (Roadone 235/75 R17.5). At the same time, the yields of gaseous product and solid residue were 15–20% lower. These differences

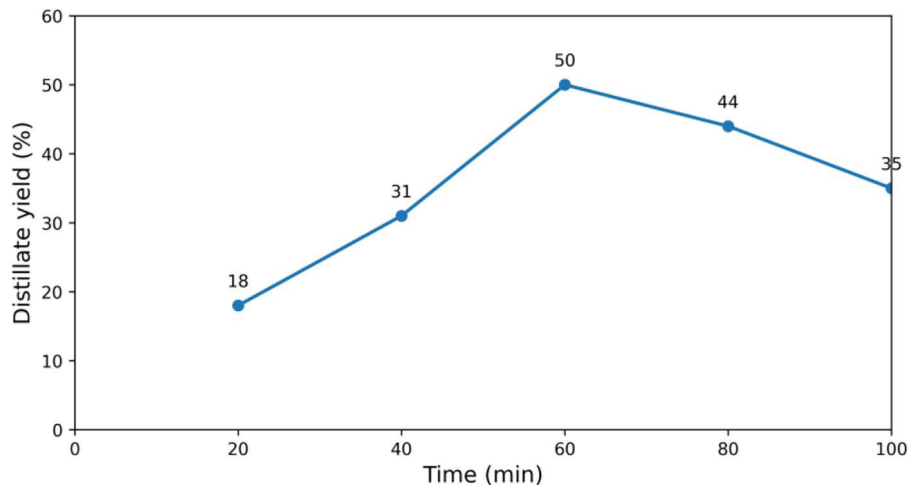


Figure 7. Effect of time on fuel-distillate yield

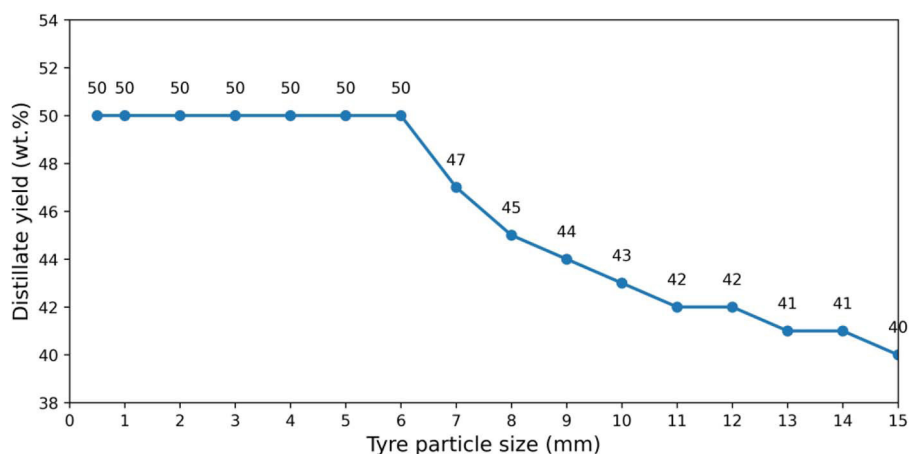


Figure 8. Effect of rubber-crumb size on fuel-distillate yield

Table 2. Material balance of thermal processing of waste tyres

Feed			Products		
Feedstock	Mass, g	Mass fraction, %	Product	Mass, g	Mass fraction, %
Waste-tyre rubber	1000	100	Fuel distillate	500	50
			Solid residue	280	28
			Gas	200	20
			Loss	20	2
Jami:	1000	100		1000	100

Table 3. Product yields during thermal processing of a waste-tyre rubber sample

Tyre sample	Fuel distillate, %	Gas, %	Solid residue, %	Loss, %
Roadone-235/75 R13.5	20-25	26-27	45-49	4
Roadone 315/80 R22.5 156/153L	45-50	18-20	30-33	2

are attributable to variations in formulation, filler content and reinforcement in the tyres.

Based on the research results, a hierarchical conceptual flowsheet for thermal processing of hydrocarbon-containing rubber and plastic wastes was developed (Figure 9). At the initial stage, the feedstock is prepared: plastic wastes are shredded, and waste truck tyres are separated into components (rubber and steel). The steel fraction is further divided into bead wires and cord wires and removed by magnetic separation.

The separated waste-tyre rubber is thermally processed (pyrolyzed) at 400 °C for 1 h, while plastic wastes are thermally processed at 500 °C for 20 min. In the process, the formed vapors are condensed to obtain a liquid fuel distillate, and non-condensable gases and solid carbonaceous residue are also produced.

On the basis of the hierarchical conceptual scheme, a technology for thermal processing of rubber and plastic wastes was developed. The technological system consists of four sections:

- Preparation of waste tyres for processing—shredding and component separation;
- Thermal processing of shredded waste tyres after removing excess/non-rubber components;
- Cooling the vapour mixture formed during pyrolysis in a water condenser and separating the gas and fuel distillate;
- Purification of sulfur-containing compounds from the tyre-derived fuel distillate.

1) Feed preparation (shredding and separation). The bead ring of the waste truck tyre is cut in cutter (1). The tyre is then milled in grinder (2) to particle form. During milling, steel cords in the breaker and cushion layers are also fragmented.

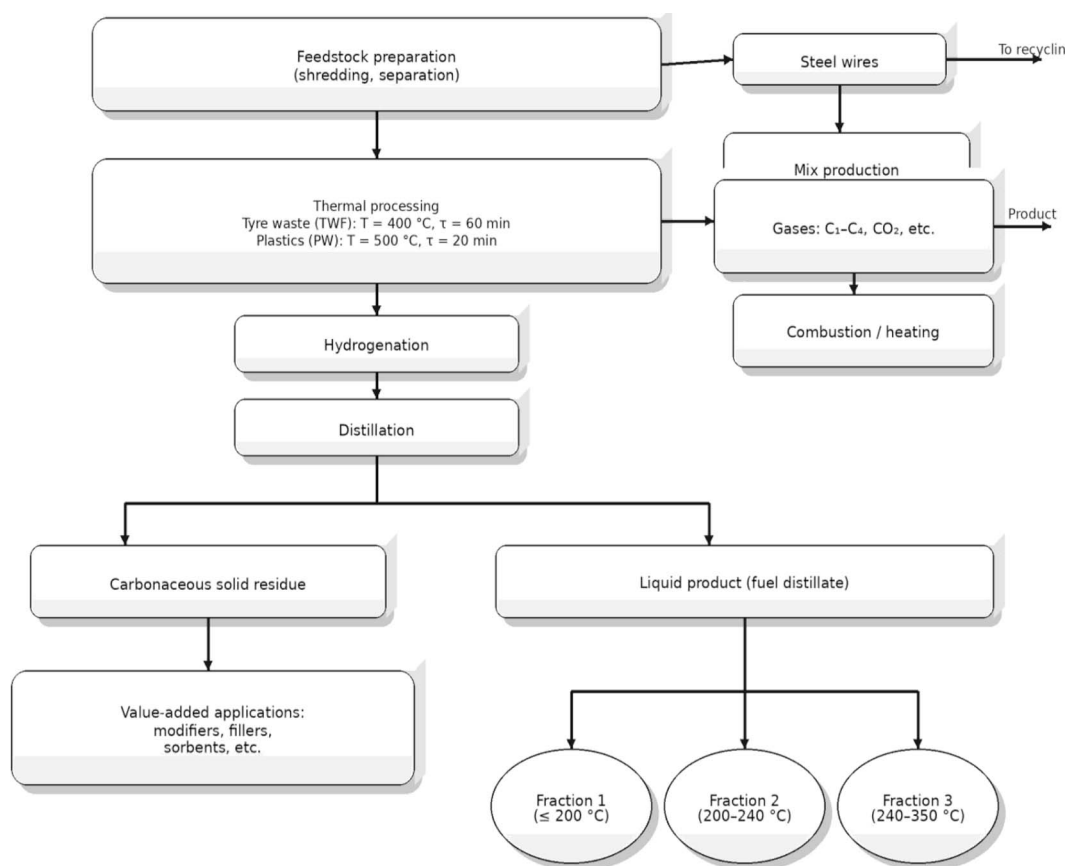


Figure 9. Hierarchical conceptual scheme for thermal processing of rubber and plastic wastes

The crushed feedstock is cleaned from steel fragments in the magnetic separator (3).

- 2) Thermal processing (pyrolysis) of the cleaned rubber particles. The rubber granules are fed to the drum reactor (4) and pyrolyzed at 550 °C under oxygen-free conditions. Pyrolysis produces a gaseous mixture and a solid residue (carbon black/char). The solid residue is discharged from the bottom of the reactor into the solid-residue hopper.
- 3) Cooling and phase separation of pyrolysis vapors. The gaseous mixture formed in the drum reactor (4) is condensed in the water cooler (5), and the condensed mixture is separated in the separator (6) into gas, liquid distillate and aqueous phase.
- 4) Removal of sulfur-containing compounds from the tyre-derived distillate. The distillate separated in the separator is cooled to 0 °C in the freon cooler/reactor (7). Concentrated H₂SO₄ is then introduced from the top, and the distillate is contacted with sulfuric acid at 0 °C. Because the sulfonated products formed are unstable, after 2 h the reaction mixture is treated with a 10% NaOH solution to convert sulfonic acids

into their corresponding sodium salts, facilitating separation.

Pyrolysis of rubber-based wastes forms products such as fuel distillate, gas and solid residue (carbon black/char). The hydrocarbon-group composition of the fuel distillate obtained at 230–550 °C was analyzed by gas chromatography–mass spectrometry (GC–MS). The identified hydrocarbon groups and their mass fractions are summarized below.

GC–MS results indicate that the obtained fuel distillates are very complex mixtures and that most compounds fall within the C₆–C₂₄ carbon-number range. The contents of alkanes and alkenes in the distillates obtained from tyres and from plastics did not differ significantly; in fact, they were present in very low amounts (alkenes: 0.93% in the tyre distillate and 0.81% in the plastic distillate).

According to the GC–MS data, the tyre-derived distillate consists mainly of C₉–C₂₄ hydrocarbons. Compounds with concentrations above 8% were identified as 1-methyl-4-isopropenyl cyclohexene (D-limonene), o-ethyltoluene and

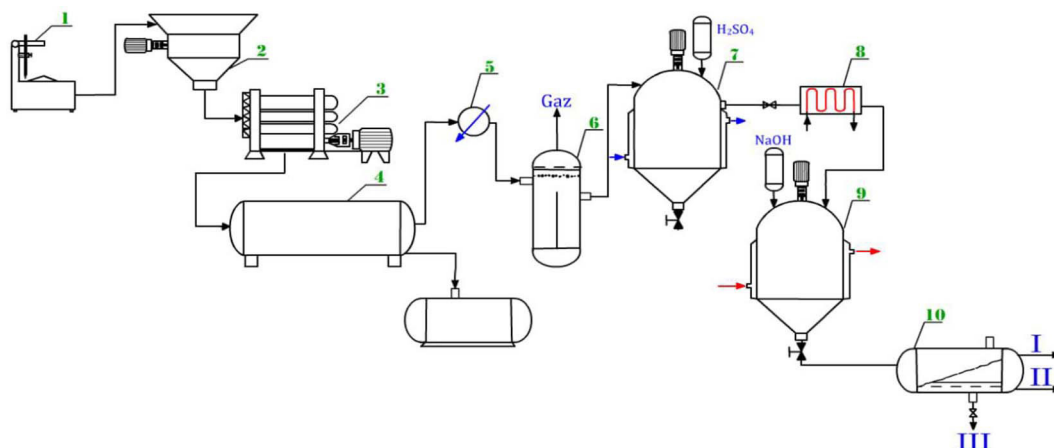


Figure 10. Technology for thermal processing of rubber and plastic wastes: 1 – tyre bead ring cutter; 2 – grinder; 3 – magnetic separator; 4 – drum reactor; 5 – water cooler; 6,10 – separators; 7 – freon cooler/reactor; 8 – H₂SO₄ mixer; 9 – NaOH mixer; 11 – distillate storage tank; 12 – sodium-salt product tank; 13 – solid residue hopper; 14 – gas outlet

Table 4. Hydrocarbon group composition of the tyre-derived fuel distillate

Hydrocarbon group	Content, wt. %
Naphthene	37,81
Olefin	0,93
Aromatic hydrocarbons	61,26

2-isopropyltoluene. The highest concentration corresponds to 1-methyl-4-isopropenylcyclohexene.

The results show that the distillate produced by pyrolysis of tyre wastes can be used as a feedstock for manufacturing valuable monocyclic aromatic compounds. For example,

o-ethyltoluene can serve as a solvent for various substances; 2-isopropyltoluene is used in limited amounts in perfumery compositions; and 1-methyl-4-isopropylbenzene is used as a fragrance component.

1-Methylnaphthalene is mainly used as an analytical reagent for determining the cetane number of fuels. In addition, it is used as a high-boiling solvent and as an intermediate in the synthesis of α -naphthylcarboxylic acid and other organic products.

Alkylbenzenes can form from waste tyres not only during pyrolysis but also as a result of Diels–Alder reactions. Fairburn et al. (2023) showed

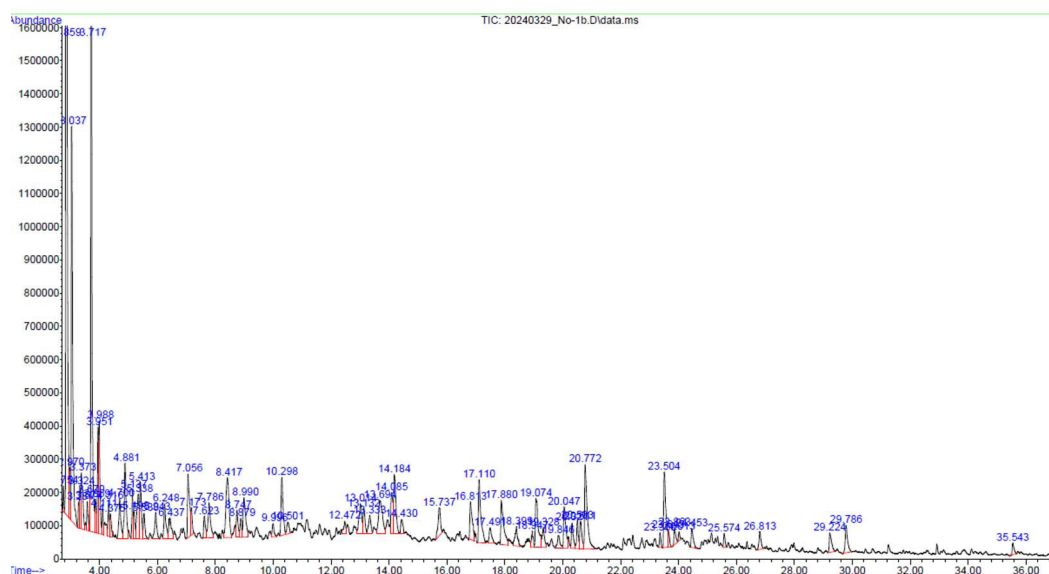


Figure 11. GC–MS chromatogram of the tyre-derived pyrolysis distillate

Table 5. Chemical composition of the fuel distillate obtained from rubber-based wastes

No.	Compound name	Content, %	Molecular weight, g/mol	Molecular formula
1	D-Limonene (or 1-methyl-4-isopropenylcyclohexene)	36.18	138	C ₁₀ H ₁₈
2	Penten 2 siklopentan (as reported)	0.68	138	C ₁₀ H ₁₈
3	o-Ethyltoluene (1-ethyl-2-methylbenzene)	9.97	120	C ₉ H ₁₂
4	o-Cymene (2-isopropyltoluene or 1-methyl-2-isopropylbenzene)	13.34	134	C ₁₀ H ₁₄
5	1,3,5-Trimethylbenzene	1.59	120	C ₉ H ₁₂
6	2,2-Dimethyl-3-methylene-bicyclo[2.2.1]heptane	0.45	112	C ₁₀ H ₁₆
7	1-Methyl-4-isopropylbenzene	2.48	134	C ₁₀ H ₁₄
8	1,2,4-Trimethylbenzene	2.19	120	C ₉ H ₁₂
9	1-Methyl-4-isobutylbenzene	0.86	148	C ₁₁ H ₁₆
10	1,2-Dimethyl-4-ethylbenzene	1.49	134	C ₁₀ H ₁₄
11	1-Methyl-4-isopropenylbenzene	1.88	132	C ₁₀ H ₁₂
12	3-Methyl-2-butenylbenzene	1.5	146	C ₁₁ H ₁₄
13	1-Methyl-2-cyclopropenylbenzene	0.39	130	C ₁₀ H ₁₀
14	1-Butenyl-2,2,3-dimethylbenzene	1.2	160	C ₁₂ H ₁₆
15	1,1-Dimethyl-1H-indene	0.74	160	C ₁₁ H ₁₂
16	Naphthalene	1.11	128	C ₁₀ H ₈
17	Aniline	2.08	93	C ₆ H ₅ NH ₂
18	1,2,3-Trimethylindene	1.34	158	C ₁₂ H ₁₄
19	1-Methylnaphthalene	4.09	142	C ₁₁ H ₁₀
20	Benzothiazole	2.07	135	C ₇ H ₅ NS
21	2,3-Dimethylnaphthalene	2.1	156	C ₁₂ H ₁₂
22	Dimethylbenzo[b]thiophene	0.50	162	C ₁₀ H ₁₀ S
23	Phenol	0.73	94	C ₆ H ₅ OH
24	2-Methylphenol (o-cresol)	0.67	108	C ₇ H ₈ O
25	1,3-Dimethylnaphthalene	0.88	156	C ₁₂ H ₁₂
26	1,7-Dimethylnaphthalene	3.28	156	C ₁₂ H ₁₂
27	1,6,7-Trimethylnaphthalene	2.73	170	C ₁₃ H ₁₄
28	2,4-Dimethylquinoline	0.43	157	C ₁₁ H ₁₁ N
29	1,4,6-Trimethylnaphthalene	0.18	170	C ₁₃ H ₁₄
30	2,3,6-Trimethylnaphthalene	0.62	170	C ₁₃ H ₁₄
31	3,4'-Dimethyl-1,1'-biphenyl	0.31	182	C ₁₄ H ₁₄
32	1,2,3,4-Tetramethylnaphthalene	0.68	184	C ₁₄ H ₁₆
33	Pentadec-1-ene	0.93	210	C ₁₅ H ₃₀
34	Anthracene	0.33	178	C ₁₄ H ₁₀

that high-molecular-weight PAHs can be formed via Diels–Alder reactions between aromatic compounds. Aromatic hydrocarbons present in higher amounts may therefore contribute to alkylbenzene formation via this pathway (Figure 12).

Alkylbenzene compounds in the distillate

The alkylbenzenes present in the distillate can be explained by formation mechanisms involving a diene-type Diels–Alder synthesis pathway (Figure 13).

Mechanisms for the formation of alkylbenzenes via Diels-Alder diene synthesis

Diels–Alder reactions occur between conjugated dienes and substituted alkenes to form substituted alkylcyclohexene systems. These alkylcyclohexenes can subsequently undergo dehydrogenation, yielding o-ethyltoluene, 2-isopropyltoluene, 1-methyl-4-isopropylbenzene and other related products.

Table 6 lists sulfur-containing compounds identified in the distillate; the corresponding

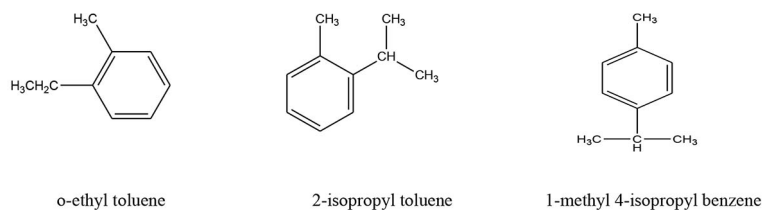


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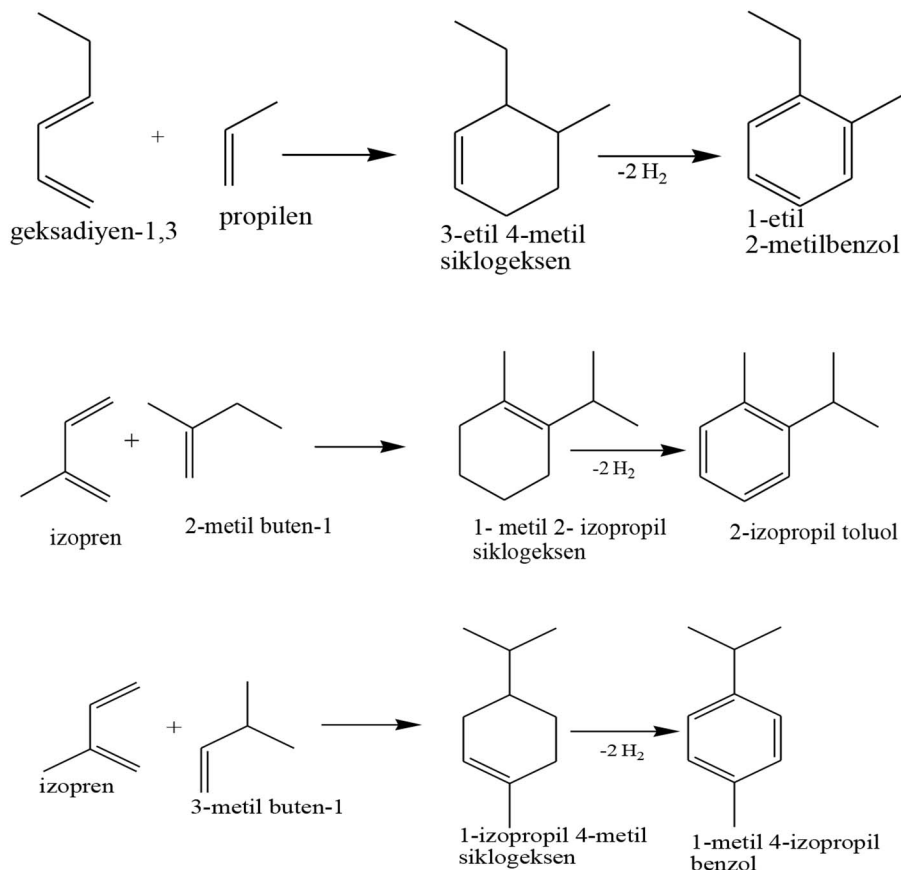


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GC–MS spectra were assigned with approximately 90% confidence.

It is known that low-sulfur crude oils contain <0.5 wt.% sulfur compounds, medium-sulfur oils contain 0.51–2 wt.%, and high-sulfur oils contain >2 wt.% sulfur. In the tyre-derived distillate obtained in this work, the sulfur content was 0.798 wt.%. This indicates that sulfur cross-links in vulcanized rubber contribute to

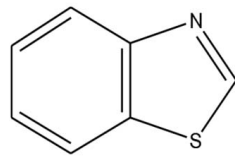
sulfur transfer into the distillate during thermal conversion (Figure 14, 15).

Possible bond cleavage during thermal processing of tyre waste can be considered as follows. The bond dissociation energies of C–S–C, C–S–S–C and C–S_x–C bonds are 273, 227 and 251 kJ/mol, respectively, whereas C–C bonds have higher dissociation energies (347–356 kJ/mol) (Chen, Rodrigues, and Ferronato 2026). This suggests that during thermal processing the sulfur-containing cross-links in rubber are cleaved more readily than the C–C backbone, contributing to the formation of sulfur-containing species.

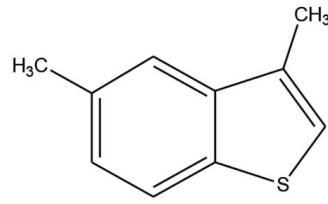
Subsequently, during pyrolysis of tyre waste, larger sulfur-containing compounds such as sulfur-bearing PAH derivatives can form and

Table 6. Sulfur compounds detected in the distillate

No.	Compound name	Amount, ml (per 100 ml of distillate)
1	Benzothiazole	2.07
2	Dimethylbenzo[b]thiophene	0.5



Benzotiazol



3,5-Dimetilbenzo[b]tiofen

Figure 14. Missing title

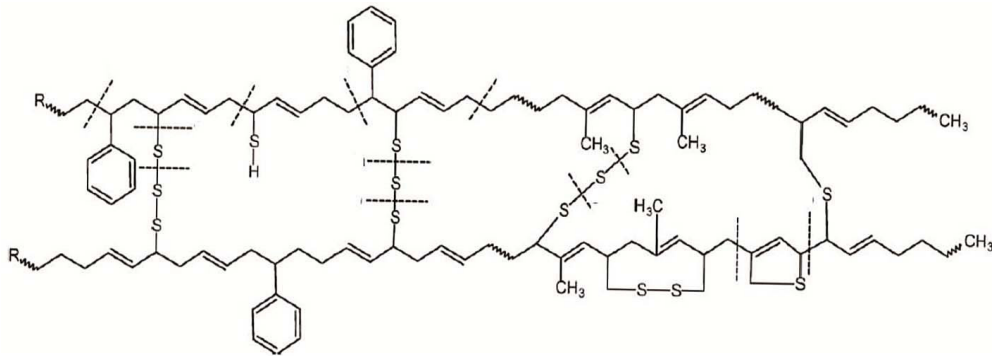


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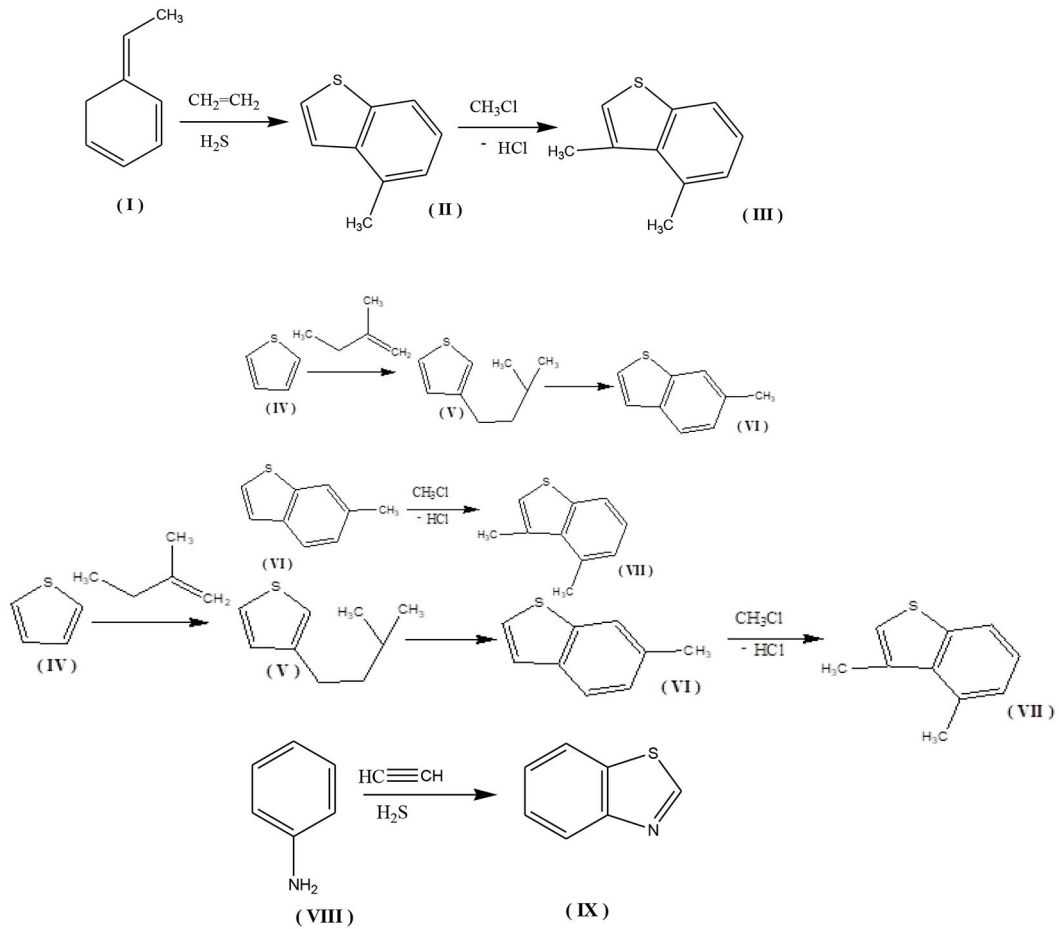


Figure 16. Missing title

participate in reactions (I–IX). Thermal conversion of sulfur-containing compounds proceeds through a sequence of radical reactions and rearrangements (Figure 16).

The proposed mechanism for sulfur-containing compounds detected in the tyre-derived distillate may explain the formation of sulfur-substituted PAHs. Ahoor and Zandi-Atashbar (2014) reported that, at certain stages of thermal processing of tyre waste, alkylthiophenes and olefins can form, which can further react to yield larger sulfur-containing aromatic structures (Figure 17).

High temperature affects individual stages of sulfur-compound conversion and suppresses the excessive formation of their PAH derivatives.

In addition, heavy oil fractions and other species formed during tyre-waste pyrolysis can react with each other. As a result, hydrogenation reactions of sulfur-containing compounds may occur, and hydrogen sulfide can form through reactions between hydrogen donors and sulfur-containing fragments:

Thus, the concentration of sulfur-containing compounds in the tyre-derived distillate decreases due to hydrogenation reactions (Akhmedova, Khayitov, and Nuraddinov 2024).

The physicochemical properties of the distillate obtained from thermal processing of waste tyres are presented in Table 7.

The sulfur content of the fuel distillate obtained from waste rubber was determined in accordance with GOST 19121-73 using the lamp

combustion method. Based on the experimental results, a mechanistic approach for desulfurization of the rubber-derived fuel distillate was developed. One of the most effective methods for removing condensed (fused) aromatic hydrocarbons containing sulfur from rubber-waste-derived fuel distillates is sulfonation with sulfuric acid accompanied by complex formation reactions.

Studies have been conducted on the introduction of a sulfo group ($-\text{SO}_3\text{H}$) into the molecules of 3-methyl- and 3,5-dimethylbenzo[b]thiophenes isolated from petroleum. These studies indicate that the resulting sulfonic-acid derivatives are unstable under ambient conditions. Therefore, the sulfonated products formed during the reaction should be isolated in the form of their salts (Usmanov, Usmanov, and Kukaniev 2012).

Analogous reactions were investigated for the interaction of sulfuric acid with 3,5-dimethylbenzo[b]thiophene and benzothiazole present in the fuel distillate obtained from waste rubber. The reaction products were isolated as salts of the corresponding sulfonic acids. Thus, 3,5-dimethylbenzo[b]thiophene and benzothiazole were separated in the form of their sulfuric-acid-derived salts. By determining the reaction rate for the interaction of sulfuric acid with 3,5-dimethylbenzo[b]thiophene and benzothiazole, it was established that, at 0 °C, the process proceeds with good yield (40–90%) over 2 h when the reactants are used in an equimolar ratio consistent with their equivalents. In general terms, the

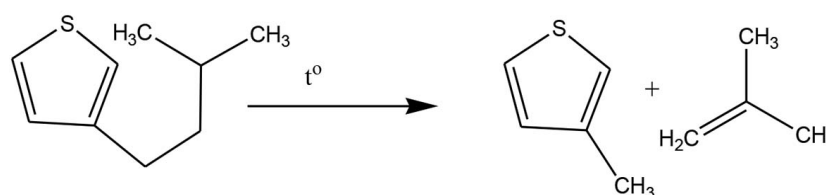


Figure 17. Missing title

Table 7. Physicochemical properties and quality parameters of the fuel distillate

No.	Quality parameter	Test method	Fuel distillate values
1	Density at 20 °C, kg/m ³	GOST 3900-2022	863.7
2	Sulfur content, wt. %	GOST 19121-73	0.798
3	Water content, wt. %	GOST 2477-2014	4.6
4	Chloride salts, mg/L	GOST 21534-2021	13.982
5	Mechanical impurities	GOST 6370-2018	0.093
6	Kinematic viscosity, mm ² /s	GOST 31391-2020	1.6
7	Fractional composition, °C: initial boiling point (IBP); 50% recovered; final boiling point (FBP)	GOST 2177-99	65 200 360

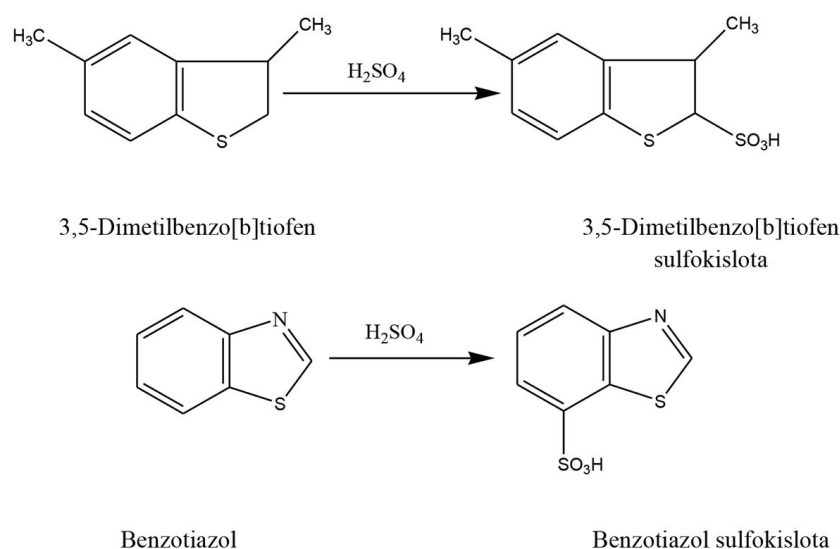


Figure 18. Missing title

reaction schemes can be represented as sulfonation of sulfur-containing compounds (Figure 18). Considering that the sulfonic-acid products formed in the reaction are unstable, after 2 h the reaction mixture was treated with a 10% sodium hydroxide solution, and the corresponding salts were isolated. In a general form, the reaction can be represented as conversion of sulfonated sulfur-containing compounds into their sodium salts (Figure 19).

In this reaction, substitution of the hydrogen atom at the 2-position of the heteroring in 3,5-dimethylbenzo[b]thiophene by a sulfo group was observed. This can be explained by the ability of the sulfur atom in the fused five-membered heterocycle to donate lone-pair electron density, activating the α -carbon and facilitating electrophilic substitution.

During the experiment, three layers formed in the test tube (bottom – water, middle – precipitate, top – distillate). A sample from the distillate

layer was taken and checked by the lamp-burning method. The results are given in Table 8.

As can be seen from Table 8, concentrated sulfuric acid followed by treatment with 10% sodium hydroxide is effective for removing sulfur-containing compounds from the tyre-derived fuel distillate.

At the next stage of the study, experiments were carried out to determine how much tyre-derived fuel distillate can be added to the feedstock for atmospheric distillation (a crude-oil and gas-condensate mixture). For this purpose, the tyre-derived fuel distillate (TWFDD) was blended with crude oil (N) and gas condensate (GC) at various ratios and the properties of the mixtures were evaluated.

Table 9 shows that adding the tyre-derived fuel distillate to the crude-oil/gas-condensate mixture increases the density. The contents of chloride salts and mechanical impurities in the

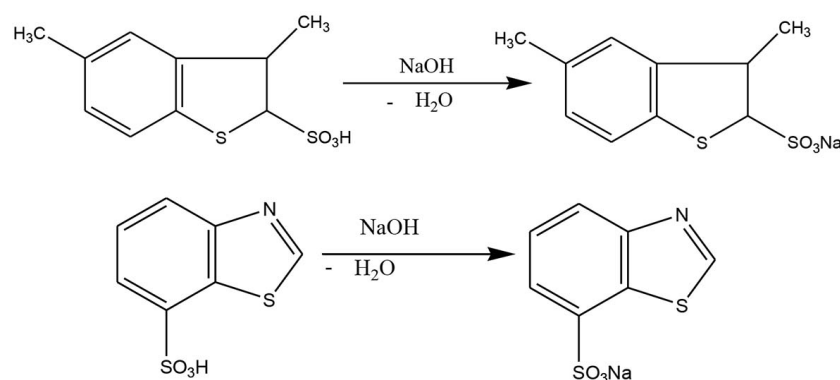


Figure 19. Missing title

Table 8. Determination of sulfur content in the rubber-derived fuel distillate

Experiment number	Reagents and their concentrations		Sulfur content, %
1	Distillate, H ₂ SO ₄ (30%)	NaOH (10%)	0.798
2	Distillate, H ₂ SO ₄ (50%)	NaOH (10%)	0.7
3	Distillate, H ₂ SO ₄ (70%)	NaOH (10%)	0.6
4	Distillate, H ₂ SO ₄ (90%)	NaOH (10%)	0.3
5	Distillate, H ₂ SO ₄ (conc)	NaOH (10%)	0.07

Table 9. Density of a crude-oil/gas-condensate mixture with tyre-derived fuel distillate at different temperatures and component ratios

T, °C	Density of mixtures of crude oil (N), gas condensate (GC) and tyre-waste fuel distillate (TWFDD) at different component ratios (vol.%); density, kg/m ³								
	20N + 80GC	30N + 70C	29N+70GC+ 1TWFDD	28N+70GC+ 2 TWFDD	27N+70GC+ 3 TWFDD	26N+70GC+ 4 TWFDD	25N+70GC+ 5 TWFDD	24N+70GC+ 6 TWFDD	23N+70GC+ 7 TWFDD
20	778.58	786.57	786.59	787.75	788.61	789.53	791.43	792.19	792.98
30	769.94	777.91	777.91	779.08	779.93	780.84	782.71	783.47	784.25
40	761.05	769.03	769.05	770.18	771.02	771.92	773.78	774.52	775.3

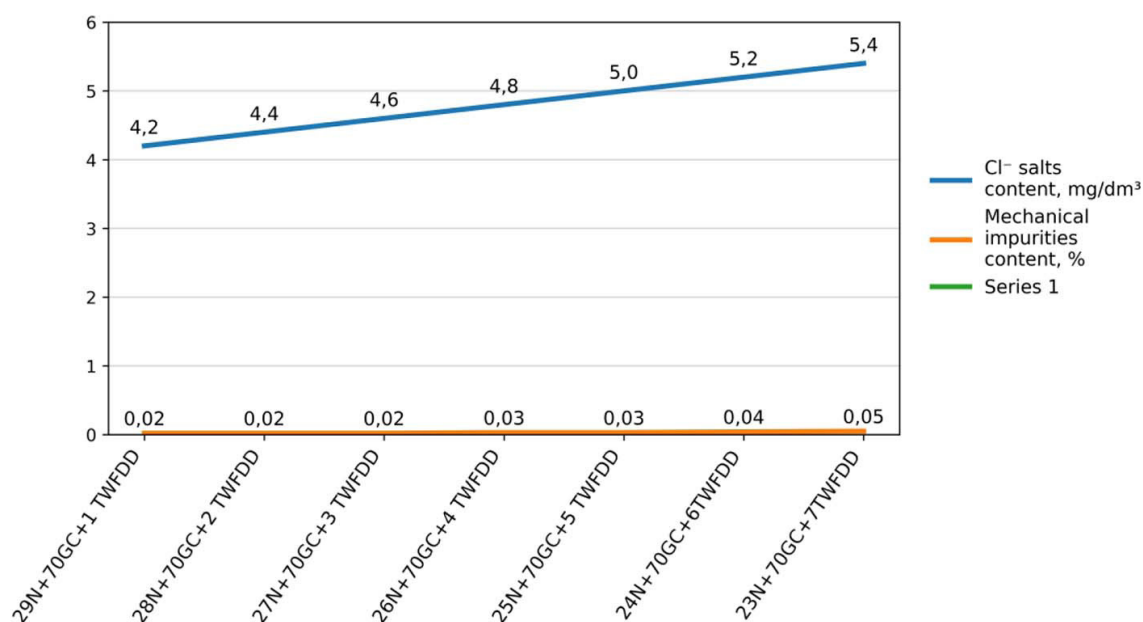


Figure 20. Chloride salts and mechanical impurities in mixtures of tyre-derived distillate and crude-oil/gas-condensate

Table 10. Results of atmospheric distillation of the crude oil, gas condensate and fuel distillate blend (15%–80%–5%)

Name	Unit, t/day	Share, %	Name	Unit, t/day	Share, %
Oil and gas condensate (20–80%)	3000	100	Crude oil, gas condensate and fuel distillate (15%–80%–5%)	3000	100
Compressed Petroleum Gases (CNG)	42.3	1.41	Compressed Petroleum Gases (CNG)	42.3	1.41
Gasoline fraction	2160	72	Gasoline fraction	2220	74
Kerosene fraction	387	12.9	Kerosene fraction	284.4	9.48
Gasoil (diesel) fraction	288	9.6	Gasoil (diesel) fraction	330.6	11.02
Fuel oil	122.7	4.09	Fuel oil	122.7	4.09

mixtures were also evaluated, and the results are shown in Figure 20.

Based on the data in Figure 20, when large amounts of tyre-derived distillate are added to the crude-oil/gas-condensate mixture, the contents of chloride salts and mechanical impurities exceed the limits specified in the technological regulations of the atmospheric distillation unit. Therefore, an addition level of 5% was considered optimal.

The addition of 5% fuel distillate increased the yields of gasoline and gasoil fractions and decreased the kerosene fraction.

When 5% fuel distillate is added, the yields of gasoline and gasoil fractions increase, while the kerosene fraction decreases.

CONCLUSIONS

Thermal conversion (pyrolysis) of end-of-life tyre rubber was demonstrated as an effective route for producing liquid fuel distillates and expanding the feedstock base for motor-fuel production. Based on thermogravimetric analysis and process-parameter screening, the optimal operating conditions for the studied tyre waste were established as 400 °C, 60 min, and a rubber-crumb size of 0.5–6 mm. Under these conditions, the liquid distillate yield reached up to 50%, and the product showed a density of 870 kg/m³ at 20 °C with an initial boiling point of 65 °C and a final boiling point of 360 °C, indicating a broad fuel-range fractional composition.

GC–MS analysis confirmed that the distillate is a complex mixture dominated by naphthenic and aromatic hydrocarbons, with minor sulfur-containing species (e.g., benzothiazole and benzo[b]thiophene derivatives). The total sulfur content of the untreated distillate was 0.798 wt.%. A practical desulfurization approach based on low-temperature sulfonation with concentrated sulfuric acid followed by neutralization to isolate sulfonates as sodium salts was developed; under the most severe treatment conditions, the sulfur content was reduced to 0.07 wt.%.

From an integration perspective, blending 5% (v/v) of the tyre-derived fuel distillate into an atmospheric-distillation feed composed of 15% crude oil and 80% gas condensate did not adversely affect the properties of the resulting fractions. The blend increased gasoline and gasoil yields while decreasing the kerosene fraction, supporting the feasibility of co-processing

tyre-derived distillates in refinery streams. Overall, the proposed technological concept provides a dual environmental and resource-efficiency benefit by reducing tyre-waste accumulation and generating valuable liquid products. Future work should focus on scale-up validation, optimization of desulfurization selectivity and reagent recovery, and comprehensive techno-economic and life-cycle assessment of the integrated process.

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