IOP Conference Series: Materials Science and Engineering

PAPER • OPEN ACCESS

Investigation of the process of grinding of a char coal obtained from tires waste pyrolysis

To cite this article: J Sidor *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **641** 012022

IOP Conf. Series: Materials Science and Engineering **641** (2019) 012022 doi:10.1088/1757-899X/641/1/012022

Investigation of the process of grinding of a char coal obtained from tires waste pyrolysis

J Sidor[1], S Budzyń[2] , C Czosnek[2], G Kozub –Budzyń[3] and B Tora[4]

[1] Faculty of Mechanical Engineering and Robotics,
[2]Faculty of Energy and Fuels,
[3]Faculty of Geology, Geophysics and Environmental Protection,
[4]Faculty of Mining and Geoengineering
AGH University of Science and Technology, Mickiewicza 30 Av., 30-059 Krakow, Poland

E-mail: tora@agh.edu.pl

Abstract. The paper contains results of examinations of grinding of char obtained from waste car tires. The grinding of the char was conducted in a laboratory vibratory mill of low vibration frequency. The examinations concerned the possibility of using a char as raw material in industry, particularly as a substitute for carbon black applied for the production of rubber. One of the basic parameters characterizing carbon black is particle size distribution as well as specific surface area. In the examinations, the char was obtained with following characteristic sizes of particles: d_{50} = 2.5 ÷ 9.3 µm , d_{90} = 13.3 ÷ 35.0 µm and specific surface area 74 ÷ 163 m^2/g matching the particle size distribution and specific surface area characteristic of carbon black, which means that in order to grind a char, the vibratory mill can be used.

Komentarz [D1]: This terminology is not clear to use in the paper.

1. Introduction

In the EU countries, around 3.4 million Mg of car tiretires are withdrawn from operation every year; in Poland it is about 0.24 million Mg. About 23% of that amount is reused. The remaining amount needs putting into appropriate use in accordance with the current regulations. This involves the reuse of the tires after retreading, energy recycling - combustion, pyrolysis - conversion to liquid and solid fuels, material recycling - after mechanical processing and modification (devulcanization and regeneration), and putting into use in different sectors - after mechanical processing[1].

The processing of waste tires and other rubber waste through pyrolysis is one of the methods of their recycling, and its products are: gas with a composition similar to that of natural gas, pyrolytic oil, and a solid residue - a char. The char contains 70 ÷ 80% of carbon, is featured by low contents of volatile matter and the presence of inorganic matter, the composition of which depends on the kind of rubber blends produced [2, 3, 4]. The carbon contained in the char comes from carbon black, but its structure and properties are different because of the influence of technological processes to which carbon black was subjected (production of rubber blends, vulcanization and pyrolysis). In the technology of rubber blends production, different additives are applied, such as vulcanizing agents and accelerators, plasticizers, fillers, pigments, anti-ageing substances, and others. These are mainly inorganic substances, which remain in the char after the pyrolysis process. Also, a significant amount of sulphur (up to 3%), which is used for vulcanization of rubber blends, stays in the char [4, 5]. The

Komentarz [D2]: What is the meaning of this notation?

IOP Conf. Series: Materials Science and Engineering **641** (2019) 012022 doi:10.1088/1757-899X/641/1/012022

properties of a char depend on the kind of rubber waste, time-temperature conditions of the pyrolysis process and type of plant in which pyrolysis is conducted [8, 9, 10].

In the technological process of rubber blends production, various kinds of organic and inorganic substances are used as additives - fillers, which aim at imparting the required physico-chemical properties to the rubber products. The basic substance used as a filler is carbon black, which, depending on the type, is characterized by the specific surface area (BET) of 20 ÷ 130 m^2/g. Carbon black is a relatively expensive component of rubber blends, therefore, in rubber products with lower quality requirements, substitute substances are applied.

Laboratory examinations showed that in certain cases carbon black can be fully or partly replaced with a char obtained from pyrolysis of waste tires, without significant changes in the properties of the resulting rubber [11]. The price of the char is much lower than that of carbon black, which makes it possible to reduce the production costs of rubber blends. This also creates the possibility to recycle waste rubber products, to the benefit of the environment, by developing a wasteless technology of utilizing rubber waste in the pyrolysis process. One of the conditions for obtaining a char, which can be used as a filler in the production of rubber blends, is its size reduction to an appropriate limit and obtaining an appropriate specific surface area [12]. A char can also be used in different sectors of industry, e.g. for producing pigments, activated carbons, plastics, as a mercury adsorbent, an additive to asphalt, as well as a component of suspensions and liquid coal, where its appropriate size reduction is also required [8-11].

The paper contains results of investigations of a very fine grinding of a char conducted in a laboratory vibratory mill with a low vibration frequency [13, 14]. The diameter of the milling chamber used in this research, corresponding to that of industrial milling chambers will, in the future, facilitate the selection of grinding parameters and the dimensions of the mill adequate for the required milling efficiency of chars on an industrial scale [15,16].

2. Characteristics of char

The basic properties of the char intended for the examinations are presented in Table 1. The char was obtained in an experimental plant for pyrolysis of organic waste operating periodically. The maximal pyrolysis temperature was 600 °C, and the residence time of waste in the reactor was 18 hours.

Table 1. Physico-chemical properties of the char.

Moisture content [%]	Ash content [%]	Volatile matter content [%]	Sulphur content [%]	Carbon content [%]	Hydrogen content [%]	BET specific surface area [m^2/g]
W	A	V	S	C	H	S_{BET}
1.1	20.2	2.2	2.66	76.3	0.95	50

Table 2. contains the determination results of particle size distribution for the char before grinding, and Fig.1 shows a typical SEM image of the char with the results of elemental analysis. The particle size distribution of the char was determined with the use of the dry method, according to the standards PN-71/C-04501 and PN-ISO 2395-2000, by means of a laboratory vibratory screen.

Table 2. Particle size distribution of the char before grinding.

Size fraction [mm]	>1.6	1.6-1.0	1.0-0.63	0.63-0.40	0.40-0.315	0.315-0.10	0.10-0.063	<0.063
Yield of size fraction [%]	0.0	6.7	14.2	12.9	8.8	6.4	32.2	18.8

Figure 1 shows the results of examinations of char conducted by means of a field emission scanning electron microscope (FESEM) FEI QUANTA 200. The results of the elemental analysis are given in Figures 1B ÷ 1F. The char contains 76.3% of the carbon element and 20.2% of ash (Table 1). The presence of inorganic matter in the char is a result of applying mineral components for rubber blends. It is composed mainly of SiO_2, ZnO, CaO, Al_2O_3, Na_2O, and Fe_2O_3 [6]. Car tires subjected to pyrolysis were not cleaned at all; therefore, the char can also contain components originating from the impurities.

Komentarz [D3]: Please choose tyre or tire.

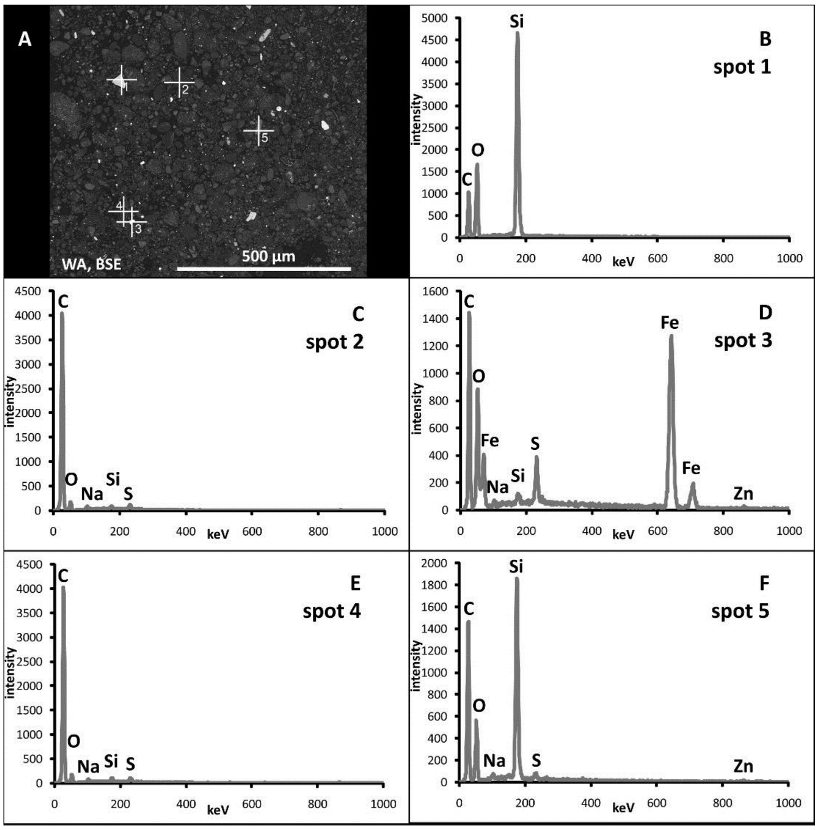

Figure 1. The results of examinations of char.

3. Objective and method of examination of char grinding

The main aim of the investigations was to obtain a ground char with a specific surface area close to that of activated carbon black and with the maximal particle size of 45 µm, at standard parameters of the mill, within the shortest possible grinding time. The material for grinding was a char from a periodically operating industrial plant for pyrolysis of organic waste, in which waste from worn out car tires was subjected to pyrolysis. The investigations of the process of char grinding were conducted in a laboratory vibratory mill, operating periodically, in a chamber with steel lining with the capacity of 2.2 dm^3. As the grinding media, steel balls were used. Their mass was 8 kg. The variable parameters were grinding time and mass of the char. Grinding time varied from 10 to 60 minutes, except one test where the grinding time was 120 minutes. The mass of the char was 0.32 kg in the sa1 to sa4 tests, and in the remaining ones it was 0.25 kg. The grinding was performed using the dry method, in a tightly-sealed chamber. The vibration frequency of the chamber was 14 Hz. The test stand with the original laboratory vibratory mill of low vibration frequency is presented in Figure 2.[13, 14].

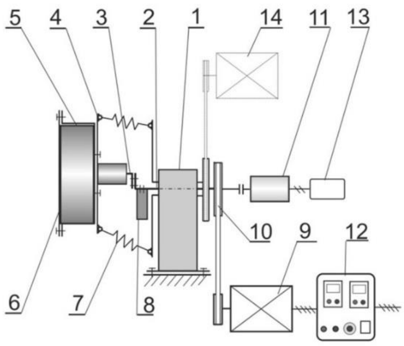

Figure 2. Constructional diagram of the vibratory mill: 1 - the unit of propulsion, 2 - the shaft of vibrator, 3 -the shaft of chamber, 4 - shield, 5 - chamber, 6 - cover of the chamber, 7 - clutch, 8 - filler, 9 - the engine of vibrator, 11 - sensor, 12 - the power system, 13 - measuring system, 14 - the engine of the chamber.

The test equipment enables investigations of the vibratory grinding process within a broad range of changes of technological parameters (in the conditions of air, inert gas, water and other liquids), stabilization of the temperature of the grinding process within the range of 20 ÷ 80 °C in chambers with capacities from 100 cm^3 to 5 dm^3 with a lining of steel and ceramics - corundum or polyamide). The parameters of vibratory motion can also be changed: the frequency of chamber vibrations within the range of 0 ÷ 25 Hz, the amplitude of chamber vibrations 2.5 ÷ 14 mm, and the chamber can also be set in additional rotary motion. The power output of the vibrator engine is 3.5 kW, and of the chamber engine (not used in these experiments), 0.75 kW - see item 14 in Figure 2.

4. Program, implementation and results of investigations

The program of preliminary investigations of char grinding involved the determination of char grinding process kinetics for the adopted mill parameters - these tests were labelled with symbols from sa1 to sa4, two tests with a lowered char mass (sa4 and sa8) and one test labelled sa9, with a grinding time two times longer when compared to the maximal time adopted in the grinding kinetics examinations. The kinetics of the grinding process concerned the impact of the char grinding time on the change of characteristic particle size fractions, particle size and the specific surface area.

The results of the investigations of particle size distribution of the char after grinding, determined with the use of an ANALYSETTE 22 apparatus (Fritsch), are shown in Table 3. Figures 4 and 5 represent the impact of the grinding time on the contents of particle size fractions 0-5 µm, 0-10 μm, as well as 0-20 μm, and the size of particles d_{97}, d_{90} and d_{50} of the char ground during particular tests. Figure 6 represents the particle size distribution for the char after 60 minutes of grinding in the test labelled as sa4.

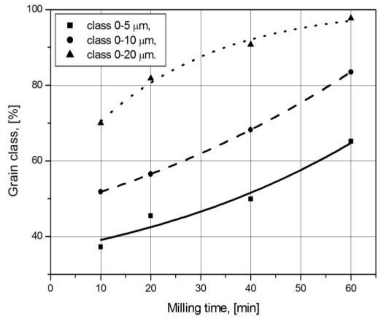

Figure 3. Impact of grinding time on size fractions content in tests sa1 – sa4.

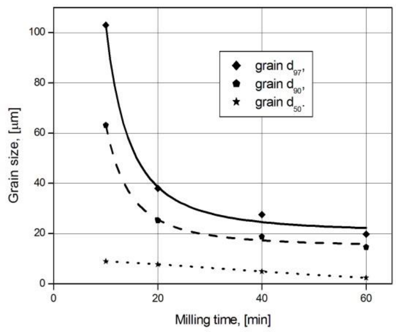

Figure 4. Impact of grinding time on particle sizes d_{97}, , d_{90}, and d_{50} in tests sa1 – sa4.

Table 3 provides also BET specific surface areas of the samples of ground char. The specific surface area results were obtained using the method of low temperature nitrogen sorption by means of a Micrometrics Gemini V 2380 apparatus. Nitrogen adsorption isotherms were determined at liquid nitrogen temperature, using nitrogen gas of 99.999% purity. Before the adsorption measurements, the samples were degassed at 200 ^{o}C for the removal of any incidentally adsorbed matter, and thus obtaining a clean surface for adsorption. The specific surface areas of the samples were calculated by means of the standard BET method using five data points on the adsorption isotherms in the P/P_0 range of 0.05 to 0.30 and taking the molecular cross-sectional area of 0.162 nm^2.

Table 3. Results of examinations of particle size distribution of the char after different grinding times.

Sample → Particle size	sa1	sa2	sa3	sa4	sa6	sa8	sa9
d_{10} [μm]	0.86	0.79	0.68	0.51	0.78	0.67	0.79
d_{37} [μm]	4.84	4.04	2.65	1.47	3.00	2.49	2.59
d_{50} [μm]	9.29	7.87	5.01	2.52	5.50	4.53	4.28
d_{80} [μm]	33.46	19.03	14.18	8.79	16.26	14.40	14.91
d_{90} [μm]	35.00	25.14	19.85	13.32	22.79	21.98	22.63
d_{99} [μm]	124.99	40.91	31.92	23.41	30.78	38.07	49.42
BET specific surface area [m^2/g]	74	88	103	141	140	141	163
Grinding time [min]	10	20	40	60	60	60	120

The impact of grinding time on the change of the specific surface area of the char is shown in figure 5. The specific surface area of the char before grinding was 50 m^2/g.

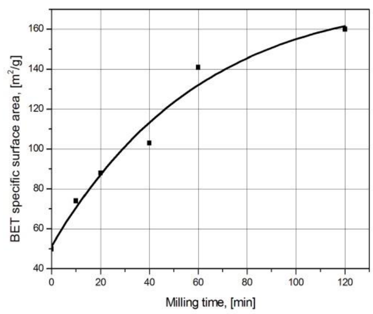

Figure 5. Impact of grinding time on the specific surface area of the char.

Observations and chemical analyses were performed using a FEI QUANTA 200 Field Emission Gun Scanning Electron Microscope (SEM) equipped with an energy dispersive spectrometer in the Phase, Structural, Textural and Geochemical Analyses Laboratory at the Faculty of Geology, Geophysics, and Environmental Protection, AGH University of Science and Technology (Krakow, Poland). Analytical conditions included low vacuum, accelerating voltage of 20 kV, 10 mm working distance, and secondary electrons (SE) imaging of particles sprinkled on the SEM mount with an adhesive carbon duct tape.
Figure 6 represents typical SEM images of the char from the tests sa2, sa8 and sa9.

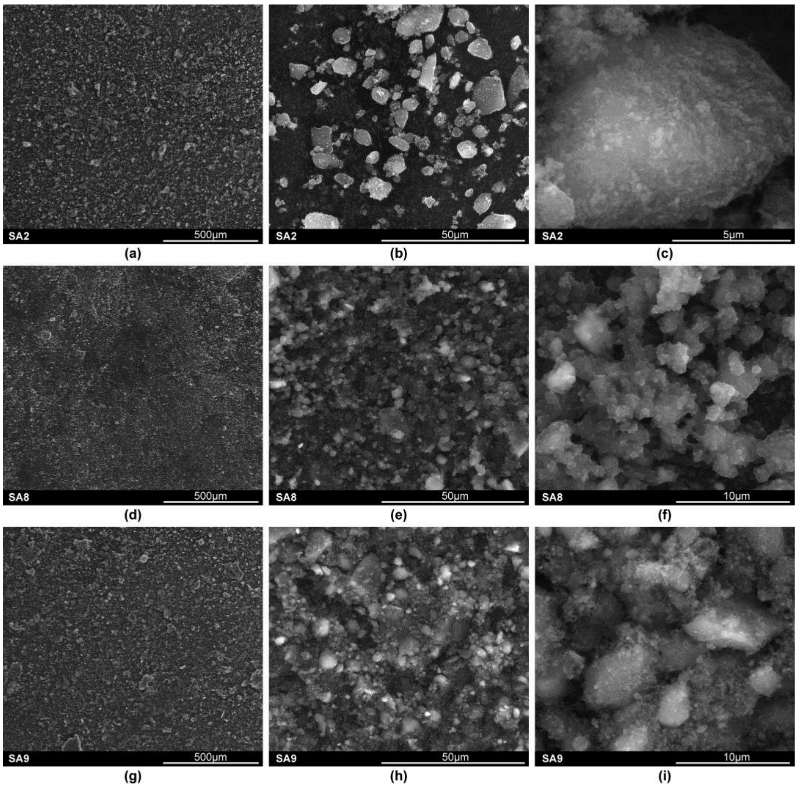

Figure 6. SEM images of the char after grinding tests: a, b, c - after 20 minutes of grinding; d, e, f - after 60 minutes of grinding; g, h, i, - after 120 minutes of grinding.

5. Conclusions

The results of preliminary investigations of char grinding conducted in a laboratory vibratory mill confirmed the possibility to use it for a very fine grinding of that material. The results of the examinations of particle size distribution of ground char contained in Table 3 as well as in Figures 3 and 4 indicate a clear impact of the grinding time on the selected size fractions and characteristic sizes of particles d_{50}, d_{80}, d_{90} and d_{99}. After 20 minutes of char grinding (test sa2), a 99% concentration of particles below 31.92 µm was obtained, while, for carbon black this requirement concerns particles of 45 µm. An increase in the grinding time up to 60 minutes (test sa6) reduced the upper limit of particle size to 23.41 µm. The results of microscopic observations (SEM) presented in Figure 7 indicate a very high dispersion ratio and the occurrence of large amounts of particles with sizes below 10 µm and 5 µm.

In accordance with the standard ASTM D1765, activated carbon black should have a specific surface area from 71 m^2/g to 130 m^2/g. The lower value of that range can be obtained in a vibratory mill already within 10 minutes of grinding. The char ground for 60 minutes had, in each of the tests, a specific surface area which was greater by nearly 8% (140 m^2/g) than the required maximal value of the specific surface area of carbon black. The specific surface area was greater by about 90 m^2/g than the specific surface area of the char before grinding (50 m^2/g). The increase of grinding time up to 120 minutes resulted in a growth of the surface area by only 23 m^2/g, without a significant change of the particle size distribution.

The particle size distribution and the specific surface area of a char are basic and indispensable, but, at the same time, not the only parameters determining its usefulness as a component for producing rubber. Therefore, in order to determine if a char is fully useful as a substitute of carbon black, it is necessary to examine the remaining properties, such as: iodine number, tinctorial strength, pH, and DBP number. The final result of determining the usefulness of the char for the production of rubber will be verified through examinations of its impact on physical and quality properties of rubber blends and rubber products.

In the paper it has been demonstrated that a char obtained from waste tires can be used to produce a material with the basic parameters (particle size distribution and specific surface area) similar to those of activated carbon black applied in the rubber industry. It has also been shown that a vibratory mill allows obtaining a char with a varying particle size distribution, including a significant amount of size fraction with dimensions of the order of a few dozen nanometers. It means that in a vibratory mill, a machine with a simple structure and a low power input, it is possible to produce powdered char, which can be used not only as a component for rubber production, but also as a valuable material for other purposes, e.g. as a component for manufacturing pigments , water-coal suspensions, a filler for polymer materials, as well as an adsorbent for removing mercury or other impurities. As a result, it is possible to reduce the costs of recycling of waste tires.

References

[1] Krajowy plan gospodarki odpadami 2022, Warszawa, 2016, Załącznik do uchwały nr 88 Rady Ministrów z dnia 1 lipca 2016 r. (poz. 784)

[1] S. Stelmach (2011) Potencjalne metody zagospodarowania karbonizatów z opon samochodowych, Archiwum Gospodarki Odpadami i Ochrony Środowiska, 13 (2011) 37-52.

[2] S. Budzyń, J. Jakóbiec, B. Tora, W. Żmuda, (2013) Laboratory analysis of rubber wastes in order to their utilization in energy sector, AGH Journal of Mining and Geoengineering, 37 (2013) 9-13.

[3] K. Jastrząb, S. Stelmach, J. Figa, (2013) Adsorbenty węglowe otrzymane ze zużytych opon przeznaczone do usuwania rtęci z gazów spalinowych, http://www.is.pcz.czest.pl/konferencje/weg2013/2008/19 (26.07.2019).

[4] Stanisław Budzyń, Barbara Tora (2015) Analysis of carbon black from tires pyrolysis, Inżynieria Mineralna = Journal of the Polish Mineral Engineering Society ; ISSN 1640-4920. — 2015 R. 16 nr 2, s. 149-154.

[5] Stanisław Budzyń, Victor Iwanicki, Andrzej Sumara, Wieslaw Żmuda, Christian d'Emal (2012) *Procédé de transformation de caoutchouc pour produire du carbonisat semi-actif et du plastifiant.* [Rubber granulate conversion process for producing a semi-active carbonized substance and a plasticizer] Patent, FR 2946054 B1

[6] Stanisław Budzyń, Victor Iwanicki, Andrzej Sumara, Wiesław Żmuda, d'Emal Christian, (2012) Rubber granulate conversion process for producing a semi–active carbonized substance and a plasticizer, Patent US 2012136112 A1 http://patenty.bg.agh.edu.pl/pelneteksty/US20120136112A1.pdf

[7] Jan J. Hycnar, Karel Honysch, Barbara Tora, Stanisław Budzyń (2017) – Physico-chemical Characteristics of Selected Alternative Fuels and their Mixtures with Carbon Fuels, Inżynieria Mineralna – Journal of the Polish Mineral Engineering Society, No 2(40), pp. 201-206

[8] Juan Daniel Martínez, Neus Puy, Ramón Murillo et all (2013) Waste tire pyrolysis – A review, Renewable and Sustainable Energy Reviews 23:179–213, DOI 10.1016/j.rser.2013.02.038

[9] Jaswinder Singh (2017) A review paper on pyrolysis process of waste tire, International Journal of Applied Research 2017; 1(13): 258-262

[10] N Cardona, F Campuzano, M Betancur, L Jaramillo and J D Martínez (2018) Possibilities of carbon black recovery from waste tire pyrolysis to be used as additive in rubber goods -a

review, IOP Conf. Series: Materials Science and Engineering 437 (2018) 012012 doi:10.1088/1757-899X/437/1/012012

[11] Barbara Tora, Stanisław Budzyń, Wiesław Żmuda, Peter Fecko, Vlastimil Kriz., (2013), The methode of organic waste pyrolysis oils utilisation] Patent PL 214925 B1 http://patenty.bg.agh.edu.pl/pelneteksty/PL214925B1.pdf

[12] Xue Zhang, Hengxiang Li, Qing Cao, (2018) Upgrading pyrolytic residue from waste tires to commercial carbon black, Waste Management & Research, 2018, Vol. 36(5) 436–444 DOI: 10.1177/0734242X18764292

[13] Jan Sidor, (2005) Badania, modele i metody projektowania młynów wibracyjnych, Rozprawy Monografie nr 150, UWND AGH, Kraków 2005

[14] Jan Sidor, (2014) Preliminary studies of production of glass micropowder in a vibratory mill, Materiały Ceramiczne - Ceramic Materials 66 (2014) 292-297.

[15] J. Sidor, (2011) The development of powder producing technology with using the vibratory mills, Powder & Bulk - Materiały Sypkie i Masowe; ISSN 1899-2021. - 2011 wyd. spec. [SyMas 2011], s. 19-23.

[16] Jan Sidor (2011) Projecting of vibrating mills. Advanced grinding: 25 th anniversary of the comminution in Bydgoszcz, eds. A. Mroziński, M. Macko, Wyd. Fundacji Rozwoju Mechatroniki, Bydgoszcz p. 225-24.

Acknowledgements

The research was supported by AGH University of Science and Technology under a subsidy No. 16.16.100. 215 and 16.16.210.476