Analysis of Carbon Black from Tyres Pyrolysis

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Abstract

The article presents the results of the analysis of the pyrolysis products (char) from waste tires. Pyrolysis was carried out in four temperature 450, 500, 550, 600°C. Yield of solid product (char) ranged from 37% for the temperature of 450°C to 43% for the temperature of 500°C. The SEM analysis of obtained samples shows that the surface properties (size) depends on the process temperature.

Keywords: waste tyre, pyrolysis, char, SEM analysis

Introduction

The pyrolysis products are carbonization product, oil and gas. Carbonization product which states for 45% of pyrolysis products is very difficult to use in industry because of additional material which serve as tyres strengthening (metal, textiles) as well as some ingredients of rubber which, during pyrolysis, stay in the solid product and lower the investment profitability. Therefore an examination of the pyrolysis was undertaken concerning pure rubber granulated product which was obtained from disintegration of used tyres and devoided from additional materials like textiles and metal elements used, except rubber, in production of tyres [2]. In Poland, the process of pyrolysis of used tyres was carried out in the seventies of the last century by Institute for Chemical Processing of Coal, but at that time the technology was not enough profitable in terms of market [1].

Char

An important property of pyrolytic char is its morphological similarity with natural carbon black.

The high ash content reduces their recycling and is used in the manufacture of tires, but can be used in the manufacture of rubber. A fundamental difference between the commercially sold carbon black and pyrolytic carbon black is the content of inorganic component (ZnO, S), as well as SiO_2 and Al_2O_3. With increasing temperature of pyrolysis a reaction between ZnO and S occurs to form ZnS, consisted of individual particles with a density higher than of pyrolytic char and the particles can be further separated. Even in our case, the zinc content in pyrolytic char determined by the X-ray fluorescence was very high, up to 7.6% of ZnO; Ba, Cr, Fe etc. occurred to 1%. The character of pyrolytic char with a porous structure is evident from the following photo documentation (Figs. 1–3).

Research

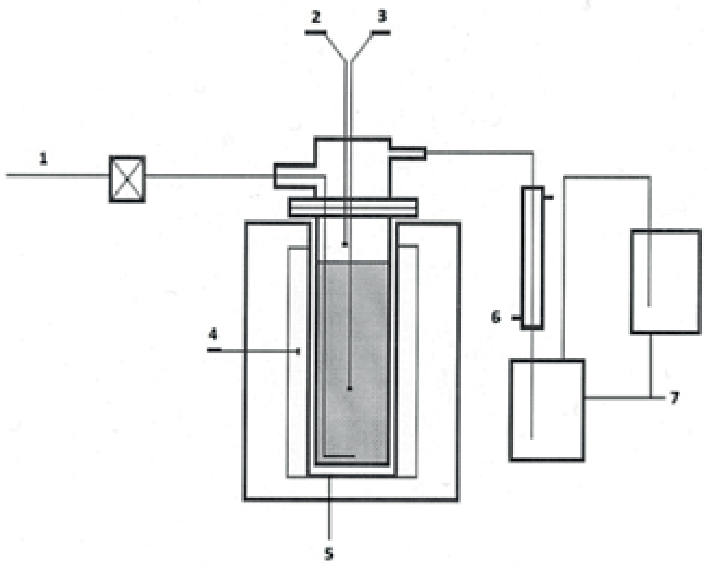
The pyrolysis analysis laboratory equipment

The installation for pyrolysis of granulated product is shown on Fig. 1. A substantial element is a retort made of heat-resisting steel which is composed of two pieces twisted with screws. The retort has a diameter of 90 mm and height equal 700 mm. At the bottom of the retort the sample of granulated rubber product is placed. Upper part, standing for retort closure, has a pipe delivering water and a pipe which removes gases from pyrolysis. The retort is placed in a 10 kW electric furnace which provides the uniform temperature in the entire height of the load and maintains the heating rate stability on the set level. The temperature is measured using thermocouple placed in the central part of the load and on its surface. The end of retort includes pipe which delivers the water to the load and pipe which carries off the volatile matter. The water is transported to the retort using peristaltic pump which allows accurate measurement and dosage control. Pyrolytic gas is condensed in the receivers.

Experimental methods

Examination of pyrolysis of rubber granulate

The sample of rubber granulate weighting approximately 430 g was prepared for the tests. After weighing the granulate was poured into the retort which was then closed and put into the furnace. After connecting the water supplying ducts and carrying off the volatile matter ducts the furnace heating was switched on taking into account heat-



1 – dosing pump
2, 3, 4 – thermoelement
5 – retort
6 – cooler
7 – collecting oil

Fig. 1. Instalation for pyrolysis

Rys. 1. Instalacja do pirolizy

Tab. 1. Energetic properties of rubber granulate

Tab. 1. Właściwości energetyczne granulate z gumy

	W^a [%]	V^a [%]	A^a [%]	S^a_t [%]	C^a [%]	H^a [%]	Q^a_s [kJ/kg]	Q^a_i [kJ/kg]
Rubber granulate	0,4	64.6	6,3	2,08	79,70	6,91	34 264	32 728

W – moisture
Index a – dry condition
V – volatile matter
A – ash content
St – sulphur content (total)
C – carbon content
H – hydrogen content
Qs – calorific value
Qi – net calorific value

Tab. 2. Yield of pyrolysis products vs temperature

Tab. 2. Wychód produktów pirolizy w zależności od temperatury

Product	Pyrolysis temperature [°C] yield [%]			
	450	500	550	600
Carbon black	43,5	43,0	37,7	36,8
Oil	47,0	48,1	52,4	52,5
Gas	9,5	8,9	9,9	10,7

ing rate. The water dosage was switched on when temperature inside the load reached 100°C. After reaching previously set terminal temperature and stabilization in the time the furnace was switched off and when it cooled, the retort was removed from the furnace and solid residue from it was weighed. The oil obtained in pyrolysis process and collected in the receiver was also weighed. Tab.1. shows results from tests on energetic properties of rubber granulate conducted in 450, 500, 550 and 600°C. The pyrolysis was carried out to the end of collecting of the oil. In this moment the furnace heating was switched off.

Table 2 shows the yields of pyrolytic products for different temperatures of the process.

With increase of temperature the amount of obtained oil increases too and the amount of solid carbonization product decreases.

Microscopic analysis of carbon black

Samples were prepared by milling and sieving to a fraction below 50 µm. For each sample,

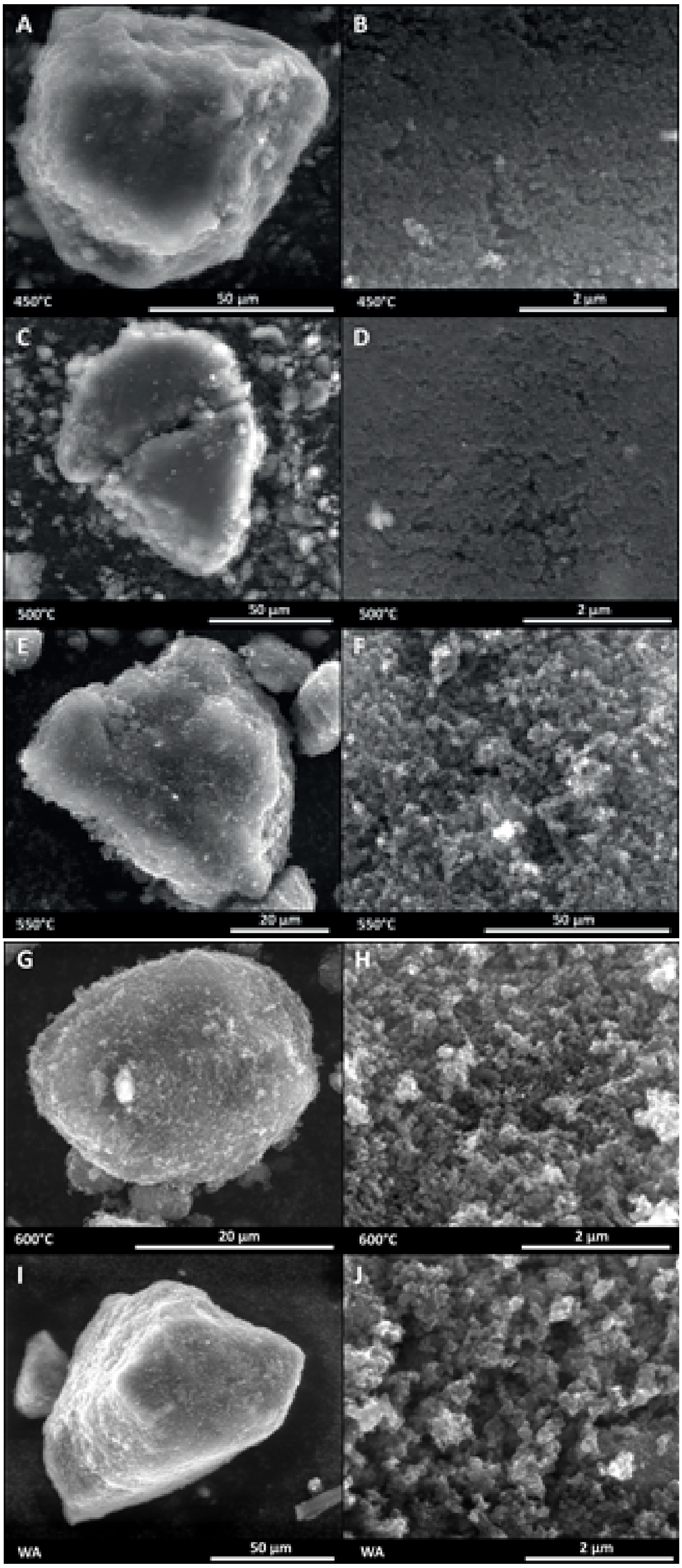


Fig. 2. Products of the pyrolysis at temperatures of 450°C (A, B), 500°C (C, D), 550°C (E, F), 600°C (G, H) and sample from industrial instalation (I, J). The secondary electrons (SE) images present development of active surface subsequent with increasing temperature conditions of pyrolysis

Rys. 2. Produkty pirolizy uzyskane w róznych temperaturach 450°C (A, B), 500°C (C, D), 550°C (E, F), 600°C (G, H) i próbka uzykana w instalacji przemysłowej (I, J). Obrazy z analizy SE przedstawiają wzrost powierzchni aktywnej w zaleznośći od temperatury procesu pirolizy

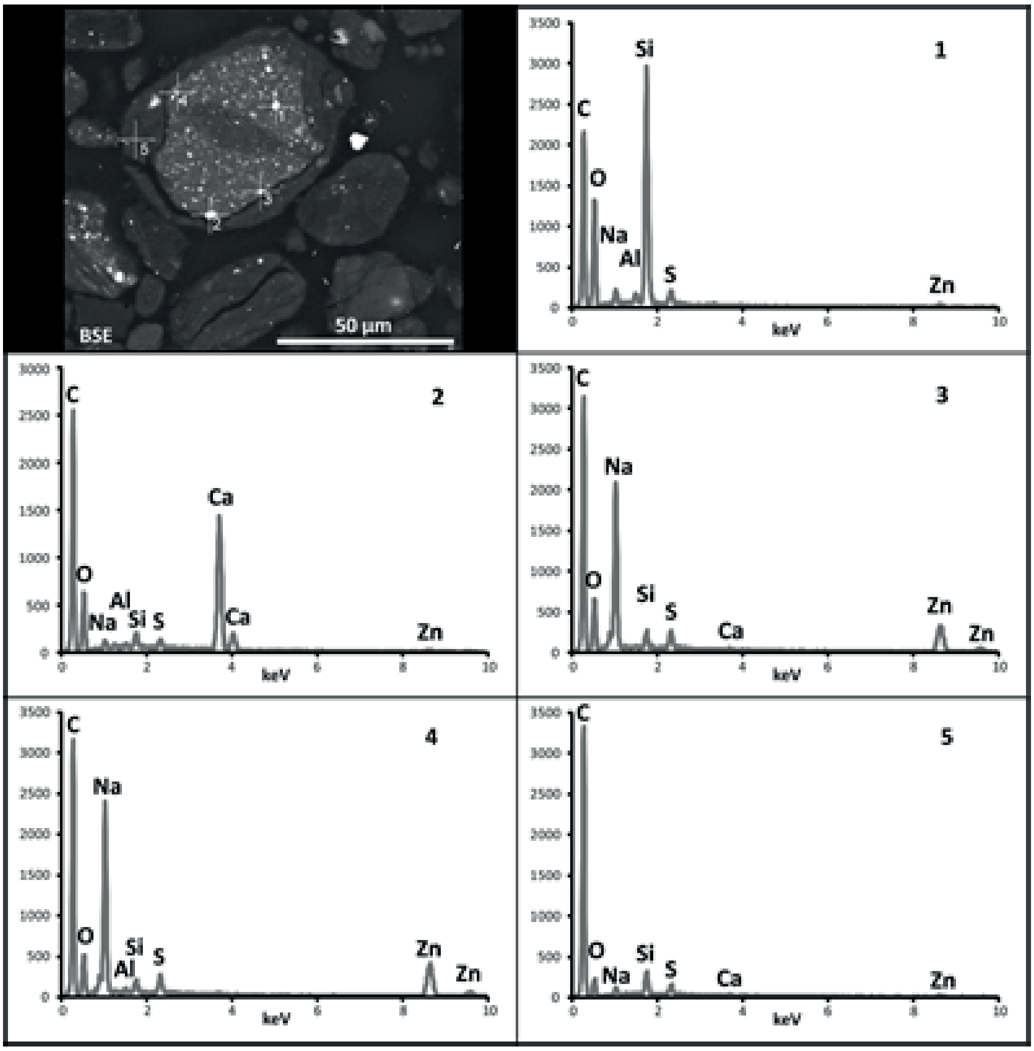


Fig. 3. Back scattered electrons (BSE) image presenting cross section of the polished sample with products of pyrolysis at 450°C. Si, Na and Ca-riched inorganic compounds form core enclosed in carbon shell. EDS spectrums represent chemistry of the analytical spots labeled 1–5 at the BSE image

Rys. 3. Analiza BSE przedstawiająca przekrój próbki produktu pirolizy w temperaturze 450°C. Składniki nieorganiczne bogate w Si, Na i Ca są zamknięte w strukturze węglowej. Obrazy EDS, oznaczone 1–5, przedstawiają skład chemiczny.

grains were mounted in Araldite epoxy and polished to obtain a cross section. Subsequently, second portion of grains was sprinkled on the SEM mount with an adhesive carbon duct tape. Textural observations and chemical analyzes were performed using FEI Quanta QUANTA 200 Field Emission Gun Scanning Electron Microscope equipped with energy dispersive spectrometer in Phase, Structural, Textural and Geochemical Analyzes Laboratory at the Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology (Kraków, Poland). The SEM was operated under low vacuum, accelerating voltage of 20 kV, 10 mm working distance, and focused electron beam on not coated samples. Back scattered electrons (BSE) imaging was used for polished grain mounts, and secondary electrons (SE) imaging for sprinkled grains.

Results and discussion

From Table 1, 2 (chernical characteristics of char), it can be seen that there is high ash content in all char samples. High ash content is due to the presence of inorganic ingredients used in tire production. The volatile matter of char was extremely low, all other pyrolytic char samples were comparable. Higher volatility in char indicates increasing amounts of pyrolytic oil condensed on the char.

Planned solid residue investigation

The solid residue contains carbon black and the mineral matter initially present in the tire. Several studies have reported the production of active carbon from waste tires [3],[4], [5]. These active carbons have been used to adsorb phenols, basic dyes and metals, phenols, butane and natural gas. Active carbon from solid product of pyrolysis process is produced by activation with an activating gas at 800–100°C. Carbon characteristics (especially specific area) are greatly influenced by the degree of the activation also by nature of activating agent (steam or CO_2) and process temperature. Based on the current technology and literature results tire chare activation below 700°C looks impractical.

The particle size of the tire rubber was found to have influence on the porosity of the resultant carbon generated from steam activation.

Acknowledgement

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Literatura – References

1. STELMACH S. 2011. "Potencjalne metody zagospodarowania karbonizatów z opon samochodowych." *Archiwum Gospodarki Odpadami i Ochrony Środowiska* 3(13): 37–52.
2. STELMACH S., WASIELEWSKI R., FIGA J. 2005. "Badania pirolizy zużytych opon samochodowych." Praca zbiorowa pod red. Wandrzasza J.W. i Pikonia K.: *Paliwa z odpadów*, 5th edition. Gliwice: Helion.
3. TORA B. 2013. "Wybrane sposoby wykorzystania produktów pirolizy odpadów" *Przegląd Górniczy* 3: 163–166.
4. TORA B., BUDZYŃ S., ŻMUDA W.A., FECKO P., KRIZ V. 2012. *Sposób wykorzystania olejów po pirolizie odpadów organicznych — [Method for using oils after the pyrolysis of organic waste]*/patent PL 393095 A1 — Zgłosz. 2010-11-30; Opubl. 2012-06-04.
5. DEPTA G., TORA B., ŻMUDA W., BUDZYŃ S. 2012. *Sposób wytwarzania ukształtowanego paliwa stałego z materiałów odpadowych*. Patent PL 394987, 2012.
6. BUDZYŃ S., BUDZYŃ B., KOZUB-BUDZYŃ G., TORA B. 2014. *Analysis of carbon black from tyres pyrolysis in: 18 Conference on Environment and mineral processing*. Pt. 2/ed. Čablík Vladimír; Ostrava: VŠB – Technical University of Ostrava.

Streszczenie

W artykule przedstawiono wyniki analizy produktów pirolizy opon samochodowych. Piroliza była prowadzona w temperaturach 450, 500, 550, 600°C. Wychód karbonizatu (produktu stałego pirolizy) wynosi od 37% dla temperatury 450°C do 43% dla temperatury 500°C. Przedstawiono wyniki analizy SEM, które wskazują, że wielkość powierzcni karbonizatu zalezy od temperatury procesu.

Słowa kluczowe: żuzyte opony samochodowe, piroliza, karbonizat, analiza SEM