M. NIESLER, J. STECKO, D. GIERAD, M. NOWAK, S. STELMACH

ISSN 0543-5846
METABK 62(2) 259-261 (2023)
UDC – UDK 629.11.012.5.002.68:621.1:66.014:669.17/662.781=111

COMPARISON OF THE CHEMICAL COMPOSITION OF CHAR FROM WASTE CAR TIRES TO THE COKE BREEZE USED IN THE IRON ORE SINTERING PROCESS

Received – Primljeno: 2022-09-14
Accepted – Prihvaćeno: 2022-12-05
Preliminary Note – Prethodno priopćenje

The increasing automotive development generates large amount of waste car tires, which cannot be landfilled and the reuse level of raw materials used in vehicles production must achieve at least 95 %. The calorific value of waste tires is very high and they can be considered as energy carries, for example in the form of char generated during pyrolysis process. The article presents the results of chemical analysis of char samples and parameters which are crucial from the environment and iron ore sintering process point of view. The results show, that char samples with high carbon content, low sulfur, zinc and pyrolysis oil content can be applied in the iron ore sintering process.

Keywords: waste car tires, pyrolysis, chemical analysis, iron ore sintering process

INTRODUCTION

Economic development and hence automotive development increases the generation of rubber waste. Car tires account for about 80 % of all collected rubber waste [1]. Annually almost 1,4 billion tires are produced in the world [2, 3].

Car tires have a complex structure and a lot of materials are used for their production, above all: natural rubber (NR), butadiene rubber (BR) and styrene-butadiene rubber (SBR). The morphological composition of car tires is as follows: rubber (40-50 %), soot (20-25 %), small amount of construction elements (steel, fibers) and additives (stabilizers, antioxidants) [4].

Since the landfills in Europe are expanding and car tires are considered to be very harmful for the environment, European Union introduced several legal acts, which among others banned the landfilling of tires and tires elements [5] and forced the necessity to reuse at least 95% of the raw materials used in vehicles production [6].

At present there are several ways of waste tires management: retreading, material recycling or energy recovery. However the amount of waste tires is constantly increasing, so new methods of the waste utilization should be developed. The calorific value of the waste tires is very high (31-32 MJ/kg), so they are considered as an attractive energy carrier [7].

M. Niesler (e-mail Marian.Niesler@imz.pl) – Łukasiewicz Research Network – Institute for Ferrous Metallurgy, Gliwice, Poland, J. Stecko – Łukasiewicz Research Network – Institute for Ferrous Metallurgy, Gliwice, Poland, D. Gierad – Energoekspert Sp. z o.o. Katowice, Poland, M. Nowak – Institute of Energy and Fuel Processing Technology, Zabrze, Poland, S. Stelmach – Institute of Energy and Fuel Processing Technology, Zabrze, Poland

The article presents the results of the possibility of using char from waste car tires generated in a pyrolysis process as a source of alternative fuel in the iron ore sintering process.

PYROLYSIS PROCESS

Application of char from a pyrolysis process can be an attractive alternative to co-incineration process in cement or power plants, since the energy recovery from pyrolysis or gasification processes can reach 70 %, while the co-incineration can reach only about 40 % of the energy recovery. Generally, pyrolysis process in an endothermal process, conducted in anaerobic environment in temperature above 400 °C [7-11]. During the waste tires pyrolysis following products are generated: 38-55 $\%_{mass}$ of oil fraction, 33-38 $\%_{mass}$ of char and 10-30 $\%_{mass}$ of gaseous fraction [8]. The heating values of the pyrolysis products are sufficient to apply them as fuels [7, 12]. Also research were conducted on using char as soot substitute and carbon adsorbent, steel slag former, steel bath carburizer and reducer in the metallurgical process [13-19].

MATERIALS AND METHODOLOGY

The research methodology includes acquiring of char samples, which are subjected to chemical analysis. The samples come from different parts of Poland (Wielkopolskie, Dolnośląskie and Świętokrzyskie voivodships), from different producers. The measurement method for C and S determination is coulometry. Al_2O_3, CaO, Cd, Co, Cu, Fe, K, MgO, Na, Ni, Pb, SiO_2 and Zn are determined by OES-ICP (Inductively Coupled Plasma Optical Emission Spectrometry). The measurement methods for the waste oil from tires pyrolysis is weight method. Cl is determined by spectrophotometric method and mercury analyzer is used for Hg determination. Also a comparison of chemical properties of char samples and coke breeze is performed.

CHEMICAL ANALYSIS OF CHAR SAMPLES AND COKE BREEZE

The chemical analysis of 6 waste tires char samples and coke breeze is presented in Table 1.

Table 1 **Chemical analysis of char samples and coke breeze**

Parameter / $\%_{mass}$	Coke breeze	Char sample					
		1	2	3	4	5	6
Al_2O_3	3,36	0,43	1,05	0,50	0,57	1,20	0,51
C	81,0	76,00	55,00	72,20	77,90	74,50	79,40
CaO	1,55	1,95	4,83	2,10	2,40	1,30	2,14
Cd	<0,01	<0,01					
Cl	0,083	0,40	0,47	1,76	0,43	0,08	0,44
Co	<0,01	<0,01					
Cu	<0,01	<0,005	0,014	0,02	0,03	0,02	0,02
Fe	1,73	0,36	1,31	0,36	0,72	0,39	0,69
Hg, ppm	n.t.[1]	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
K	0,039	0,16	0,22	0,24	0,07	0,09	0,06
MgO	0,48	0,07	0,75	0,65	0,74	<0,01	0,63
Na	0,12	0,06	0,11	0,14	0,07	0,13	0,06
Ni	<0,01	<0,01	0,012	<0,01	<0,01	0,02	<0,01
Oil	<0,01	16,5	0,56	0,12	13,10	0,45	23,90
Pb	<0,01	0,020	0,010	1,220	0,007	0,002	0,007
S	0,9	2,27	2,52	3,46	2,54	2,69	2,21
SiO_2	6,24	2,76	10,28	3,00	3,46	14,10	3,01
Zn	<0,01	1,93	2,38	2,65	2,81	3,09	2,26

[1] not tested

The results shows great diversity in the chemical composition of the tested samples, especially in the case of carbon content. C content is a crucial parameter in application in the iron ore sintering process, since it directly influences the calorific value of the material. The highest carbon content is observed in sample number 6 – almost 80 $\%_{mass}$, while the lowest carbon content is observed in sample number 2 – 55 $\%_{mass}$.

The following crucial parameter in char composition is oil, generated during the pyrolysis process. The pyrolysis oil is an undesirable component of input materials for the sintering process. With the temperature decrease the oil vapors settle on dust particles, pipelines and dust collectors and cause deterioration of dust collecting conditions. In sinter plants equipped with electrostatic precipitators incandescent fires of dust, settled on electrostatic precipitators construction elements, can occur [18, 19].

Char samples 2, 3 and 5 contains small amounts of the pyrolytic oil, below 0,6 $\%_{mass}$, while in the other samples the oil content is significantly higher – in sample 6 the oil reached almost 24 $\%_{mass}$. The results of C and pyrolytic oil content are show in Figure 1.

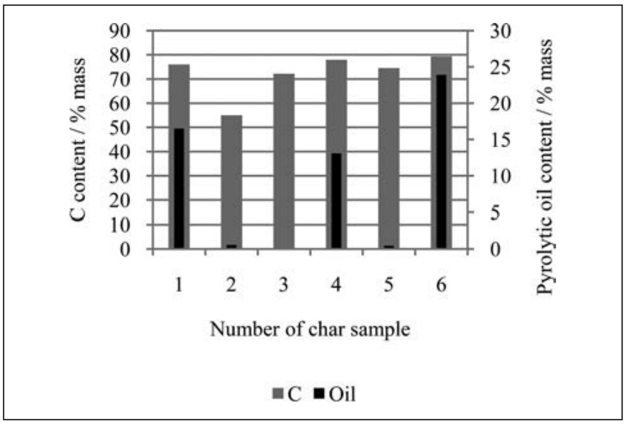

Figure 1 C and pyrolytic oil content in tested char samples

From the environmental and iron ore sintering process point of view, the sulfur and zinc content is essential and their quantity should be as low as possible. However, S and Zn are key elements in the car tires production, since they are the main vulcanization factors, enable controlling of process conduction and enhance physical properties of the rubber. The S content in tested chars varies from 2,21 $\%_{mass}$ to 3,46 $\%_{mass}$, and Zn content varies from 1,93 $\%_{mass}$ to 3,09 $\%_{mass}$. Taking into consideration both S and Zn content, sample number 1 has the most preferred composition – 2,27 $\%_{mass}$ of S and 1,93 $\%_{mass}$ of Zn. Figure 2 shows the S and Zn content in the tested samples.

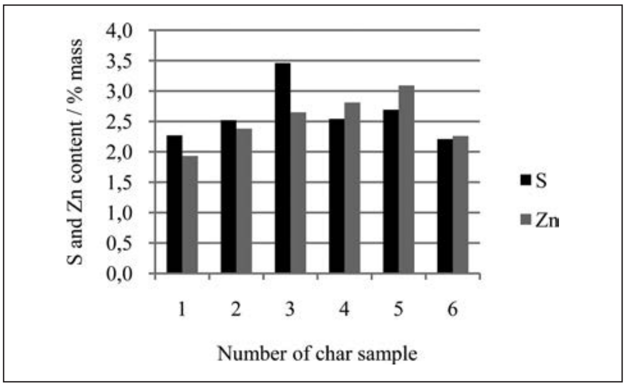

Figure 2 S and Zn content in tested char samples

DISCUSSION OF THE RESULTS

The chemical analysis assessment of the six tested samples shows that sample 1 and 6 can be applied in the iron ore sintering process. Main criteria, that were taken into account are:

- **High carbon content**. As a coke breeze (which C content is approx. 81 $\%_{mass}$) substitute, the C content in char should be as high as possible. Samples 2 and 3 are eliminated, since C content is too low (55 $\%_{mass}$ and 72 $\%_{mass}$) for the sintering process, while in the samples 1, 4, 5, 6 the C content is sufficient.

- **Low Zn and S content**. From the environment and metallurgy point of view the amount of zinc and sulfur should be as low as possible. The smallest amounts of these elements are in samples 1 and 6. Additionally, an addition of sorbent in form of hydrated lime allows to fully absorb the sulphur, while the amount of Zn cannot be easily reduced. The Zn content in sinter is undesirable, because according to the technological guidelines of the blast furnace process, the Zn content in the iron-bearing sinter should not exceed 0,015-0,020 $\%_{mass}$.
- **Pyrolytic oil content**. This is a crucial parameter which can impact the emissions to the environment and should be as low as possible. Only the sample 3 and 5 meet the requirements of BAT 31, according to which, the amount of oils in recycled materials should be below 0,5 % [16]. However the C content in sample 4 is too low for the iron ore sintering process and the amount of S and Zn in sample 6 are too high for the process and these parameters disqualify samples 3 and 5 as coke breeze substitute. The high oil content in chosen samples 1 and 6 can be reduced by application of hydrated lime, which allows to absorb the excess amount of oil.

In order to confirm the possibility of char from waste tires application in the iron ore sintering process, laboratory tests with these fuel should be conducted.

CONCLUSIONS

Based on the results of the conducted investigations it was concluded that:

- It is possible to introduce char from waste car tires to the iron ore sintering process.
- The critical parameters, which can qualify char as a coke breeze substitute are: high carbon content, low sulfur, zinc and pyrolytic oil content.
- The conducted research shows, that none of the tested sample meets all the requirements, however the sulfur and pyrolytic oil content can be easily reduced by adding hydrated lime as an sorbent.
- The chemical analysis of samples 1 and 6, shows that the C content is high enough for the iron ore sintering process and the S and Zn content is low enough for the process. However the pyrolytic oil content is too high and should be reduced by adding an appropriate absorber.

REFERENCES

[1] W. Parasiewicz, L. Pyskło, J. Magryta, Poradnik – Recykling zużytych opon samochodowych, Wydawnictwo IPG Stomil, Piastów, 2005.

[2] E. Sulman, Y. Kosivtsov, A. Sidorov, A. Stepacheva, Y. Lugovoy, Catalytic co-pyrolysis of polymeric waste and biomass as the method for energy and ecology problems solution, International Journal Of Energy And Environment 10 (2016), 100-104.

[3] M. Sienkiewicz, J. Kucinski-Lipka, H. Janik, A. Balas, Progress in used tyres management in the European Union: A review, Waste Management 32 (2012) 10, 1742-1751.

[4] Basel Convention, Revised technical guidelines for the environmentally sound management of used and waste pneumatic tyres, Columbia 2011.

[5] Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste, L 182/1 16.7.1999.

[6] Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles, L 269/34 21.10.2000.

[7] J. Martinez, N. Puy, R. Murillo, T. Garcia, M. Navarro, A. Mastral, Waste tyre pyrolysis – A review, Renewable and Sustainable Energy Reviews 23 (2013), 179-213.

[8] E. Kamińska, R. Michalski, A. Wojciechowski, Wybrane metody zagospodarowania zużytych opon, Polimery 57 (2012) 9, 656-660.

[9] G. Ferrer, The economics of tire remanufacturing, Resources, Conservation and Recycling 19 (1997) 4, 221-255

[10] M. Ischia, R. Maschio, E. Rada, M. Ragazzi, Energy recovery from tyre waste through thermal option, U.P.B. Scientific Bulletin 74 (2012) 4, 201-210

[11] C. Dębek, Modification of Pyrolytic Oil from Waste Tyres as a Promising Method for Light Fuel Production, Materials 12 (2019) 16, 880.

[12] P. Baran, D. Czarna-Juszkiewicz, P. Kunecki, M. Panek, M. Wdowin, R. Żmuda, Charakterystyka odpadu po pirolizie opon oraz analiza potencjalnego wykorzystania, Zeszyty Naukowe Instytutu Gospodarki Surowcami Mineralnymi i Energią PAN 107 (2018), 19-32.

[13] A. Sorek, M. Borecki, P. Ostrowska-Popielska, Wybrane odpady tworzyw sztucznych jako źródła paliw alternatywnych w przemyśle metalurgicznym, Prace Instytutu Metalurgii Żelaza 4 (2012), 47-57.

[16] J. Labaj, L. Blacha, A. Smalcerz, J. Wieczorek, M. Frolichova, P. Vadasz, R. Findorak, M. Niesler, Utilization of waste coal floatation concentrate for copper matte smelting, Engineering Science and Technology – An International Journal 24 (2021) 4, 996-1004.

[17] W. Stanek, M. Szega, L. Blacha, M. Niesler, M. Gawron, Exergo-ecological assessment of auxiliary fuel injection into blast furnace, Archive of Metallurgy and Minerals, 60 (2015) 2, 711-719.

[18] J. Mróz, Recykling i utylizacja materiałów odpadowych w agregatach metalurgicznych, Wydawnictwo Politechniki Częstochowskiej, Częstochowa 2006, 157.

[19] M. Hara, T. Kawaguchi, Utilization of Biomass for Iron Ore Sintering, ISIJ International 53 (2013) 9, 1599-1606.

Note: The responsible translator for English language is Martyna Nowak – Institute of Energy and Fuel Processing Technology. Poland.