THE ENERGY USE OF GRANULATE AND PYROLYSIS OIL FROM DISCARDED CAR TIRES AS A METHOD TO INCREASE ECOLOGICAL AND ENERGY SAFETY

Andrzej Tomporowski[1] – *orcid id: 0000-0002-9860-8748*
Izabela Piasecka[1] – *orcid id: 0000-0003-4028-5146*
Adam Mrozński[1] – *orcid id: 0000-0003-1839-3167*
Weronika Kruszelnicka[1] – *orcid id: 0000-0002-9909-5112*
Patrycja Bałdowska-Witos[1] – *orcid id: 0000-0003-0547-4400*
Stephan Kovalyshyn[2]
[1]University of Science and Technology in Bydgoszcz, **Poland,** *weronika.kruszelnicka@gmail.com*
[2]Lviv National Agrarian University, **Ukraine**

Abstract: On average, there are about 60 kg of rubber in a passenger car, about 67% of which are tires, about 20% of all kinds body seals, doors and windows, suspension elements amount to 5%, the rest are other elements related to the engine (seals, hoses, wires, pads, etc.). Rubber waste is too valuable resource to direct to landfills. The vast majority of recovery of used tires in Poland (over 70%) is carried out by burning tires with energy recovery. Tires in the form of granulate, mixed with coal dust, are burn in some combined heat and power plants. The paper presents results of experimental studies of possible use for energy purposes, granules and pyrolysis oil the resulting from discarded car tires for increasing ecological and energy safety. Energy properties of granulates and pyrolysis oil were investigated and the shape and size of granulate particles were analyzed. For this purpose, digital image processing (CAMSIZER device) and calorimeter were used. It was found that the products of tire recycling decommissioned from exploitationare the high-energy material with good calorific value. Based on the results of experimental studies, application conditions of rubber waste for energy purposes was formulated.
Keywords: car tire, pyrolysis oil, alternative energy, rubber granulate

1. INTRODUCTION

Manufacturing activity has one clearly defined direction, which is the cycle of production and consumption. Energy and raw materials are converted into waste and more or less dangerous emissions in this cycle (Tomporowski et al., 2017a; Tomporowski et al., 2017c). Contemporary society depends on motorization in transport and everyday life (Amari et al., 1999). In the future, this state will not change radically, because cars cannot function without tires. Every year, over 150000 tonnes

of used tires are accumulated in Poland. The global production of tires currently exceeds 2 billion units, and rubber tires -30 million tonnes (Marczuk et al., 2015). There is a necessity to recycle used car tires. Reprocessing of the rubber requires a series of time-consuming, labor-intensive and expensive operations. Obtained recirculate usually is characterized by poorer physico-mechanical properties and is not competitive compared to original rubber materials (Marczuk et al., 2015; Miranda et al., 2013; Sunthonpagasit and Duffey, 2004; Macko et al., 2017). Rubber waste is an extremely serious economic and ecological problem that counts as many years as the modern rubber industry. Due to the deteriorating state of the environment and the decreasing volume of its resources, the need to determine the possibility of using the two most important products of recycling car tires: rubber granulate (mechanical recycling - grinding) and pyrolysis oil (raw material recycling - pyrolysis) were noted (Formela et al., 2011; Seidelt et al., 2006).

2. MATERIALS AND METHODS
2.1. Materials
The basic process enabling the used car tires recycling is their comminution (Flizikowski et al., 2015; Marczuk et al., 2017; Flizikowski, 1999). The analysis covered the rubber granulate obtained as a result of three-stage tire grinding at ambient temperature (first stage: grinding in three mills stacked one above the other for pieces with dimensions 40 × 40 mm, second stage: further grinding in a grinding mill to obtain a granulate size 0.5-2.5 mm, third stage: final grinding in a twin-screw grinding extruder with a two-stage cooling system to prevent coking and igniting the product). The second tested raw material was pyrolysis oil obtained as a result of low temperature pyrolysis (maximum temperature 500°C). The process was carried out without oxygen access in the indirectly heated (diaphragmatic) pyrolysis furnace.

2.2. Equipment
Research of the possibility of using rubber granulate and pyrolysis oil for energy purposes was carried out in the Laboratory of Comminution Research in the University of Science and Technology in Bydgoszcz using the following research equipment: KL-12 calorimeter, CAMSIZER, PT 100 sample divider, OPTA-TECH SN series stereoscopic microscope with a digital camera, AS 220.R2 analytical scale.
The KL-12 calorimeter allows to measure the heat of combustion of solid and liquid substances. The measurement method complies with the requirements of PN-ISO 1928: 2002, iPN-C-04062: 1986. The measurement consists in the complete combustion of a fuel sample in an oxygen atmosphere under pressure in a calorimetric bomb submerged in water and on the measurement of the water temperature increase.
CAMSIZER enables the simultaneous measurement of particle size and shape of powders and granulates in accordance with ISO 13322-2: 2006. It works on the principle of digital image processing. Using the vibrating conveyor, the sample is transported to the measuring field in which it moves between the source of scattered light and two CCD cameras (Tomporowski et al., 2017b).

2.3. Research methodology
In the first stage of the research, the rubber granulate was analyzed. Using the PT 100 sample divider, the input material was divided into 10 samples with a mass of 10

g each. The samples were subjected to granulometric analysis on the CAMSIZER device. The following parameters were determined for them: $p3$ [%] – relative frequency, $Q3$ [%] – distribution function, volume percent, $SPHT3$ – spherical particle frequency, $Symm3$ – frequency of symmetrical particles, $b/l3$ – ratio of length to width, PDN – number of particles per size class (Tomporowski et al., 2017b). The results were averaged. In the next stage, the shape and size of the particles were analyzed under the OPTA-TECH stereoscopic microscope.

The second stage was the assessment of selected parameters of the rubber granulate and pyrolysis oil combustion, using a KL-12 calorimeter. Ten each material samples, weighing 1 g, were subjected to testing and the results were averaged. The following parameters have been determined: H [%] – hydrogen content, Q_{sr} [$J \cdot g^{-1}$] – heat of combustion in working condition, Q_{sa} [$J \cdot g^{-1}$] – heat of combustion in the analytical state, Q_{ir} [$J \cdot g^{-1}$] – calorific value in in working condition, Q_{ia} [$J \cdot g^{-1}$] – calorific value in the analytical state.

2.4. Analytical methods

The particle size and shape analysis was carried out using the CAMSIZER device and a stereoscopic microscope. The measurement of selected combustion parameters was carried out with a KL-12 calorimeter. The calorimeter works on the principle of measuring characteristic heat balance temperatures. The entire measurement process follows the graph shown in Figure 1.

The calorimeter work is divided into 5 cycles shown in figure 1. The individual cycles inform about the calorimeter state. Cycle:

0 Turning on the calorimeter and stabilizing the temperature inside the calorimeter (duration: about 2 min).

1 temperature $T1$ registration and measurement a 5 minutes time interval.

2 temperature $T2$ registration and fuel sample ignition in a calorimetric bomb. This cycle lasts for n-minutes, until reaching the maximum temperature.

3 temperature $T3$ registration and the measurement of next time segment equal to 5 minutes,

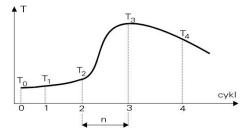4 Temperature $T4$ registration and work termination.

Fig. 1. Example of the calorimetric measurement process
Source: (Szymański et al., 2006).

Combustion heat (Qs) is understood as the heat amount released when the fuel mass unit is completely combusted, measured after condensation of water vapor released during combustion and after cooling the combustion products to the initial temperature of the components involved in the combustion and reduced by the amount of heat generated in the synthesis and dissolution of H_2SO_4 and HNO_3 (Szymański et al., 2006).

The combustion heat of the fuel sample is calculated automatically using the following equation:

$$Qs = K \cdot (T3 - T2 - k) \qquad (1)$$

where:
Qs – heat of combustion of the fuel sample,
K – calorimeter constant,
$T2$, $T3$ – characteristic balance temperatures,
k – correction for heat exchange of the calorimeter with the environment:

$$k = 0.5 \cdot \left[0.2 \cdot (T2 - T1) + 0.2 \cdot (T4 - T3) \right] + 0.2 \cdot (n - 1) \cdot (T4 - T3) \qquad (2)$$

where:
n – the number of minutes in cycle number 2 (the main period),
$T1$, $T4$ – characteristic balance temperatures (Szymański et al., 2006).

The calorific value (Qi) is the heat of fuel combustion reduced by the amount of heat necessary to evaporate the water contained in the fuel and resulting from the combustion of hydrogen contained in the fuel. The calorific value of the tested sample is calculated as:

$$Qi = Qs - 24.42 \cdot (8.94 \cdot H - W) \qquad (3)$$

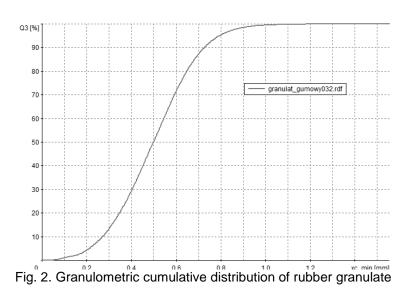where:
Qs – heat of combustion,
H – hydrogen content in the test sample,
W – moisture content in the test sample (Szymański et al., 2006).

The fuel working condition is called the state of the fuel that has been extracted or used and has parameters that have not been able to adapt to the surrounding atmosphere (moisture, ash). In contrast, the analytical state describes such state of fuel samples that have moisture equivalent to ambient moisture (Szymański et al., 2006).

3. RESULTS AND ANALYSIS

The particle size and shape analysis was carried out using digital image processing (CAMSIZER device), thanks to which the particle size distribution of all tested fractions was obtained in samples from 1 to 10. The averaged test results are shown in table 1 and figure 2.

Fig. 2. Granulometric cumulative distribution of rubber granulate

The largest percentage share (10.8%) of the particles was recorded in the range (0.450-0.500) mm. The frequency of occurrence of spherical particles, depending on the considered size range, ranged from 0.307 to 0.827, while the frequency of occurrence of symmetrical particles ranged from 0.710 to 0.841. The smallest number of particles in the tested sample was characterized by size classes above 0.850 mm, while the largest – classes below 0.300 mm.

Table 1

Rubber granulate fraction percentage share with division into size classes

Size class, mm		p3, %	Q3, %	SPHT3	Symm3	b/l3	PDN
0.000	0.150	2.1	2.1	0.827	0.841	0.738	1778284
0.150	0.200	2.2	4.3	0.728	0.826	0.597	148425
0.200	0.250	3.8	8.1	0.732	0.833	0.606	126324
0.250	0.300	5.3	13.4	0.712	0.827	0.603	94226
0.300	0.350	7.3	20.7	0.693	0.819	0.594	82566
0.350	0.400	8.7	29.4	0.692	0.821	0.605	66630
0.400	0.450	10.2	39.6	0.682	0.819	0.603	54706
0.450	0.500	10.8	50.4	0.662	0.807	0.602	41633
0.500	0.550	10.7	61.1	0.674	0.815	0.625	32030
0.550	0.600	10.5	71.6	0.662	0.810	0.623	24867
0.600	0.650	8.8	80.4	0.659	0.804	0.641	16951
0.650	0.700	6.9	87.3	0.667	0.810	0.649	10902
0.700	0.750	4.9	92.2	0.635	0.796	0.640	6115
0.750	0.800	3.2	95.4	0.634	0.796	0.660	3292
0.800	0.850	1.9	97.3	0.672	0.798	0.703	1273
0.850	0.900	1.2	98.5	0.644	0.792	0.705	717
0.900	0.950	0.7	99.2	0.623	0.781	0.678	284
0.950	1.000	0.3	99.5	0.488	0.776	0.681	100
1.000	1.200	0.4	99.9	0.458	0.710	0.605	144
1.200	1.400	0.1	100.0	0.307	0.782	0.237	6
1.400	1.600	0.0	100.0	1.000	0.000	0.000	0

The next step in the research procedure was to analyze the particles shape and size under the OPTA-TECH stereoscopic microscope. The particles in the test sample were characterized by varied size and shape. Irregularly shaped particles with sharp jagged edges were observed. It was found that asymmetrical particles with elongated shape prevail. Figure 3 shows an example of single particles microscopic image with their dimensions.

Figure 4 and table 2 illustrate the calorimetric measurement process results for the rubber granulate and pyrolysis oil tested samples. In the case of rubber granulate, the water temperature in the calorimeter during sample ignition was 21.759°C and its maximum temperature (24.538°C) was reached after 12 minutes. The higher water temperature was recorded when the pyrolysis oil was ignited – 24.629°C, and the maximum temperature (27.240°C) was reached after just 8 minutes. Pyrolysis oil ignition takes place at a temperature approx. 50°C. The difference between the water temperature during sample ignition and the maximum temperature was 2.779°C for the rubber granulate, whereas in the case of pyrolysis oil it was 2.611°C.
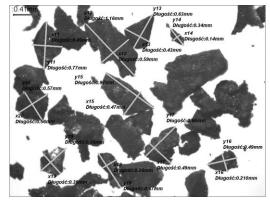
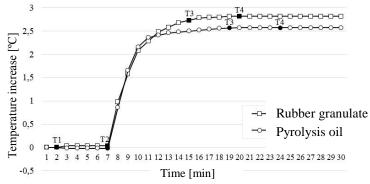Fig. 3. Shape and size analysis of rubber granulate particles (mag. × 60)

Fig. 4. Increase of water temperature during the calorimetric measurement process for rubber granulate and pyrolysis oil

Table 2
Selected parameters of the calorimetry measurement for granulate and pyrolysis oil

Parameter	Unit	Rubber granulate	Pyrolysis oil
$T1$	°C	21.723	24.645
$T2$	°C	21.759	24.629
$T3$	°C	24.538	27.240
$T4$	°C	24.534	27.212
n	min.	12	8

The measurements results of selected combustion parameters carried out with the KL-12 calorimeter are presented in table 3. The rubber granulate was characterized by a higher value of heat of combustion (34875 $J \cdot g^{-1}$) and the calorific value (33695 $J \cdot g^{-1}$) compared to pyrolytic oil (heat of combustion: 33242 $J \cdot g^{-1}$, calorific value: 32063 $J \cdot g^{-1}$). The hydrogen content for all samples was comparable and was about 5.4%.

Table 3
Selected burning parameters for rubber granulate and pyrolysis oil

Parameter	Symbol	Unit	Rubber granulate	Pyrolysis oil
Analytical hydrogen	H_a	%	5.405	5.400
Analytical combustion heat	Q_{sa}	$J \cdot g^{-1}$	34875	33242
Combustion heat in working state	Q_{sr}	$J \cdot g^{-1}$	34875	33242
Analytical calorific value	Q_{ia}	$J \cdot g^{-1}$	33695	32063
Calorific value in working state	Q_{ir}	$J \cdot g^{-1}$	33695	32063

Table 4

The weight of the residue after burning of rubber granulate and pyrolysis oil samples

Measurement	Unit	Rubber granulate	Pyrolysis oil
Mass of clean crucible	g	6.1156	4.9475
Crucible mass with sample	g	7.1156	5.9475
Crucible mass after sample burning	g	6.2046	4.9735
resulting residue mass	g	0.0890	0.0260
Percentage share of residue	%	8.9	2.6

4. SUMMARY AND CONCLUSION

The evaluation of the possibility of using rubber granulate and pyrolysis oil samples from used car tires for energy purposes was carried out. The products of mechanical and raw material recycling of end-of-life tires are a product with good calorific value. Rubber granulate has a higher value of combustion heat (34875 $J \cdot g^{-1}$) and the calorific value (33695 $J \cdot g^{-1}$) in comparison to pyrolysis oil (heat of combustion: 33242 $J \cdot g^{-1}$, calorific value: 32063 $J \cdot g^{-1}$). The water temperature in the calorimeter when igniting the rubber granulate was lower and amounts to 21.759°C, and its maximum temperature (24.538°C) is reached only after 12 minutes. During the pyrolysis oil sample ignition a higher water temperature 24.629°C was noted, and its maximum temperature (27.240°C) was reached earlier, after 8 minutes. The rubber granulate, despite the higher calorific value, after burning, however, leaves more residues, constituting 8.9% of the feedstock mass, which can be a serious problem in the field of environmental protection.

Due to limited possibilities of using tires in the form of raw material and their good calorific value, they can be used as a supplementary fuel (mainly in cement plants). 2. The contents in tires, among others sulfur and zinc oxide, makes however, that under normal burning conditions toxic substances are realeased. For this reason, in tire incinerators special reduction devices must be used (Bignozzi and Sandrolini, 2006).

In the case of a traditional car tire, the highest mass percentage is synthetic (24.17%) and natural rubber (18.21%), carbon black (19%), coated steel wire (11.4%), silica (9.65), oil (6.12%), textile fibers (4.7%), zinc oxide (1.58%), sulfur (1.28%), stearic acid (0.96%) and recycled rubber (0.5%) (Ivan, 2012). It is extremely important to increase the importance of renewable raw materials during the production of tires, eg. obtaining rubber from a Guayule plant instead of just a traditional rubber tree, as well as replacing fossil raw materials with renewable materials, e.g. synthetic petroleum oil can be produced from butadiene on the basis of bioethanol, fillers currently produced from crude oil or coal can be produced from vegetable fats and oils or to obtain silica from inedible rice husks, which is currently used for burning (Sharma et al., 2000).

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