

# PROPERTIES OF THE GASOLINE FRACTION OBTAINED FROM THE PYROLYSIS OF TIRES

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## INTRODUCTION

Rubber pieces together with tires constitute about 6.7% of the vehicle's weight. These are necessary for the proper functioning of the car, hence their elimination is impossible. Among others, rubber pieces ensure proper flow of liquids and gases, sealing, absorbing energy through shock absorbers or suspension elements, noise reduction as well as vibrations. Waste tires do not degrade in the natural environment for over 100 years. They create waste that is environmentally harmful and should be removed or used industrially. It is estimated that approximately 1 billion of waste tires per year are arriving [1]. Left in landfills, cause numerous threats, including fire hazards. The effects of such a fire can be catastrophic for soil fertility, groundwater, flora and fauna. Uncontrolled combustion of tires can also cause the emission of significant amounts of sulfur and nitrogen oxides to the atmosphere. In the European Union, the amount of used tires increases by more than 2.5 million tons every year [1].

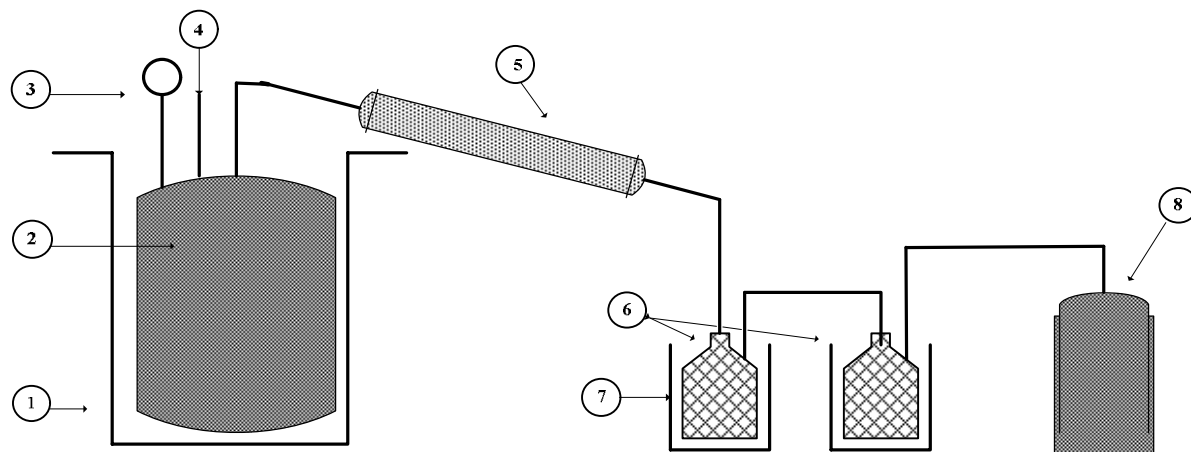
The European Parliament's adoption of directives: Landfill 1993/31 / EC [2], End-of-Life Vehicle 2000/53 / EC [3] was the basis for the management of used tires in the European Union. According to Directive Landfill 1999/31/EC, the storage of all used tires was prohibited in 2003, and from 2006, also disintegrated tires. The End-of-Life Vehicle Directive 2000/53/EC obliged vehicle owners to remove tires from cars before handing them over for scrap. The implementation of these provisions was aimed to increase the management of used tires. Used tires, not suitable for retreading, belong to waste, which should be properly managed in such a way that it does not pose a threat to the natural environment and man. In accordance with the embargo on the burial and storage of all used tires, as well as their components, several methods were proposed: product recycling, material recycling, pyrolysis, energy recovery [1].

The pyrolysis process is a process that involves heating whole or fragmented waste tires at a temperature of 400-700 °C without access to oxygen and other oxidizing agents. As a result of this process, gaseous, liquid and solid products are formed, which can and should be further processed to obtain more valuable products. As a result of the waste tires pyrolysis process, the following products can be obtained: solid residue 35-42%, pyrolytic oil 20-40%, 15-20% of gaseous product, 10-15% of steel [4]. The gas phase consists mainly of aliphatic hydrocarbons, hydrogen and hydrogen sulphide. The liquid phase is aromatic hydrocarbons, and the solid char residue, oxides and zinc sulphide as well as steel, when the whole tires are subjected to pyrolysis. Gas or oils obtained in the pyrolysis process, products can be used, among others, for as fuels/fuel components. After the refining process, the solid char can be used as a pigment in paint coatings, varnishes, thermoplastics, as well as in printing ink. Coatings and varnishes can be used in the automotive, marine and cable industries, as well as for covering the surface of vats used in various production processes. Soot can also be used as a filler for rubber mixtures, improving the abrasion resistance and strength of products [5].

The aim of this work was to conduct the series of waste tires pyrolysis process and analysis of the obtained liquid as a potential source of the gasoline fraction. The obtained gasoline fraction was verified in accordance with the applicable, commercial standards.

## MATERIALS AND METHODS

Pyrolysis experiments were performed in laboratory scale apparatus, presented in Figure 1. Pyrolysis experiments were carried out in a fixed bed reactor up to the final temperature of 500 °C. In the typical experiment, 100 g of the waste tires grains of fragmentation below 5 mm was loaded to the batch reactor and then the reactor temperature was increased at the steady rate of 5 °C/min till desired final temperature was reached. At this point, the experiment was held at a constant (final) temperature for 30 minutes till the process was completed. Before the start of the experiment, the reactor was purged with argon for 15 minutes at a flow rate of 20 l/h to remove air from the apparatus system. The gaseous pyrolysis products were flowing through a water condenser, where they were condensed and cooled in a water jacket and next in a cold trap maintained at temperature ~ -5 °C. Oil fraction were additionally dried over molecular sieves 4A. The hermetically closed glass bottles with oils were stored at reduced temperature (~ 3-5 °C). Pyrolysis process was carried out 15 times to determine the products yield along with deviations under the established process conditions.



*Fig. 1. Pyrolysis process setup.*

*1 – electric furnace, 2-reactor, 3- manometer, 4- thermocouple, 5-cooler, 6-liquid receivers, 7-cooling mixture, 8-gas receiver*

The obtained pyrolysis oil fraction was divided into fuel fractions by atmospheric distillation: gasoline fraction boiling up to the temperature of 210 °C and diesel oil fraction boiling in the range of the temperature 210-360 °C. The above mentioned collected fractions were stored in hermetically closed glass bottles under reduced temperature (~ 3-5 °C). In order to analyze the basic properties of the gasoline fraction as a potential fuel, the obtained liquid was analyzed with the applicable standards for commercial gasoline (PN-EN 228:2012: „Fuel for motor vehicles. Unleaded gasoline. Requirements and test methods”).

## RESULTS

The yield of the pyrolysis products along with the deviations obtained during the 15-fold process was collected in the Table 1. It can be noticed, that the process is repeatable, and the oil yield is comparable to the one obtained by other authors [6, 7].

Table 1

**. Waste tires pyrolysis – products yield**

	Yield, mas. %	Deviation, %
Pyrolysis oil	48.93	1.1
Solid char	40.86	2.2
Gaseous products	10.21	2.2

The efficiency of the pyrolysis oil distillation process was analyzed three times. Gasoline fraction was obtained with the efficiency of 63.4 vol. %, fuel oil fraction was obtained with the efficiency of 25.2 vol. %. The remaining part of the liquid did not distill under established atmospheric distillation conditions (up to the temperature of 360 °C, atmospheric pressure).

The determined characteristics of the gasoline fraction are summarized in Table 2. Selected properties were compared with the commercial gasoline requirements.

Table 2

**Properties of the gasoline fraction obtained from the waste tires pyrolysis oil**

No.	Parameter	Standard	Unit	Result	Requirements of PN-EN 228:2012
1	Colour	Visual assessment	-	dark brown	clear transparent
2	Sulfur content	PN-EN 24260:2002	mg/kg	4200	max. 10
3	Chlorine content	PN-EN 24260:2002	mg/kg	17	-
4	Density at 15°C	PN-EN ISO 12185:2002	kg/m <sup>3</sup>	874	720-775
5	Water content	IEC 60814:1997	mg/kg	900	-
6	Freezing point	PN-ISO 3015:199	°C	<60	-
7	Vapor pressure	EN 13016-1:2007	kPa	11	min. 45
8	Bromine number	PN-68 C-04520	gBr <sub>2</sub> /100g	88.1	-
9	Heat of combustion	PN-81 G-04513	MJ/kg	46.1	-
10	Determination of hydrocabons content with FIA method	PN-EN 228:2012	% V/V	Parafins: 28.9 Olefins: 62.5 Aromatics: 8.6	Parafins: n/a Olefins: max. 18 Aromatics: max. 35

The analysis of the data summarized in Table 2 allows to conclude that the obtained gasoline fraction cannot be used directly as a commercial fuel.

The obtained fuel fraction is characterized by a very high value of the bromine number (88.1 gBr<sub>2</sub>/100g), demonstrating a high content of olefins. High olefins content was also confirmed by Fluorescent Indicator Adsorption (FIA) analysis (62.5 % V/V) The presence of the above-mentioned compounds may negatively affect the processes storage. Olefins are characterized by low thermal stability, therefore tend to form resins and deposits in the intake system of the engine, which affects its performance and exhaust purity. A significant reduction in their content is therefore necessary before commercial application of pyrolysis oil as a fuel.

The vapor pressure is an important characteristic of gasoline due to the performance and emission of the spark-ignition engine, it should be adjusted seasonally, depending on the prevailing temperatures. A low value of the vapor pressure (11 kPa) prevents the proper operation of the engine. Another, important factor is water and chlorine content. Both influencing corrosivity of the liquid. Water content influences also high density of the product. Sulfur content needs to be reduced due to the sulfur oxides formed in the fuel combustion process (environmental issue).

In order to improve the quality of the pyrolytic oil and/or the obtained fuel fractions, the obtained liquids should be subjected to refining processes, eg. hydrotreating. Properly selected hydrotreatment parameters (process parameters and the catalyst) will hydrogenate unsaturated hydrocarbons and remove sulfur from the liquid. Before refining process, water should be removed to prevent catalyst poisoning.

## CONCLUSIONS

In the pyrolysis of waste tires, significant amount of the liquid product, up to 49 mass %, can be obtained. Liquid separation in the atmospheric distillation process allows the gasoline fraction production with the yield of ca. 63.4 vol. %. Despite the large amount of liquid product obtained and the attractiveness of the raw material, which are waste tires, the properties of the gasoline fraction significantly differ from the commercial requirements for gasoline. The drying process and hydrorefining for strong reduction of unsaturated hydrocarbons content and sulfur amount reduction is necessary for improving the fuel-properties of the liquid.

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