

RECOVERY OF TIRES WASTE THROUGH THERMAL CRACKING

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ABSTRACT

The article addresses a topic of global interest related to the recovery of rubber waste. In the context of the increase in the demand for tires worldwide, the concern for the management of used tires by introducing them into the economy is legitimate. The research proposes thermal cracking as a recycling method for used tires. Through the thermal conversion process at a temperature of 500°C and a pressure of 40 bar, gaseous and liquid fuel products as well as a solid residue are obtained.

Keywords: Tire, Recovery, Fuels, Thermal Cracking

INTRODUCTION

The general name “rubber” includes linear or weakly cross-linked polymers that have elastic properties at operating temperature.

Rubber is an important source of raw material for world industry, being used for various purposes. The multitude of applications is due to the vulcanization process of the rubber which determines an improvement of its mechanical properties. [1]

The tire industry is the largest consumer of natural and synthetic rubber. The increase in demand for tires has inevitably led to an increase in waste and the need to recycle used tires. End of Life Tire (ELT) recycling and disposal represent major challenges in waste management due to the structure and chemical composition of tires. [2]

The recovery of waste from used objects made of rubber mixtures, has of course in addition to the economic value, a real ecological value in the sense of minimizing rubber waste.

Considering the limited natural resources of the planet as well as the exponential growth of the rubber industry, it is necessary to continue research in the field in order to find an efficient way to recycle rubber waste.

Rubber is an energy-intensive material that wears out regardless of the purpose for which it is used.

Globally, each year approximately 1000 million tires cannot be reused or retreaded. It is estimated that in 2030 the number of used tires will increase to 1200 million tires/year. [3]

The three-dimensional cross-linked structures of rubber resulting from vulcanization together with stabilizers and additives incorporated during production make tires resistant to natural degradation. [4]

The ELT waste stream is an important environmental problem worldwide because it produces severe air, water and soil pollution. The ELT waste stream constitutes more than 2% of the total amount of solid waste. This waste stream is not biodegradable and belongs to the category of non-hazardous waste. Unfortunately, poor ELT management is still a common phenomenon in many economies, with almost half of the ELT waste stream being dumped into landfills remains untreated. [5]

Used tires thrown into landfills take up a lot of space, and due to their curved shape, they can be a breeding ground for mosquitoes and rodents. [6]

Used rubber tires stored in industrial areas or in warehouses represent a danger to the environment because they contain flammable materials and can cause fires. These fires are very difficult to extinguish and emit toxic gases such as: SO₂, metal particles, polycyclic aromatic hydrocarbon (PAH), formaldehyde, carbon monoxide, acrolein (VOC) that pollute large areas and have negative effects on the population health. [7]

If emission factors (PAHs, metal particles and VOCs) are used to estimate emissions from accidental pollution according to Air Pollution 42, it should be taken into account that emissions from the open burning of tires generally depend on the burning rate. Thus, greater emission potential is found at lower burn rates (such as in a smoldering fire).

Table 1 Emission factors for PAHs resulting from burning 1 kg of tire

Crt. Nr.	Pollutant / PAH	Emission factor [mg/kg tire]
1	Acetonaphthene	718.20
2	Acetonaphthylene	570.20
3	Anthracene	265.60
4	Benzopyrene	173.80
5	Benzofluoranthene	501.1
6	Benzanthracene	7.90
7	Chrysene	48.30
8	Dibenzeneanthracene	54.50
9	Fluoranthene	85.70
10	Indopyrene	58.60
11	Naphthalene	0.00
12	Phenanthrene	28.00
13	Pyrene	35.20
	Total PAH	2547.1

Table 2 Emission factors for metal particles resulting from burning 1 kg of tire

Crt. Nr.	Pollutant / metal particles	Emission factor [mg/kg tire]
1	Aluminum	3.07
2	Antimony	2.94
3	Arsenic	0,05
4	Barium	1.46
5	Calcium	7.15
6	Chromium	1.97
7	Copper	0.31
8	Iron	11.80
9	Lead	0.34
10	Magnesium	1.04
11	Nickel	2.37
12	Selenium	0.06
13	Silicon	41.03
14	Sodium	7.68
15	Titanium	7.35
16	Vanadium	7.35
17	Zinc	44.98
	Total	140.9

Table 3 Emission factors for VOC resulting from burning 1 kg of tire

Crt. Nr.	Pollutant / (VOC)	Emission factor [mg/kg tire]	Crt. Nr.	Pollutant / (VOC)	Emission factor [mg/kg tire]
1	Methyl biphenyl	12.71	20	Ethylmethyl benzene	537.60
2	Fluorene	191.27	21	Inden	472.74
3	Methylnaphthalene	620.67	22	Isocyano benzene	283.78
4	Benzaldehyde	825.04	23	Isocyano naphthalene	10.75
5	Benzene	1526.39	24	Limonene	48.11
6	Benzodiazine	13.12	25	Methylethylene benzene	166.41
7	Benzofuran	40.62	26	Methyl benzene	1129.80
8	Benzothiophene	50.37	27	Methyl cyclohexene	3.91
9	Biphenyl	190.08	28	Methyl hexadiene	15.59
10	Butadiene	117.14	29	Methyl indene	80.41
11	Cyanobenzene	203.81	30	Methyl naphthalene	144.78
12	Cyclopentadiene	67.40	31	Methyl thiophene	4.39
13	Dihydroindene	9.82	32	Phenol	337.71

Crt. Nr.	Pollutant / (VOC)	Emission factor [mg/kg tire]	Crt. Nr.	Pollutant / (VOC)	Emission factor [mg/kg tire]
14	Dimethylbenzene	323.58	33	Propyl naphthalene	26.80
15	Dimethylhexadiene	6.22	34	Propyl benzene	19.43
16	Dimethylnaphthalene	35.28	35	Styrene	618.77
17	Ethylbenzene	568.72	36	Thiophene	17.51
18	Ethylenemethyl benzene	562.44	37	Trichlorofluoro methane	138.10
19	Ethyl benzene	138.94	38	Trimethyl benzene	195.59
	Total VOC			9755.8	

If we consider a tire with an average weight of 7 kg as a reference, its open combustion emits into the atmosphere: metal particles 0.99g, polycyclic aromatic hydrocarbons (PAH) 17.83g, volatile organic compounds (VOC) 68.29g.

The lands where the tire warehouses are located are affected by the harmful and toxic chemical substances in the composition of the tires such as: metals (Fe, Mn, Zn), additives, (stabilizers, plasticizers or flame retardants), they permeate the soil, and have negative effects on plant development. [8]

Currently, used tires can be completely recycled. Thus, millions of tires take the recycling route. Most come from the touring car fleet as well as buses and trucks. The recycling industry has developed due to the efforts made in the field of used tire collection, treatment techniques and research into the fields of application of recovered raw materials.

There are three main reasons why the recovery of used tires is a priority: reducing excessive stocks, ensuring their proper use by returning them to the economy, and last but not least, preserving natural resources. For this reason, reducing the amount of waste and the scarcity of raw materials through the continuous use of resources is the way to a sustainable economy. [9]

Thermal, mechanical, physical, chemical and biological methods can be applied to the management and devulcanization of rubber waste. To recover energy from rubber, thermolysis and pyrolysis are the two thermal methods used to degrade rubber with the aim of obtaining energy.

The mechanical process costs in the destruction of the rubber structure by grinding, the rubber powder is used in civil engineering projects, (asphalt pavement, playgrounds, light fillings, protective barrier, shock and vibration absorbers, as a substitute for sand gravel, material of filling, etc. [10]

The thermomechanical devulcanization process uses extrusion and the recovered rubber is used in various SBR blends.

Chemical devulcanization uses chemicals such as organic solvents (peroxides or green solvents). Most of the elastomeric properties of the devulcanized rubber are preserved, and it can be used in the manufacture of new rubber products. [11]

From the category of physical methods of rubber degradation, the most frequently applied are those with ultrasound and microwaves. The devulcanized rubber obtained by the microwave process has good fluidity and a high degree of reuse. [12]

Another rubber degradation process is the biological one that involves the intervention of microorganisms that adhere to the surface of the rubber, and produce enzymes that facilitate the devulcanization of the rubber. Soil contains various types of microbes, including bacteria and fungi, which can degrade rubber. The biological method is in the beginning phase and has the advantages of milder operating conditions and zero emissions of toxic gases compared to the other methods, but also precautions because the microorganisms cannot be controlled. [13]

Depending on the scope, the used tires will be cut small (turned into chips or powder) to be used. As an alternative for the recovery of rubber, it is used to obtain fuels through the pyrolysis process. Some of the fuels derived from used tires are used together with conventional fuels such as coal to obtain energy. [14]

Investigations were also carried out in order to demonstrate the feasibility of using used rubber in the composition of concrete and the effects of its use on the properties of the obtained mixture.

Waste rubber is also successfully used in geotechnical applications such as improving the resistance of soils by reinforcing them with pieces of used rubber, using rubber powder in different percentages in bitumen, to improve the behavior of the asphalt binder at high temperature and for buildings seismic isolation. [15]

This study is part of the current trend to find options for the recovery of rubber waste with important environmental benefits. The research proposes the recovery of used tires by thermal cracking into combustible products (liquid and gaseous). Among the rubber waste, car tires were chosen, considering the large volume of this type of waste accumulated in recent years. In the experiment, the yields and the quality of the decomposition products obtained were analyzed.

EXPERIMENTAL

In the absence of oxygen, rubber waste is transformed at temperatures of 500-700°C through thermo-chemical conversion into liquid gas and solid residue containing carbon, ash and metals.

The thermal cracking recycling experiment was carried out on a micropilot plant, with an autoclave type reactor, in which 300g of used tire, cut into thin strips, heated to a temperature of 500°C under a pressure of 40 bar was introduced.

The heating was started and at 350°C (the temperature at which the cracking reactions are considered to start) notes has begun to be taken: the time and the pressure at each 20°C interval until the imposed reaction temperature of 500°C was reached. The reaction system is maintained at the imposed temperature and pressure for 15 minutes, the time necessary to obtain the desired cracking depth. The obtained products are evacuated from the autoclave, first the gases in the range of 2÷5 bar, after which the liquid is removed from the base of the autoclave. The obtained gases are measured and analyzed chromatographically. The product remaining in the autoclave, consisting of liquid

hydrocarbons and carbon black particles is separated, and the liquid is distilled TBP, collecting a fraction of gasoline with a final 180°C and middle distillate with a final 340°C.

The obtained liquid fractions are weighted on the analytical balance in order to establish the material balance and product yields.

The characterization of the obtained products sought the determination of: density, liquid fraction, sulfur content in liquids and gas composition. Sulfur content was determined by the X-ray fluorescence method using a PW4025/45 MiniPal II X-ray spectrometer.

RESULTS AND DISCUSSIONS

The products obtained by the thermal cracking of waste tire are: gases (measured with a gas meter and characterized by Bunsen Schilling relative density and chromatographic analysis), the liquid fraction (separated by TBP distillation in middle distilled gasoline) and residue. For the separated products, the sulfur content was determined by X-ray spectrometry.

Table 4 Material balance

	Amount	Yields	Characteristics	
	[g]	[%wt.]	Density d420	Sulfur [%]
Raw material - used tire	300	100	-	-
Products:				
Gases	31.4	10.46		-
Gasoline	26.9	8.96	0.792	0.06
Medium distilled	56.8	18.93	0.883	0.10
Liquid residue	55.6	18.53	-	0.18
Solid residue + losses	129.3	43.10	-	-
Total	300	100.00	-	-

From the data presented in table 4, it can be seen that the thermal degradation of used rubber waste generates by breaking the molecules: gases, gasoline and middle distillates.

Thermal cracking reactions proceed by radical chain mechanism. This mechanism forms radicals at the tertiary carbon atoms for isoparaffins, but also towards the center of the molecule in the case of n-paraffins. Polymers are structures with long chains and only about 10% of the total number of carbon atoms in the polymer molecule are branched chains, so that free radicals are formed according to both variants, but mostly in the linear structure. For this reason, mostly distillate-type products are formed.

The reaction temperature of 500°C in turn justifies the small number of breaks of the radicals, which will ultimately lead to products with a higher number of carbon atoms in the molecule, so to distillates.

The composition of the gases determined chromatographically is presented in table 5.

Table 5 Composition of the gases obtained during the thermal cracking of rubber waste

Component	Composition [%]
Methane	69.37
Ethan	11.65
Ethene	5.27
Propane	13.71
Total	100.00

It was found that through the thermal processing of used rubber waste, light and medium distillates are obtained, which can be used as fuels after further processing.

By heating to 500°C, tire waste decomposes into gases, light and medium distillate, liquid and solid residue.

CONCLUSIONS

By thermal cracking of used tires, 27.89% light and medium distillates are obtained, which can be used together with similar petroleum fractions obtained from thermal processes (coking, viscosity reduction) or as fuels, after further processing.

An inconvenience in the utilization of gases and liquid products obtained in the form of fuels is their high content of sulfur compounds.

Through thermal treatment, 10.46% gases are also obtained which can be used as fuel gases for heating systems or in situ steam generation.

The liquid residue resulting from the process of 18.53% can be used mixed with fuel oil for the formulation of burner fuels.

In addition to the decomposition products in the gas and liquid phase, a solid residue consisting of carbon black particles and solid residues from the solid texture of the tire or plasticizers is also obtained.

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