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Use and Environmental Impact of Substitute Fuels in the Iron Ore Sintering Process

Abstract: The aim of the article is to present the results of the conducted research considering the application of substitute fuels in the iron ore sintering process and determination of RDF (*Refuse Derived Fuel*) potential as a substitute for part of the coke breeze in the sintering process. The tested substitute fuels were: biochars from sawmill sawdust, woodchips and sunflower husks, chars from waste car tires and "Blue Coal". The results show, that there is a possibility to replace a part of the coke breeze in the sintering process with these substitute fuels. Thanks to the substitute fuels, it is possible to obtain higher production efficiency, better sinter strength and lower CO_2 and SO_2 emissions. The tests were performed in a unique semi-industrial installation to simulate the sintering processes equipped in an innovative exhaust gas neutralization system. The article also presents potential perspectives for Refuse Derived Fuels application in the sintering process. The metallurgical industry is constantly seeking for a new fuels, in order to meet the requirements of the European Green Deal in the field of circular economy and industry decarbonization.

Key words: iron ore sintering process, waste car tires, biochar, Refuse Derived Fuel, Solid Recovered Fue

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1. Introduction

European Green Deal is a set of policy initiatives established by the European Commission, whose primary goal is to make the European Union climate-neutral by 2050. The assumptions of the Green Deal are presented in the Communication from the Commission entitled "The European Green Deal" [1]. The European Commission has established 10 key points under the Green Deal [2]:

1. "Climate-neutral" Europe
2. Circular economy
3. Buildings and renovations
4. Zero-pollution
5. Ecosystems and biodiversity
6. "From farm to fork" strategy
7. Transport
8. Money
9. R&D and innovation
10. External relations

Energy-demanding industrial sectors, which are not able to reduce the emissions by direct electrification, seek energy carriers, which are more ecological and neutral in terms of CO_2 emissions. The European Green Deal combines two aspects, i.e. the reduction of greenhouse gas emissions and the preparation of the European industry for a climate-neutral economy. The European Union countries have committed themselves to increasing the share of renewable energy sources, which, in turn, translates into an increasing share of renewable energy in their energy mix. Furthermore, the aforesaid cost is expected to decrease in the years to come. In addition, according to the Green Deal assumptions, the introduction of the circular economy concept favours production based on recycled materials [3].

In order to achieve climate neutrality by 2050, the transition of the iron and steel industry towards low-carbon manufacturing is essential. A lot of the European steelmaking plants are interested or have already started the construction or operation of pilot, demonstration or full-scale plants for the low-carbon manufacturing of steel [4].

The global production of steel in 2023 was 1.85 billion tonnes, whereas in the European Union, the production of steel amounted to 126 million tonnes [5]. The CO_2 emissions from the fuel preparation process in sintering plants amount to 0.2 t_{CO2}/t_{steel}, from the iron-making process in the blast furnace are 1.2 t_{CO2}/t_{steel} and from the steel-making process in the basic oxygen furnace amount to 0.2 t_{CO2}/t_{steel} [4]. In general, the basic fuel in the sintering process is coke breeze, however, it is sometimes replaced by anthracite [6, 7].

The metallurgical industry is constantly searching for new fuels to be used as fossil fuel substitutes [8–18]. The energy carriers which could be used in the sintering process as more ecological and neutral in terms of CO_2 emissions are, for instance, biomass and waste (refuse-derived fuels, tyre chars, etc.). In addition, the reuse of waste additionally is consistent with the assumptions of the circular economy policy.

Residual biomass, especially from the agricultural sector, is regarded as a valuable renewable energy source. In Europe, the agricultural industry generates 442,000 Gg of residues. In terms of biomass used for energy-related purposes, agricultural biomass in Europe represents 27 % of the overall biomass supply [11].

Combustible waste is considered as a potential energy carrier, the management of which should be complementary with the circular economy concept. Attractive combustible waste includes the so-called

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refuse-derived fuel (RDF), i.e. non-hazardous waste with waste code 19 12 10. Refuse-derived fuels are obtained by blending, crushing or grinding municipal or industrial waste (recovery process R12 – exchange of waste for submission to any of the operations numbered R1 to R11). Refuse-derived fuel is a very heterogeneous material, the properties of which can be "customised" (i.e. to satisfy customer-specific requirements) [12]. In general, refuse-derived flues are stored in a loose form, yet they are also available in the form of pellets (Figure 1).

The EN ISO 21640:2021 standard was established to enable the efficient trade in RDFs, promote their safe use in energy conversion and increase public trust in the above-named fuels. The standard provides a classification and specification system for solid recovered fuels (SRF), be defined as a specific part of RDF.

Figure 2 presents a simplified flow chain related to SRF, from the input of non-hazardous waste to the end use of SRF. The EN ISO 21640:2021 standard covers the areas from the point of acceptance to the point of delivery. The fuel is not considered to be SRF until it is specified and classified according to the aforesaid document. Requirements concerning how the input waste should be collected and how to use SRF are not part of the standard.

The classification system (Table 1) for SRF is based on limit values concerning three important fuel characteristics, i.e. net calorific value (NVC), chlorine content (Cl) and mercury content (Hg). Each of the classification characteristic is divided into 5 classes. A combination of the class numbers makes up a class code. For instance, a classification for an SRF sample with an average NCV of 19 MJ/kg, average Cl content of 0.5 % and Hg content (80. percentile) is NCV 3; Cl 2; Hg 2.

Presently, the largest SRF and RDF recipients in Poland are cement plants. The waste is processed in recovery process R1, principally as a fuel or another means used to generate energy. Data considering the amount of generated and processed waste were acquired from the Polish Ministry of Climate and Environment. The amount of processed SRF/RDF (Figure 3) in cement plants increased from 1.59 million Mg in 2020 to 1.83 million Mg in 2022, which constitutes approximately 90 % of all processed SRF/

Table 1. Classification system for SRF [13]

Classification characteristic	Statistical measure	Unit	Classes				
			1	2	3	4	5
Net calorific value (NCV)	Mean	MJ/kg (ar)	≥ 25	≥ 20	≥ 15	≥ 10	≥ 3
Chlorine (Cl)	Mean	% mass (d)	≤ 0.2	≤ 0.6	≤ 1.0	≤ 1.5	≤ 3
Mercury (Hg)	Median	mg/MJ (ar)	≤ 0.02	≤ 0.03	≤ 0.05	≤ 0.10	≤ 0.15
	80 percentile	mg/MJ (ar)	≤ 0.04	≤ 0.06	≤ 0.10	≤ 0.20	≤ 0.30

ar – as-received, d – dry basis

Fig. 1. Refuse-derived fuel in the loose form (left) and as pellets (right)

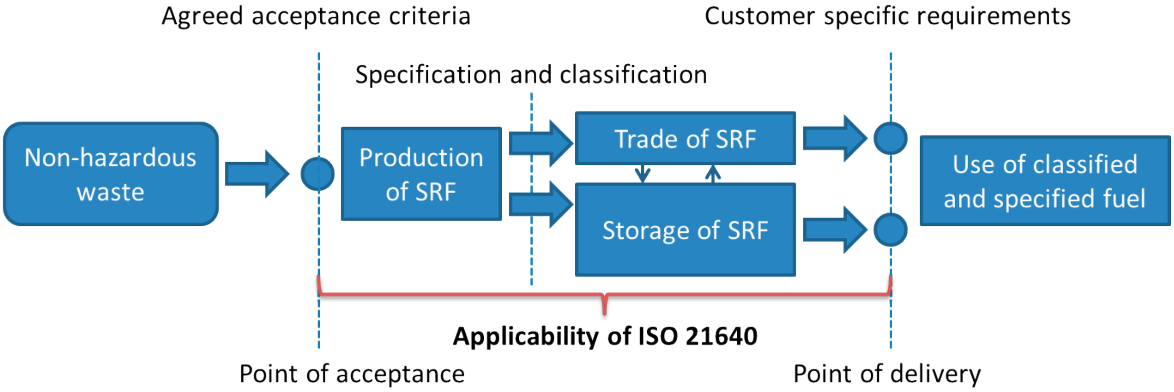

Fig. 2. Solid Recovered Fuel chain – applicability of ISO 21640 [13]

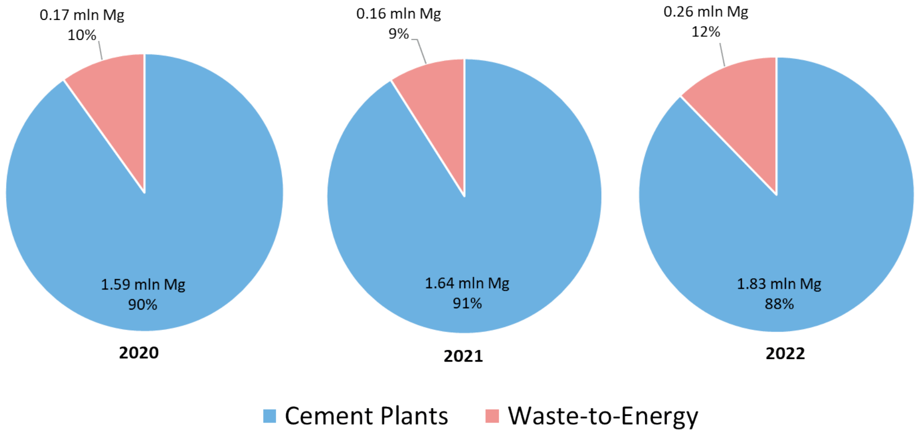

Fig. 3. Amount of processed SRF and RDF in Poland in the years 2020–2022

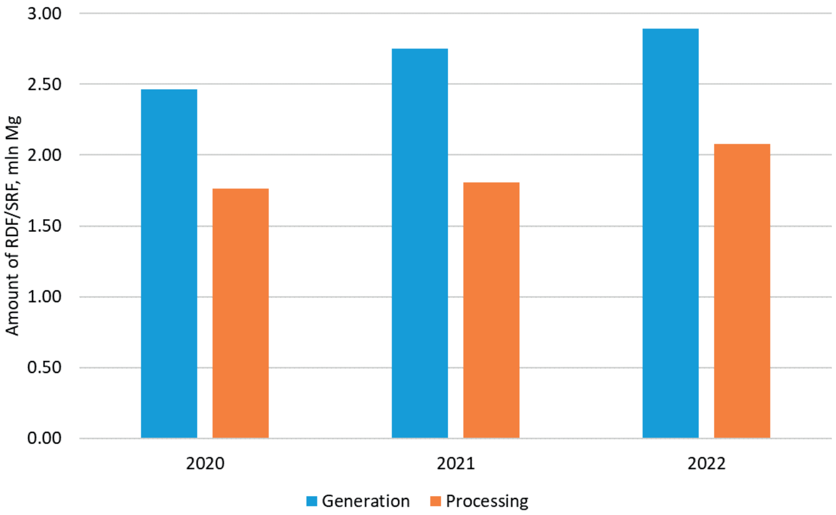

Fig. 4. Amount of generated and processed RDF/SRF in Poland in the years 2020–2022

RDF. The remaining part (approximately 10 %) is processed in waste-to-energy plants, including:

- municipal incineration plants in Warsaw, Białystok, Szczecin and Konin,
- CHP plant Fortum in Zabrze, fired only with RDF,
- other installations, using energy from waste for their own purposes.

The amount of processed SRF/RDF is lower than the amount of generated SRF/RDF (see Figure 4). The difference between generation and processing amounted to 0.70 m Mg in 2020, 0.94 m Mg in 2021 and 0.81 m Mg in 2022. As can be seen, there is still an unresolved potential of combustible waste.

Waste car tyres could also be regarded as energy carriers for metallurgical processes as their higher heating value can reach between 31 MJ/kg and 32 MJ/kg. Globally, almost 1.4 billion tyres are produced annually. The European Union has passed several legal acts banning tyre- and tyre-element-based landfilling and introducing the necessity to reuse at least 95 % of the raw materials used in vehicle production. As a result, waste car tyres are considered useful in the sintering process [14].

However, biomass and other waste products are characterised by unfavourable properties including poor grindability, low energy density, high moisture content, irregular structure (shape and size) and non-uniform composition, usually limiting their direct use as a fuel, particularly in metallurgical processes. One of the methods enabling the improvement of biomass and waste properties is pyrolysis. The main advantages resulting from the process of pyrolysis include an increased calorific value, decreased moisture content, reduced transport and storage costs as well as the reduction of energy consumption required for grinding and milling [11].

The article discussed the application of biochars obtained from biomasses, chars from waste car tyres and Blue Coal as well as the RDF potential in the sintering of iron ores.

2. Materials

The materials used in the research-related tests were chars obtained from biomass and waste car tyres and “Blue Coal”.

Biomass feedstocks used for biochar preparation were residual sawmill sawdust (in the form of pellets), residual woodchips and sunflower husks. The biochars were produced in pilot installation for the conversion of solid fuels in a circulating fluidised bed, located at the Institute of Fuel and Energy Technology in Zabrze. The pyrolysis process of biomass of grain size <10 mm was performed at a temperature of approximately 800 °C and a capacity of 100 kg/h [11].

Chars from waste car tyres were obtained from various Polish producers located in different parts of Poland (Wielkopolskie, Dolnośląskie and Świętokrzyskie Voivodeships). Waste car tyres were processed in the process of pyrolysis without the access of oxygen [14–16].

"Blue Coal" is a thermally processed (partly degassed) thermal coal which can be applied in a conventional domestic heat source. This fuel was developed by a scientific consortium of the Institute of Fuel and Energy Technology (ITPE) and Polchar Sp. z o.o. Compared to the combustion of "regular" coal, "Blue Coal" combustion leads to the reduction of emissions (CO, volatiles, B(a)P, dust, PAHs and NO_X). The properties of "Blue Coal" are similar to those of coke (applied in various metallurgical processes). Part of Łukasiewicz – GIT and ITPE cooperation involved the performance of research on the application of "Blue Coal" as a substitute for coke [17]. A related table presents data contained in reference publications in relation to the chemical analysis of chars from RDF (subsequently compared to test materials).

In terms of RDF and its heterogeneous nature, the content of sulphur may differ significantly; the RDF 2 char contained 1.2 % of sulphur, whereas the RDF 4 char contained 0.0 %.

The chemical analysis, particularly as regards the carbon content, revealed that the use of RDF could constitute another promising direction as regards the replacement of fossil fuels in the metallurgical industry. However, the strongly heterogeneous nature and considerably varying contents of chemical elements in RDF should also be taken into account.

Table 2 contains chemical analysis-related data concerning the following samples:

- one sample of comparative sinter – 100 % of coke breeze in the fuel;
- three samples of chars from waste car tyres obtained from different producers;
- two samples of "Blue Coal" – crushed and fine;
- three samples of biochars from residual pelletised sawmill sawdust (SDP), residual wood chips (WdC) and sunflower husks (HS);
- five RDF samples.

Carbon content is an essential parameter for the sintering process, requiring a specific amount of energy to take place properly. The highest carbon content was observed in RDF 1 char (93.9 %), the crushed sample of "Blue Coal" (82.36 %) and in the biochar obtained from pelletised sawdust (SDP), i.e. 82.0 %. The content of carbon in those fuels was higher than that in the coke breeze (81.0 %). In terms of the process and environmental aspects, the sulphur and zinc contents are crucial and should be as low as possible. The content of zinc in tyre char samples was relatively high (restricted within the range of 1.93 % to 3.09 %) if compared to that in the coke breeze (where it was below the limit of determination) and that in the biomass samples (where the Zn content amounted to than 0.013 %). The content of sulphur in tyre char samples 1 and 2 (above 2 %) was significantly higher in comparison with that in the coke breeze and the remaining samples (below 1 %). In terms of RDF and its heterogeneous nature, the content of sulphur may differ significantly; the RDF 2 char contained 1.2 % of sulphur, whereas the RDF 4 char contained 0.0 %.

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Table 2. Chemical analysis of the samples, i.e. biochars, chars from waste car tyres, Blue Coal and chars from RDF (based on [11, 12] and [14–22])

Parameter	Unit	Coke Breeze	SDP biochar	WdC biochar	SH biochar	Crushed "Blue Coal"	Fine "Blue Coal"	Tyre char 1	Tyre char 2	Tyre char 3	RDF 1 char	RDF 2 char	RDF 3 char	RDF 4 char	RDF 5 char
Al_2O_3	wt%	3.36	0.067	0.068	0.043	n.d.	n.d.	0.43	1.20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CaO	wt%	1.55	0.66	0.90	1.66	n.d.	n.d.	1.95	1.30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cd	wt%	<0.01	n.d.	n.d.	n.d.	n.d.	n.d.	<0.01	<0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	wt%	<0.01	n.d.	n.d.	n.d.	n.d.	n.d.	<0.01	<0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	wt%	<0.01	<0.01	<0.01	0.09	n.d.	n.d.	<0.005	0.02	0.14	n.d.	n.d.	n.d.	n.d.	n.d.
Fe	wt%	1.73	0.59	0.17	0.24	n.d.	n.d.	0.36	0.39	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
K	wt%	0.039	0.15	0.16	1.43	n.d.	n.d.	0.16	0.09	n.d.	n.d.	n.d.	n.d.	0.02	n.d.
MgO	wt%	0.48	4.36	0.23	1.33	n.d.	n.d.	0.065	<0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Na	wt%	0.12	<0.01	0.019	<0.01	n.d.	n.d.	0.06	0.13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	wt%	<0.01	n.d.	n.d.	n.d.	n.d.	n.d.	<0.01	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	wt%	<0.01	n.d.	n.d.	n.d.	n.d.	n.d.	0.020	0.002	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SiO_2	wt%	6.24	3.24	0.64	0.48	n.d.	n.d.	2.76	14.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	wt%	<0.01	<0.01	0.01	0.013	n.d.	n.d.	1.93	3.09	2.91	n.d.	n.d.	n.d.	0.05	n.d.
C	wt%	81.0	82.0	75.0	73.0	82.36	71.16	76.00	74.50	75.1	93.9	73.7	80.2	61.3	77.2
S	wt%	0.9	0.31	0.33	0.15	0.40	0.61	2.27	2.69	0.97	0.9	1.4	0.3	0.0	0.6
Cl	wt%	0.083	0.02	0.04	0.09	n.d.	n.d.	0.40	0.08	n.d.	n.d.	n.d.	1.9	8.5	n.d.
Hg	ppm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<0.1	<0.1	n.d.	n.d.	0.009*	n.d.	n.d.	n.d.

* wt%, n.d. – no data

strongly heterogeneous nature and considerably varying contents of chemical elements in RDF should also be taken into account.

3. Experimentation

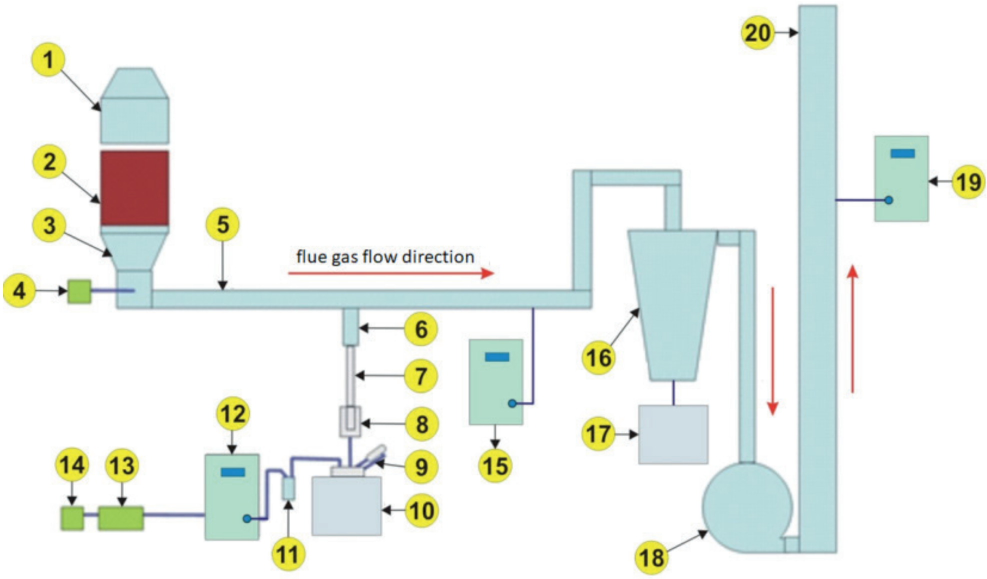
Experiments involving the simulation of the sintering processes were performed using a semi-industrial installation consisting of a sintering site equipped with sintering pans of working heights of 550 mm and 300 mm and a 250 kW ignition furnace. The installation also features an innovative exhaust gas neutralisation system (belonging to Łukasiewicz – GIT, Poland). The gas purification process was performed using a catalytic ceramic filter of high thermal resistance, enabling gas purification up to 400 °C. The filter was additionally provided with a sorbent dosing system (used to improve the neutralisation of harmful gas components). The schematic diagram of the installation is presented in Figure 5, whereas Figure 6 contains a photograph of the semi-industrial sintering process installation.

Sintering process tests were performed in accordance with all the procedures and conditions applied for industrial sintering belts operated at integrated steel plants (i.e. the composition of the sintering mixture, retention time in the ignition furnace, pressure, sintering mixture height, addition of calcium oxide, mixture basicity and amount of sinter return). The blends for the sintering process contained iron ores in the form of concentrates, low silica ores and fine-grained iron ore, fluxes (dolomite and limestone) and coke breeze or its blends with alternative fuels (biochars, chars, “Blue Coal”). The unit consumption of the mixture blends in the tests was as follows [11–17]:

- 46.4 kg/Mg of sinter (79 %) of coke breeze and 12.3 kg/Mg of sinter (21 %) of pelletised sawdust (SDP);
- 50.6 kg/Mg of sinter (90 %) of coke breeze and 5.9 kg/Mg of sinter (10 %) of wood chips (WdC);
- 51.3 kg/Mg of sinter (88 %) of coke breeze and 6.9 kg/Mg of sinter (12 %) of sunflower husks (SH);
- 0.00 kg/Mg of sinter (0 %) of coke breeze and 59.39 kg/Mg of sinter (100 %) of crushed “Blue Coal”;
- 31.5 kg/Mg of sinter (45 %) of coke breeze and 37.8 kg/Mg of sinter (55 %) of fine “Blue Coal”;
- 46.87 kg/Mg of sinter (78 %) of coke breeze and 13.11 kg/Mg of sinter (22 %) of tyre char 1;
- 52.2 kg/Mg of sinter (89 %) of coke breeze and 6.5 kg/Mg of sinter (11 %) of tyre char 2;
- 47.2 kg/Mg (79 %) of sinter of coke breeze and 12.7 kg/Mg of sinter (21 %) of tyre char 3.

4. Results and discussion

Table 3 presents the results of the sintering tests, sintering process parameters, sinter strength and chemical composition. I addition, the table presents the results of sintering tests conducted by Han J. et al. [18]: RDF 0 % and RDF 35 %, corresponding to the RDF substitution ratio. It was possible to observe that the production efficiency in most of the samples was higher than that related to the comparative sinter. In terms of the biochar from sunflower husks (HS) as well as tyre char 2 and tyre char 3, the production efficiency was slightly lower than that related to 100 % coke breeze. In turn, as regards tyre char 1, the production efficiency was only significantly lower (29.73 Mg/m^2/24 h) – marked red. In terms of RDF, it was also possible to observe an increase in production efficiency from 32.40 Mg/m^2/24 h to 37.92 Mg/m^2/24 h. As mentioned before, from the environmental point of view, the contents of zinc and sulphur are significant and should be as low as possible. The content of Zn in the sinters from biochars and “Blue Coal” samples was similar to that of the



1. Natural gas burner
2. Sintering bed
3. Temperature measurement
4. Dust collection before the ceramic filter input
5. Flue gas pipeline
6. Collection point (stub pipe)
7. Thermostated probe
8. Cellulose filter (filter cup)
9. Absorber of organic compounds
10. Condenser with bottle for condensate
11. Moisture absorber
12. Suction pump with control system
13. Exhaust gas analyser (GA40Tplus)
14. Exhaust gas analyser (GA20)
15. Analyser – continuous raw gas analysis
16. Ceramic filter
17. Dust collection from ceramic filter tank
18. Fan
19. Analyser – continuous purified gas analysis
20. Stack

Fig. 5. Schematic diagram of a semi-industrial scale installation for the sintering of iron ores

Fig. 6. Semi-industrial installation for the sintering of iron ores (left) equipped with a gas purifying system (right)

comparative sinter (approximately between 0.01 % and 0.012 %). In turn, the content of zinc in the sinter obtained from all tyre char samples was significantly higher, i.e. restricted within the range of 0.023 % to 0.049 % (marked red). As regards the content of sulphur, the sinters obtained from crushed Blue Coal and tyre char 2 were characterised by a similar content of sulphur in comparison with that of the comparative sinter (marked green). In the sinters obtained from sawdust pellets and fine Blue Coal the S, the content of sulphur exceeded 0.020 %. In the remaining samples, the content of sulphur was nearly twice as high as that present in the comparative sinter. Another essential parameter of the sinters is strength. The addition of tyre chars resulted in the obtainment of slightly higher strength, whereas the addition of RDF led to strength reduction. In other samples, the strength was comparable with that of the comparative sinter.

Table 4 presents the average composition of exhaust gases on the dirty side (before the catalytic ceramic filter) and on the clean side (in the emitter). Emission parameters such as CO_2, CH_4, SO_2 and NO_X were measured in a continuous way using stationary analysers, whereas dust was measured periodically. Dust was separated on a specially designed cellulose filter and weighed before and after the measurement. The dust concentration was determined on the basis of the difference in weight. Three sintering tests were performed in each series of tests (the results presented in Table 4 are averaged). It was possible to notice that the cleaning system made it possible to obtain a significant reduction in CO_2, CH_4, SO_2, NO_X and dust. In addition, the above-named Table presents the results of sintering tests performed by Han J. et al. [18]: RDF 0 % and RDF 35 %, corresponding to the RDF substitution ratio. The concentration profiles of CO, CO_2, SO_2 and NO_X in flue gases were measured online using a gas analyser located before dust collectors. The results presented are averaged.

The use of biochars resulted in slightly higher CO_2, CO and NO_X emissions in comparison with those in the exhaust gases generated during sintering with coke breeze only. An exception was the content of NO_X in the exhaust gas formed during the process involving the use of SDP biochar, in relation to which the concentration amounted to 190 ppm. The elevated level of CH_4 in the biochars from woodchips (29 ppm) and sunflower husks (29 ppm) was probably related to the higher content of volatile matter in the biochars. The sintering process with biochar application revealed a significant decrease in SO_2 emissions, which was the result of the lower content of sulphur in the biomasses (marked green).

The use of crushed and fine "Blue Coal" had a diverse impact on flue gases. The CO_2 and NO_X (crushed "Blue Coal") contents were lower, whereas the contents of CO, CH_4, SO_2 and dust were higher.

The contents of O_2, CO_2 and NO_X in flue gases from the sintering blends with tyre chars were comparable to the emission resulting from the use of coke breeze only, which indicated the correct course of the sintering process. The stable CO content in the process gases was essential from the sintering technology point of view. The fuels used in the process transferred their chemical energy at the appropriate level to the sintering blend. The contents of CH_4, SO_2 and dust in the flue gases from sintering blends with tyre chars were higher than those in the flue gases obtained only from coke breeze. The significant dust emissions could be attributed to the blowing of some of the chars during the sintering process.

The use of RDF resulted in a decrease in CO_2 and SO_2 concentration from 7.77 % to 5.93 % and 15 ppm to 5 ppm respectively. However, the concentration of CO and NO_X increased from 0.23 % to 0.42 % and 109 ppm to 158 ppm respectively. A decrease in the emission of CO and NO_X would require the application of the flue gas recirculation process.

In order to lower the SO_2, NO_X and dust emissions, it was necessary to apply preventive measures. The use of hydrated lime as a sorbent was accompanied by the complete absorption of the sulphur contained in the process gases (marked green). The sorbent probably also absorbed part of the CO_2, which was a positive effect, enabling a decrease in the emission of greenhouse gases. A decrease in the emission of NO_X and dust necessitated the use of a ceramic filter with a catalyst on the layer. Through the oxidation of combustible components and neutralisation to CO_2, N_2 and H_2O, the ceramic filter enabled the integrated reduction of pollutants.

The higher contents of CO and CH_4 could result from the incomplete combustion of the substitute fuels during the process.

Table 5 presents the contents of polyaromatic hydrocarbons (PAHs), dioxins and furans (PCDD/PCDF) in the dust collected from the catalytic ceramic filter after the sintering process with coke breeze and biochars. The highest contents of PCDD/PCDF and PAH as well as toxic equivalent TEQ could be observed in the dust after the sintering process with sunflower husks. The elevated level of PAHs and PCDD/F was also detected in the biochar obtained from woodchips, reaching 5.7 mg/sample (PAHs) and 166.8 ng/sample (PCDD/F). The lowest content of dioxins/furans was found in sawmill sawdust biochar

Table 3. Parameters of the sinters (based on [11–17, 18])

Parameter	Unit	Comparative sinter	Biochar SDP	Biochar WdC	Biochar SH	Crushed BlueCoal	Fine BlueCoal	Tyre char 1	Tyre char 2	Tyre char 3	RDF 0 %	RDF 35 %
Sintering process parameters												
Production efficiency	$Mg/m^2/24$ h	37.06	39.86	38.66	36.51	40.66	38.1	29.73	36.23	37.01	32.40	37.92
Unit consumption of coke breeze	kg/Mg of sinter	57.6	46.4	50.6	51.3	0.0	31.5	46.87	52.2	47.2	n.d.	n.d.
Unit consumption of alternative fuel	kg/Mg of sinter	0.0	12.3	5.9	6.9	59.39	37.8	13.11	6.5	12.7	n.d.	n.d.
Sintering time	min	21.92	19.54	20.58	21.53	19.48	20.51	27.14	22.27	21.44	n.d.	n.d.
Sinter strength												
Strength ISO T	%m/m	70.81	70.57	70.76	70.58	69.72	69.83	73.26	71.89	73.08	65.80	60.20
Chemical composition of sinter												
Fe	wt%	54.63	54.35	54.58	54.43	54.92	54.70	55.43	54.59	53.84	n.d.	n.d.
FeO	wt%	8.31	6.32	6.30	6.18	8.71	6.93	5.35	8.13	6.33	n.d.	n.d.
SiO_2	wt%	9.25	10.25	9.73	9.75	9.65	9.62	9.65	9.25	9.80	n.d.	n.d.
CaO	wt%	10.78	10.92	11.15	11.09	10.16	10.60	10.38	10.78	11.44	n.d.	n.d.
Al_2O_3	wt%	0.66	0.56	0.57	0.58	1.26	1.31	0.54	0.66	0.52	n.d.	n.d.
TiO_2	wt%	0.015	0.019	0.019	0.018	0.210	0.034	0.013	0.015	0.013	n.d.	n.d.
MgO	wt%	1.38	1.31	1.24	1.26	1.25	1.22	1.25	1.38	1.34	n.d.	n.d.
P	wt%	0.026	0.021	0.024	0.023	0.040	0.036	0.019	0.026	0.019	n.d.	n.d.
Mn	wt%	0.024	0.016	0.029	0.030	0.028	0.028	0.022	0.024	0.023	n.d.	n.d.
S	wt%	0.017	0.024	0.035	0.031	0.018	0.023	0.035	0.017	0.032	n.d.	n.d.
K_2O	wt%	0.027	0.023	0.029	0.033	0.072	0.077	0.016	0.026	0.019	n.d.	n.d.
Na_2O	wt%	0.031	0.030	0.037	0.036	0.071	0.069	0.044	0.039	0.037	n.d.	n.d.
Zn	wt%	0.012	0.010	0.010	0.010	0.012	0.011	0.046	0.023	0.049	n.d.	n.d.
Cl	wt%	0.012	0.005	0.010	0.006	0.033	0.029	0.024	0.0063	0.013	n.d.	n.d.

Table 4. Average composition of flue gases from tests of sintering of iron ores (based on [11, 15, 17, 18])

Parameter	Unit	Comparative sinter	Biochar SDP	Biochar WdC	Biochar SH	Crushed BlueCoal	Fine BlueCoal	Tyre char 1	Tyre char 2	Tyre char 3	RDF 0%	RDF 35%
Content in raw exhaust gases (dirty side)												
O_2	vol.%	13.5	12.9	13.91	12.31	13.86	12.98	13.95	13.0	13.1	n.d.	n.d.
CO_2	vol.%	8.24	8.65	8.48	9.14	7.30	8.00	7.14	8.7	8.5	7.77	5.93
CO	vol.%	0.96	1.20	1.21	1.16	1.52	1.97	1.08	1.3	1.4	0.23	0.42
CH_4	ppm	19	17	29	25	48	29	30	36	33	n.d.	n.d.
SO_2	ppm	134	64	89	47	255	302	249	228	328	15	5
NO_x	ppm	216	190	227	259	203	218	173	225	210	109	158
Dust	mg/Nm^3	222	342	279	265	803	624	n.d.	570	491	n.d.	n.d.
Content in cleaned exhaust gases (clean side)												
O_2	vol.%	17.89	17.69	17.71	17.69	n.d.	n.d.	n.d.	18.6	18.3	n.d.	n.d.
CO_2	vol.%	4.20	4.30	4.08	4.21	n.d.	n.d.	n.d.	2.9	3.1	n.d.	n.d.
CO	vol.%	0.52	0.62	0.64	0.57	n.d.	n.d.	n.d.	0.5	0.6	n.d.	n.d.
CH_4	ppm	13	17	9	17	n.d.	n.d.	n.d.	16.3	9.3	n.d.	n.d.
SO_2	ppm	0	0	0	0	n.d.	n.d.	n.d.	<0.1	<0.1	n.d.	n.d.
NO_x	ppm	116	102	113	131	n.d.	n.d.	n.d.	77.7	81.0	n.d.	n.d.
Dust	mg/Nm^3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<0.1	<0.1	n.d.	n.d.

Table 5. Contents of PAHs, PCDD and PCDF in the dust collected from the catalytic ceramic filter (based on [11])

Component	Coke Breeze	Biochar SDP	Biochar WdC	Biochar SH
PAHs, mg/sample	1.6	2.5	5.7	6.3
Sum of PCDD and PCDF, ng/sample	155.2	116.7	166.8	264.3
Toxic Equivalent TEQ	17	14	19	29

(116.7 ng/sample, marked green); the content was 25 % lower than that related to coke breeze (155.2 ng/sample). Hence, taking into consideration the amounts of PAHs and PCDD/F generated during the process and appearing in the process gas, it was concluded that biochars from residual WdC or SDP could be efficiently used as substitutional fuel in the iron-ore sintering process.

In order to evaluate the sintering process with substitute fuels in terms of environmental protection, the process was performed in a manner meeting the environmental requirements of Best Available Techniques-related (BAT) conclusions concerning iron and steel production [23]. The following BAT conclusions were fulfilled:

- BAT 20 concerning the reduction of dust emission. In relation to the bag filter, the dust emission level was < 1–15 mg/Nm^3, whereas, in relation to the advanced electrostatic precipitator, the emission amounted to < 20–40 mg/Nm^3. The application of the ceramic filter allowed decreasing the level of dust below the determinability limit of < 1.0 mg/Nm^3.
- BAT 22 concerning the reduction of sulphur oxide emission. The SO_2 BAT-associated emission level should be < 350–500 mg/Nm^3 in relation to the injection of adequate adsorption agents. The adsorbent (hydrated lime) made it possible to decrease the emission of SO_2 below the determinability limit.
- BAT 23 concerning the reduction of nitrogen oxide emission. The NO_X BAT-associated emission level in relation to NO_X and selective catalytic reduction (SCR) was < 120 mg/Nm^3. The application of the "end-of-pipe" technique including ceramic inputs enabled a significant decrease in the emission of NO_X.

5. Conclusions

The above-presented tests concerned the iron-ore sintering process involving the use of substitute fuels as part of coke breeze justified the formulation of the following conclusions:

1. The substitute fuels should be characterised by high carbon content. The content of carbon in sawmill sawdust and crushed "Blue Coal" was similar to that in the coke breeze and slightly lower in the remaining substitute fuels. Refuse-derived fuel (RDF) could also contain high amounts of carbon, i.e. even up to 93.9 %.
2. Substitute fuels should be characterised by low zinc and sulphur contents. The content of zinc in the tyre chars was very high (1.93–3.09 %) and, because of this fact, approximately 10 % content was permissible in the sinter blend. The content of zinc in the biochars was similar to that in the coke breeze. In turn, the content of zinc in RDF was slightly higher (0.05 %). The addition of the sorbent in the form of hydrated lime made it possible to fully absorb the sulphur. The content of zinc could not be easily

reduced and, by transferring to steel, it was responsible for the deterioration of steel properties. The high content of sulphur in substitute fuels could be reduced by using the sorbent in the exhaust gas neutralisation system.

3. The production efficiency concerning the test fuels was similar to or higher than that related to the coke breeze. Only in terms of tyre char 1, the efficiency of production was significantly lower.
4. The application of the catalytic ceramic filter and hydrated lime as a sorbent enabled a significant NO_X reduction and the complete elimination of SO_2 in exhaust gases.
5. The presence of PCDD/F and PAH was noted for biochars and was higher in comparison to that in the coke breeze. Only the content of PCDD/F in sawmill sawdust was lower than that in the coke breeze.
6. The experiments revealed that biochars, “Blue Coal” and chars from waste car tyres could be used in the iron-ore sintering process.
7. The overview of scientific reference publications combined with high availability and the requirements of the European Green Deal indicate that combustible waste (RDF/SRF) can be used in the iron ore sintering process. Related experiments concerned with RDF/SRF in the sinter blend will be conducted in the semi-industrial iron ore sintering process installation.

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