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Investigation of fly ash from co-combustion of alternative fuel (SRF) with hard coal in a stoker boiler

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Abstract: Results of fly ashes from combustion of hard coal and co-combustion of alternative fuel (SRF) with coal in the stoker boiler WR-25 type studies have been shown. Samples of fly ashes were acquired during industrial combustion tests of hard coal and blend of coal with 10% SRF. The scope of comparative research included: chemical composition, contents of combustible parts and trace elements and also of microscopic analysis. The specific surface area SBET was established and tests of water extract were conducted. Chemical composition of mineral substance of both studied ashes is similar. Main ingredients are: SiO₂, Al₂O₃, Fe₂O₃ and CaO. Fly ash from co-combustion of SRF with coal in a stoker boiler is characterized by high contents of combustible parts (on 30% level), higher than ash from hard coal combustion. Both tested ashes are characterized by specific surface area SBET on the level of 8–9 m²/g. In porous structure mesopores are dominant (>60%), and their volume is higher for fly ash from co-combustion of SRF with coal. Fly ash from co-combustion of waste is characterized by high contents of not show leachability exceeding acceptable values for wastes different than hazardous. The microscopic structure of fly ashes from combustion of hard coal and co-combustion of alternative fuel studies showed crucial differences, especially in reference to organic material. Presented research results have shown that fly ash from co-combustion of SRF with coal in a stoker boiler showed crucial differences, especially in reference to organic material. Presented research results have shown that fly ash from co-combustion of SRF with coal in a stoker boiler can obtain the status of non-hazardous waste.

Introduction

Manufacturing and usage of alternative fuels is a chance of recovering energy contained in waste, not only in the installations designed for this purpose but also in such branches as cement and energy production (Fyffe et al. 2016, Thiel and Thomé-Kozmiensky 2012, Del Zotto et al. 2015, Wasielewski and Sobolewski 2015, Żygadło 2018, Wasielewski et al. 2018). According to the system developed by the European Center for Accreditation (CEN), the term SRF (solid recovered fuel) is defined as solid fuel prepared from non-hazardous waste to be utilized for energy recovery in incineration or co-incineration plants and meeting the classification and specification requirements laid down in EN 15359 (EN 15357 2011). However, the SRF cannot be considered as fossil fuel. Co-combustion of fuels from waste in energetic installations has many years of tradition in European Union countries, although in domestic conditions it is currently in the initial development phase (Sobolewski et al. 2006). However, it arouses great interest, mainly due to the possibility of reducing the costs of electricity and heat production (Wasielewski and Sobolewski 2015). Fuels from waste are a cheaper energy carrier in comparison to fossil fuels and also contain a biodegradable fraction (Jagustyn et al. 2014). This enables the classification and settlement of the generated electricity and heat as coming from renewable sources and reduces the costs of CO₂ emissions (Wasielewski and Bałazińska 2018).

One of the interesting issues (for both environmental and economic reasons) regarding co-combustion of the SRF and fossil fuels is the characteristics of the co-combustion by-products, including fly ash. The possibilities of managing fly ash from fossil fuel combustion and biomass combustion/ co-combustion are the subject of many studies (Basu et al. 2009, Ahmaruzzaman 2010, Saraber 2012, Attarde et al. 2014, Uliasz-Bocheńczyk et al. 2015). Commercial use of fly ashes is limited due to strict standards regarding their quality. Physical and chemical properties of fly ash depend on the type of combusted material as well as on the technology used in the combustion process (Ahmaruzzaman 2010, Jarosiński 2013, Uliasz-Bocheńczyk et al. 2015). Fly ashes are dusty materials and they exhibit very uniform grain distribution. Ash grains arisen in conventional boilers have a spherical shape of particles size in the range of $0.01 \div 350 \ \mu m$ but fly ashes from the fluidized bed boilers are particles of very irregular shapes and elongated edges usually in size not exceeding 100 µm (Wójcik et al. 2017, Ahmaruzzaman 2010). Fly ash



density falls in the range of 1900÷2800 kg/m³, but usually reaches the value of 2000 kg/m³ (Bastian 1980). In Poland, annually about 4.2 million Mg of fly ash is created, mainly from combustion/co-combustion of fossil fuels and biomass processes, of which only a small part is transferred to the recycling process, especially in construction and road sector (Wójcik et al. 2017). Apart from construction application, there are known also examples of utilization of fly ashes as the adsorbents of pollutants from sewage (Polowczyk et al. 2010, Janos et al. 2003, Jain et al. 2003). One of the methods of managing highly alkaline ashes from fluidized boilers formed during the combustion of hard coal is their agricultural usage as unconventional calcium-magnesium fertilizers (Basu et al. 2009, Bielińska et al. 2009). Fly ashes find their application in mining as constituents of the cavities backfilling (Plewa et al. 2013).

Fly ashes properties from co-combustion of wastes and coal processes can differ from the products of combustion/ co-combustion of fossil fuels and biomass. Pollutants occurring in waste, especially heavy metals, during their co-combustion with fossil fuels undergo concentration in fly ash and hinder its economic usage. These fly ashes, when classified as hazardous waste, will not find economic usage, at the same time raising significantly costs of their storage. Therefore, research of solid by-products from the cocombustion with wastes has significant meaning, especially in the aspect of comparing them with solid products of fossil fuels combustion. Thus far national experiences in this field are fairly modest and mainly concern co-combustion of SRF in fluidized bed boiler (Sciubidło and Nowak 2018) or sewage sludge combustion (Szarek and Wojtkowska 2018). Only one national combined-heat-and-power (CHP) plant in Zabrze conducts SRF co-combustion with hard coal and biomass in a fluidized bed boiler on industrial scale. Co-combustion of waste with coal in different types of boiler installations in Poland so far has not entered a phase of commercial operations, but there have been many industrial research activities/tests conducted (Wasielewski et al. 2018, Stelmach and Wasielewski 2008). There is no information found about the fly ash from stoker--fired boilers in the literature corresponding to the study of fly ash properties from co-firing SRF with fossil fuels in various types of boilers.

The paper presents selected test results of the solid combustion by-products (with significant emphasis on fly ash) acquired during industrial tests of SRF co-combustion with hard coal in the stoker boiler, type WR-25. These installations belong to the most widespread in Polish district heating systems. The physical and chemical properties of fly ash from co-combustion of SRF with hard coal in stoker boilers have not been the subject of detailed research in Poland.

Materials and research methodology

Industrial research of SRF co-combustion with hard coal was conducted in boiler installation of District Heating Facility in Racibórz, Poland. The boiler WR-25 (SEFAKO) used in the test constitutes a high-temperature water tube boiler with travelling grate and forced draught. The boiler is equipped with a single step fly ash precipitation system, which consists of cyclone batteries.

2 series of tests were conducted:

- combustion of hard coal,
- combustion of coal blend with 10% mass contribution of SRF.

Fuel blend was made at the storage yard/landfill from weighed portions of hard coal (45 Mg) and alternative fuel (5 Mg) with use of a loader. Both coal and SRF mixture were transported to boiler coal hoppers, then loaded on a grate, securing a constant thickness of the loaded fuel layer. During both tests, the boiler was working with similar capacity.

The SRF constituted the mixture of fractions: plastics (approx. 30%), wood (approx. 30%), paper and cardboard (approx. 20%), fabric (approx. 10%), and rubber (approx. 10%) that came from the municipal waste sorting installation. According to the information obtained from the manufacturer – the SRF manufacturing process involved crushing of a waste material for granulation size < 20 mm and compacting without additional binder using a prototype extruder. Compacting of SRF was aimed at improving its transport characteristics. The material had a compact form (fragments below 40 mm). SRF appearance is depicted in Figure 1.

Samples of the combusted materials and their mixture (taken every 60 minutes during the test from the surface of travelling grate) were subjected to averaging/blending then to tests that comprised: technical and ultimate analyses and also chemical composition of ash and determination of trace elements (Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Cd, Hg). Bulk density was also determined. Separate characteristics have



Fig. 1. The appearance of the alternative fuel used in the tests



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been established according to the test methodology described in Polish Standards and also in technical procedures of the Institute for Chemical Processing of Coal. Samples of fly ash were taken every 60 minutes from the hopper of cyclones dedusting equipment, then after averaging/blending they were subjected to tests in a range of: chemical composition, contents of combustible parts (loss on ignition), contents of trace elements and also of microscopic analysis. For both samples of fly ash the specific surface area S_{BET} was established. Tests of water extract (the so-called Test of Agreement) were also conducted. During both tests, samples of slag were also collected and contents of combustible parts and trace elements were determined. The results of these studies were subjected to comparative analysis. Table 1 presents a collective summary of indicators along with a reference to the standard methods according to which the analyses were carried out.

Tests of Agreement were conducted according to PN-EN 12 457-4 standard and Regulation of the Minister of Economy of 16 July 2015 regarding issuing permission to store waste on landfills (Journal of Laws of 2016 item 1277, enclosure 3).

Parameters of the porous structure of both fly ashes were established based on the measurement of the adsorption/ desorption N_2 isotherms as an adsorbate at 273K in a 3Flex analyzer (Micrometrics) in relative pressure range of 0–0.99 (adsorption) and also of 0.99–0.10 (desorption). Before isotherms measurement, the samples were degassed in the temperature of 423K in vacuum for about 24 hours.

Microscopic analysis was conducted with use of the AxioImager M1m polarizing microscope (Carl Zeiss/Germany). Samples for microscopic analysis have been prepared by embedding them in an acrylic resin and polishing using of the automatic grinding and polishing machine (Struers), polishing discs and also diamond suspensions and silicon oxide suspension. Observation of samples was conducted in the polarized reflected light in the presence of Lambda plate , using magnification of 500 times in oil immersion.

Results and discussion

The results of establishing the physical and chemical properties of every combusted material are shown in tables 2–4.

SRF used in industrial tests is characterized by good energetic parameters, close to hard coal in a range of contents of moisture and lower heating value (LHV). The content of ashes in SRF is lower than in hard coal. In comparison to the tested coal – SRF has higher volatiles content and lower sulphur content. SRF has 5 times more chlorine than the tested hard coal. Increased content of chlorine can have an influence on the higher hydrogen chloride, polychlorinated dioxins and furans emission during its combustion. High content of chlorine creates also corrosion threat for metal elements in the boiler installation and in the flue gas cleaning system (Thiel and Thomé-Kozmiensky 2012, Del Zotto et al. 2015). These threats can be reduced by a small (10%) share of alternative

Fuerrisetien	Test method/standard				
Examination	coal, blend of coal and SRF	SRF			
Moisture content	PN-ISO 589:2006, met. B1	PN-EN 15414-3:2011			
Ash content	PN-ISO 1171:2002	PN-EN 15403:2011			
Volatile matter	ISO 562:2010	PN-EN 15402:2011			
Coal content	ISO 29541:2010	PN-EN 15407:2011			
Hydrogen content	ISO 29541:2010	PN-EN 15407:2011			
Sulphur content	ISO 19579:2006	PN-EN 15408:2011			
Nitrogen content	ISO 29541:2010	PN-EN 15407:2011			
Chlor content	PN-G-04534:1999	PN-EN 15408:2011			
Fluor content	PN-82/G-04543	PN-EN 15408:2011			
High heating value	ISO 1928:2009	PN-EN 15400:2011			
Lower heating value	ISO 1928:2009	PN-EN 15400:2011			
Bulk density	PN-EN ISO 17828:2016	Q/LP/37/A:2011			
$\begin{array}{l} \mbox{Chemical composition of ashes (SiO_2, Al_2O_3, \\ \mbox{Fe}_2O_3, \mbox{CaO}, \mbox{MgO}, \mbox{P}_4O_{10}, \mbox{SO}_3, \mbox{Mn}_3O_4, \mbox{TiO}_2, \\ \mbox{BaO}, \mbox{SrO}, \mbox{Na}_2O, \mbox{K}_2O) \end{array}$	Q/LP/55/B:2016, ICP-OES fly ash: Q/LP/62/B:2016	Q/LP/65/B:2016 fly ash: Q/LP/62/B:2016			
Metals content (Pb, Cg, Cu, Cr, Ni, V, Sb, Co, As, Mn)	Q/LP/57/B:2014 slag and fly ash: Q/LP/63/A:2012	Q/LP/66/A:2014 slag and fly ash: Q/LP/63/A:2012			
Mercury content	Q/LP/32/A:2011 fly ash Q/LP/33/A:2011	Q/LP/54/A:2016 fly ash: Q/LP/33/A:2011			
Flammable parts	Q/LP/40/	'A:2011			

Table 1. Indicators of the analysed samples of combusted materials, fly ashes and slags



fuel in the fuel mixture. SRF used for the research, despite submitting to compacting process, has 3-time lower bulk density than combusted hard coal.

The concentration of main oxides in hard coal and SRF is different, because of different origin of studied fuels. The main compounds are similar: SiO_2 and Al_2O_3 , Fe_2O_3 and CaO. However the SRF ash contains significantly more CaO, which can favorably reduce SO_2 emission during co-combustion of a mixture of that material with hard coal. The mineral substance of SRF has less Fe_2O_3 . The total content of the alkaline oxides (Na₂O and K₂O) in both ashes is similar, although proportions of its contents are slightly different. Alternative fuel has more K₂O.

Chemical composition of the mineral substance of both fly ashes is similar. Dominant ingredients are: SiO_2 , Al_2O_3 , Fe_2O_3 and also CaO. Their total content constitutes about 85% of the composition. The SiO₂ content in fly ash is lower in relation to

the burned materials. Simultaneously, the content of CaO in byproducts of co-combustion of waste is higher than in by-products of hard coal combustion, similarly like in mineral substance composition of combusted materials. Alkaline oxides (Na₂O and K₂O) in the analyzed products appear in total on a similar level (approx. 4.60–4.78%) which is however higher than that reported in other studies (Ściubidło and Nowak 2018). The content of Na₂O in fly ash from combustion of SRF is noticeably higher than in fly ash from combustion of hard coal.

SRF contains significantly more (over 4-times) heavy metals in comparison to hard coal, especially: Cr, Pb, Cd, Sb, V and Co, which is related to raw material's origin, from which this fuel is made. Low share of alternative fuel in a blend is a reason why heavy metals contents in a blend are only slightly higher than those determined for coal feedstock itself.

The content of trace elements in fly ash from waste co-combustion processes is the subject of many studies (Diaz et

Iable 2. Physical and chemical properties of combusted materials						
Parameter	Unit	Hard coal	SRF	Blend of coal and 10% SRF		
Moisture content, W _t ^r	%	5.30	6.50	7.17		
Ash content, A ^d	%	23.9	16.9	20.9		
Volatile matter, V ^{daf}	%	32.89	61.69	45.51		
Coal content, C ^d	%	65.5	62.3	64.9		
Hydrogen content, H ^d	%	3.57	4.98	4.19		
Sulphur content, S ^d ,	%	0.52	0.37	0.44		
Nitrogen content, N ^d	%	1.11	1.16	1.23		
Chlor content, Cl ^d	%	0.200	0.884	0.540		
Fluor content, F ^d	%	0.011	0.010	0.090		
High heating value, Q ^a s	kJ/kg	25568	25910	25700		
Lower heating value, Q ^r i	kJ/kg	23776	23768	23348		
Bulk density, (BD) ^r	kg/m ³	1024	398	882		
Bulk density. (BD) ^d	ka/m ³	970	372	814		

Table 2. Physical and chemical properties of combusted materials

Where, indices d, daf, r, a mean: dry, dry ash free, as received and analytical state, respectively.

Table 3. Chemical composition of ashes and fly ashes from combusted materials (%)

Component	Hard coal	SRF	Blend of coal and 10% SRF	Fly ash from combustion of coal	Fly ash from combustion of blend of coal and 10% SRF
SiO ₂	56.87	51.14	55.20	45.14	44.91
Al ₂ O ₃	22.40	16.33	16.02	24.16	21.25
Fe ₂ O ₃	6.25	6.42	7.89	9.53	8.95
CaO	2.86	10.28	6.02	6.76	9.07
MgO	2.51	2.61	2.93	3.71	4.31
P ₄ O ₁₀	0.40	0.51	0.43	1.72	1.29
SO ₃	2.42	3.70	3.49	1.27	2.03
Mn ₃ O ₄	0.10	0.15	0.15	0.14	0.17
TiO ₂	1.02	1.98	1.13	1.16	1.50
BaO	0.13	0.14	0.12	0.45	0.35
SrO	0.06	0.05	0.05	0.29	0.20
Na ₂ O	0.84	2.24	1.62	1.76	2.46
K ₂ O	3.00	2.16	2.23	2.84	2.32



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al. 2006, Wu et al. 2013). Fly ash from co-combustion of waste has in total higher amounts of heavy metals in comparison to the product of coal combustion, which directly results from its greater contents in the combusted material. This is confirmed by observations of other researchers (Ściubidło and Nowak 2018, Wu et al. 2013). In the fly ashes obtained, the contents of heavy metals are generally higher than in slags. It concerns especially the contents of Hg and As. In fly ash from SRF co-combustion with hard coal, the heavy metal content is arranged in the following sequence of decreasing order: Mn> Cr> Pb> V> Cu> Sb> Co> As> Cd> Hg, while in ash from hard coal combustion it is: Mn> V> Pb> Ni> Cu> Cr> Co> As> Sb> Cd> Hg. Heavy metals in coal combustion processes immediately devolve to slag or fly ash or they evaporate, and then they precipitate on fly ash particles surface in cooler elements of a flue gas tract. That is why fly ash particles are often enriched in harmful elements (Parzentny and Róg 2007). In order to minimize the trace element emission during co-combustion of coal and SRF, besides reducing the trace element content in SRF, utilizing coal with high S and aluminosilicates content and SRF with low Cl-content would be desirable (Wu et al. 2013).

In tables 5–6, the results of other research of byproducts of combustion/co-combustion of hard coal and SRF are gathered. Table 4 presents the combustible particles content in by-products of hard coal combustion and co-combustion of SRF with coal.

It was stated that byproducts of co-combustion of waste and hard coal are characterized by high contents of combustible parts, higher in comparison to hard coal combustion. The content of combustible part (loss on ignition) is especially high in fly ashes. The increase of unburnt carbon in fly ash from co-combustion of SRF with hard coal is confirmed by the observations of other researchers (Wu et al. 2009). Similar results were obtained during other industrial tests also carried out in a stoker boiler (Wasielewski et al. 2018). Incomplete combustion of coal and alternative fuel blend contributes to increased losses from a boiler. The high share of unburnt carbon in fly ash from co-combustion of waste also limits their use in concrete production (Szarek, and Wojtkowska, (2018). It should be noticed, however, that abiding required level of burnout of process byproducts obligation was not legislatively defined for co-combustion of waste in contrast to the process of its combustion. Compacted elements of alternative fuel with 40 mm grain size are less homogenous material than hard coal. They burn slightly different and also require good contact with air (oxygen carrier) in a combustion zone. The boiler with horizontal travelling grate does not provide good conditions for a motion of a single particle of combusted material, which results in the occurrence of the increased loss on ignition in slag from burning the alternative fuel blend with hard coal. Big contents of the unburnt carbon in fly ash can have also a positive impact on possibilities of its usage. It should be acknowledged that adsorptive properties of fly ash are correlated with the contents of unburnt carbon of porous structure, which has dominant input in an adsorption ability of this material (Wang et al. 2005). Adsorptive properties of fly ashes and opportunities of their application for cleansing, among others, industrial sewage have been confirmed in many research results. Fly ashes can be successfully used as adsorbents for removing metal ions (Hequet et al. 2001,

Metal Hard coal SRF	Blend of co	Blend of coal	Hard coal		Blend of coal and 10% SRF		
	экг	and 10% SRF	slag	fly ash	slag	fly ash	
Pb ^d	15.40	102.00	24.16	69.8	207.0	55.7	243.0
Cd ^d	0.271	2.830	0.536	1.180	4.000	0.948	4.960
Cu ^d	22.6	67.3	28.1	40.7	162.0	195.0	163.0
Cr ^d	27.8	645.0	90.1	116	150	617	439
Ni ^d	34.2	21.8	33.1	70.7	197.0	87.4	157.0
Hg ^d	0.088	0.074	0.089	0.032	1.453	0.018	1.277
Vď	4.56	25.00	6.61	165	288	103	175
Sbd	1.45	42.90	5.61	5.2	16.9	14.8	54.5
Co ^d	6.43	8.70	6.72	24.8	52.9	20.9	40.7
As ^d	3.81	2.82	3.71	3.15	33.00	1.88	23.00
Mn ^d	152	192	157	653	645	505	658
Sum	268.6	1110.4	355.7	1149.6	1757.3	1601.6	1959.4

Table 4. Metals content in combusted materials, slags and fly ashes obtained during the tests (mg/kg d.m.)

Where indices d mean dry state.

Table 5. Combustible particles content in slags and fly ashes obtained during the tests (%)

Parameter	Hard	coal	Blend of coal and 10% SRF	
	slag	fly ash	slag	fly ash
Flammable parts, Vc ^d	5.78	29.13	15.48	33.47

Where indices d mean dry state, and c - combustible parts.



Polowczyk et al. 2010, Sarbak and Kramer-Wachowiak 2012), pigments (Wang et al. 2005, Janos et al. 2003, Jain et al. 2003), phenols and other organic compounds (Wang et al. 2008, Styszko and Drobniak 2015) from sewage.

Parameters of the surface structure determined based on BET isotherm for the tested fly ashes samples are presented in Table 6.

The specific surface area values of fly ash samples are varied and depend on the composition of samples. Fly ashes have a predominantly inorganic fraction and a minor organic fraction (unburnt carbon). The higher S_{BET} values are due to the higher unburnt carbon contents and the values are in the range from 4 to 300 m²/g. This type of material shows mainly mesoporous character of surface (Girón et al. 2013, Hower et al. 2017). Zeolites and mesoporous molecular sieves from fly ash show the highest values of S_{BET} and the lowest values correspond to the finest fraction (Ściubidło 2016, Ściubidło and Nowak 2012).

The executed research confirmed the presence of porous structure in both samples of fly ash. It was stated that fly ash from co-combustion of SRF has a slightly higher specific surface area as well as the total volume of pores in comparison to fly ash from coal combustion, which correlates with the increased content of unburnt carbon. The specific surface area of fly ash from co-combustion of SRF with hard coal in the boiler with mechanical stoker of WR-25 type is 2-times smaller than fly ash from blend combustion of lignite with 10% share of SRF in a fluidized bed boiler (Ściubidło and Nowak 2018). Mesopores volume dominates (more than 60% of volume) in the porous structure of both fly ashes. Fly ash from co-combustion of SRF with hard coal is characterized by nearly 2-time bigger volume of macropores than fly ash from combustion of coal.

Microscopic studies have shown big structural differentiation of both fly ashes, which illustrate examples of microphotographs featured in Figures 2 and 3.

Table 6. Selected structural parameters of the tested fly ash samples determined on the basis of the N₂ adsorption isotherm.

Material	Specific	Pore volume (cm³·10 ^{·3} /g)			
	Specific surface, S _{BET} (m²/g)	Total pore volume, V _{tot} (p/p0 =0.99)	Volume of macropores, V _{macro}	Volume of mesopores, V _{meso}	Volume of micropores, V _{micro} (p/p ₀ =0.01)
Fly ash from combustion of coal	8.54	13.73	2.84 (20.7%)	8.52 (62.0%)	2.37 (17.3%)
Fly ash from combustion of blend of coal and 10% SRF	8.74	17.51	4.57 (26.1%)	10.60 (60.5%)	2.34 (13.4%)

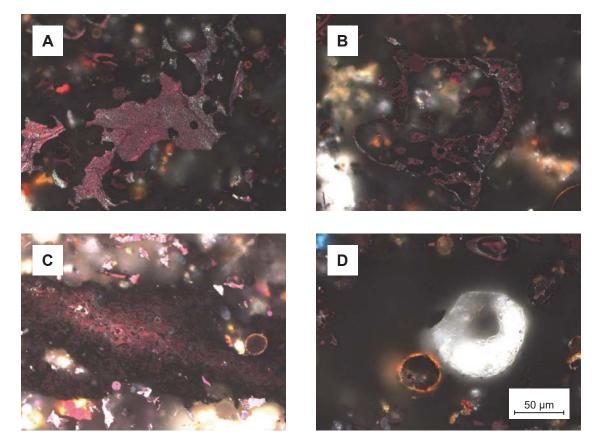


Fig. 2. Example photomicrographs of unburnt carbon particles from hard coal combustion in a stoker boiler

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Fly ash from the combustion of coal is less diversified in terms of morphology of carbonized organic particles than fly ash from co-combustion of waste and coal. Identification of unburnt carbon fractions was performed basing on the classification created as a result of the activity of the Fly Ash Working Group of ICCP (Suarez-Ruiz et al. 2015). Fly ash from the coal combustion contains mainly the anisotropic carbonates in the form of porous particles with diversified shape and size (Fig. 2A,B), as well as isotropic residue of inert organic ingredients coming from unburnt inert macerals in bituminous coal (Fig. 2C) and also mineral cenospheres (Fig. 2D). Unburnt carbon substance resembles by its texture a coal coke which means that coal particle was entrained with waste/ flue gases and subjected to pyrolysis process, but did not get combusted. The shape of particles indicates that coal particle underwent transition through a plastic state, the effect of which is the anisotropic optic texture creation, and pores present in a structure are the effect of loss of volatiles by carbon substance. The same particles were observed by other scientists (Hower et al. 2017) studying the bituminous-coal-derived UCs.

In a fly ash structure from co-combustion of bituminous coal and SRF occur, outside observed structures for fly ashes from combustion of coal, also additionally the isotropic, more or less porous carbonized particles (Fig. 3B) and also weakly anisotropic fine-crystalline amorphous particles of soot (Fig. 3C,D), likely of rubber origin. In comparison to fly ash that comes from the combustion of coal, fly ash from co-combustion of coal and SRF contains significantly more unburnt carbon of soot characteristics. About 30% of organic char particles of unburnt fuel are of the SRF origin. Those particles do not present the appearance of typical coal derived unburnt carbons

(Hower 2017). Particles of weakly anisotropic, amorphous carbon are characterized by diversified size and shape. The typical porous structure is not observed. Observed carbonized particles exhibit rather irregular, non-spherical shape, and their edges in a crosswise cut are more frayed, which can point to enlarged grains surface. The carbonized grains do not show signs of passing through a plastic state or other physical and chemical transformation. Usually, they are covered by a thin layer of pyrolytic carbon or soot. Many inorganic metallic particles can also be observed (e.g. aluminium – Fig. 3A).

In the case of an installation that undertakes co-combustion of waste with fossil fuels, the procedure of solid waste codification is changed. Wastes generated during the co-combustion of fossil fuels and biomass in boiler installations are classified within group 10 – wastes from thermal processes. On the other hand, co-combustion of fuels and wastes causes that the boiler installation is treated as an installation of the thermal waste conversion. As a result, all the wastes generated in this installation are classified within group 19 – waste from installations and equipment used for waste management. Solid by-products generated in waste co-combustion installations can be classified into the following types of waste:

- 19 01 11* slags and furnace ashes containing hazardous substances,
- 19 01 12 slags and furnace ashes different than 19 01 11 and also
- 19 01 13* fly ashes containing hazardous substances,
- 19 01 14 fly ashes different than mentioned in 19 01 13.

The classification to adequate type of waste (hazardous or different than hazardous) depends on research results. The fly ashes from co-combustion of SRF with coal can be

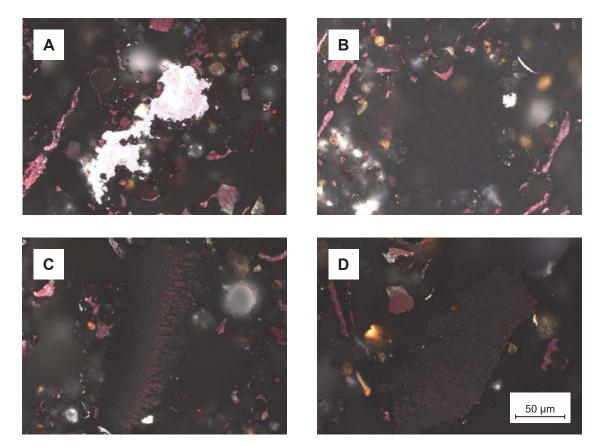


Fig. 3. Example photomicrographs of unburnt carbon particles from combustion blend of hard coal and 10% SRF in a stoker boiler.

characterized by a high leachability of contaminants and thus their economic use may be restricted. This problem was the subject of research to assess the quality of fly ash from biomass combustion/co-combustion with coal (Uliasz-Bocheńczyk et al. 2015, Plewa et al. 2013). In Table 7 the results of water extract of fly ashes from combustion/co-combustion of hard coal with SRF research are shown. The results of these studies were compared with the legal values for non-hazardous and inert wastes (Journal of Laws of 2016 item 1277, enclosure 3).

The so-called "agreement tests" carried out for both tested fly ashes did not exhibit any parameters exceeding permissible values, which allows for treating them as wastes different than hazardous (19 01 14) and significantly widens industrial usage possibilities. This means also significantly lower costs of their storage. This is also an interesting phenomenon and different in relation to fly ashes from combustion of biomass, which usually show high leaching of contaminants (Mirowski et al. 2018).

Conclusion

The conducted research showed similarities and differences of the physical and chemical properties and structure of the fly ash from the combustion process of hard coal and co-combustion of SRF with coal in a stoker boiler. Chemical composition of mineral substance of both studied fly ashes is similar. Fly ash from co-combustion is characterized by high contents of heavy metals, significantly higher in comparison to combusted materials but also slags. Nevertheless, these metals and other pollutants, do not show leachability exceeding acceptable values for wastes different than hazardous. Fly ash from co-combustion of SRF with hard coal in a stoker boiler is characterized by high contents of combustible parts, higher than ash from hard coal combustion. Contents of unburnt carbon can influence an adsorptive properties of fly ash. Microscopic structure of fly ashes from combustion of hard coal and co-combustion of SRF studies showed crucial differences, especially in organic material. Fly ash structure contains elements distinctly showing the origin of the combusted material. Optic morphology of ash from co-combustion of coal with waste is characterized by an evidently visible higher surface development.

The presented research results have shown that fly ash from co-combustion of SRF with coal in a stoker boiler can obtain the status of non-hazardous waste. This can influence potential possibilities of its management or neutralization through storage.

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 Table 7. Results of investigations of water extract of fly ashes from hard coal combustion and SRF co-combustion with coal (mg/kg d.m.)

	Μ		
Parameter	Fly ash from combustion of hard coal	Fly ash from combustion of blend of coal and 10% SRF	Limited value
Arsenic	<0.20	<0.20	2
Barium	0.28	0.45	100
Cadmium	<0.01	<0.01	1
Total Chromium	<0.01	0.17	10
Copper	<0.01	<0.01	50
Mercury	0.0001	0.0002	0.2
Molybdenum	0.26	<0.20	10
Nickel	0.01	<0.01	10
Lead	<0.01	<0.01	10
Antimony	<0.20	<0.20	0.7
Selenium	<0.20	<0.20	0.5
Zinc	<0.01	0.01	50
Chlorides	339.0	1985.0	15000
Fluorides	52.6	43.8	150
Sulphates	9706	7837	20000
Total Organic Carbon (TOC)	10.8	16.2	800
Total Dissolved Solids (TDS)	16080	17105	60000

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References

- Ahmaruzzaman, M. (2010). A review on the utilization of fly ash, Progress in Energy and Combustion Science, 36(3), pp. 327–363, DOI: 10.1016/j.pecs.2009.11.003.
- Attarde, S., Marathe, S. & Sil, A. (2014). Utilization of fly ash in construction industries for environment management, *International Journal of Environmental*, 3(2), pp. 117–121.
- Bastian, S. (1980). *Betony konstrukcyjne z popiolem lotnym*, Wydawnictwo Arkady, Warszawa. (in Polish)
- Basu, M., Pande, M., Bhadoria, P.B.S. & Mahapatra, S.C. (2009). Potential fly-ash utilization in agriculture: A global review, *Progress in Natural Science*, 19(10), pp. 1173–1186, DOI: 10.1016/j.pnsc.2008.12.006.
- Bielińska, E.J., Baran, S. & Stankowski, S. (2009). Ocena przydatności popiołów fluidalnych z węgla kamiennego do celów rolniczych, *Inżynieria Rolnicza*, 115(6), pp. 7–15. (in Polish)
- Del Zotto, L., Tallini, A., Di Simone, G., Molinari, G. & Cedola, L. (2015). Energy enhancement of solid recovered fuel within systems of conventional thermal power generation, *Energy Procedia*, 81, pp. 319–338, DOI:10.1016/j.egypro.2015.12.102.
- Diaz-Somoano, M., Unterberger, S. & Hein, K.G. (2006). Prediction of trace element volatility during co-combustion processes, *Fuel*, 85, pp. 1087–1093
- EN 15357:2011. (2011). Solid recovered fuels Terminology, definitions and descriptions.
- EN 15359:2011. (2011). Solid recovered fuels Specifications and classes.
- Fyffe, J.R., Breckel, A.C., Townsed, A.K. & Webber, M.E. (2016). Use of SRF residue as alternative fuel in cement production, *Waste Management*, 47(PB), pp. 276–284, DOI: 10.1016/j. wasman.2015.05.038.
- Girón, R.P., Ruiz, B., Fuente, E., Gil, R.R. & Suárez-Ruiz I. (2013). Properties of fly ash from forest biomass combustion, *Fuel*, 114, pp. 71–77, DOI: 10.1016/j.fuel.2012.04.042.
- Hequet, V., Ricou, P., Lecuyer I. & Le Cloirec, P. (2001). Removal of Cu2+ and Zn2+ in aqueous solutions by sorption onto mixed fly ash, *Fuel*, 80(6), pp. 851–856, DOI: 10.1016/S0016-2361(00)00153-8.
- Hower, J.C., Groppo, J.G., Graham, U.M., Ward, C.R., Kostova I.J., Maroto-Valer, M.M. & Dai, S. (2017). Coal-derived unburned carbons in fly ash: A review, *International Journal of Coal Geology*, 179, pp. 11–27, DOI: 10.1016/j.coal.2017.05.007.
- ISO 562:2010 Hard coal and coke Determination of volatile matter.
- ISO 1928:2009 Solid mineral fuels Determination of gross calorific value by the bomb calorimetric method and calculation of net calorific value.
- ISO 19579:2006 Solid mineral fuels Determination of sulfur by IR spectrometry.
- ISO 29541:2010 Solid mineral fuels Determination of total carbon, hydrogen and nitrogen content – Instrumental method.
- Jagustyn, B., Wasielewski, R. & Skawińska, A. (2014). Podstawy klasyfikacji odpadów biodegradowalnych jako biomasy, *Ochrona Środowiska*, 4, pp. 45–50. (in Polish)
- Jain, A. K., Gupta, V.K. & Bhatnagar, A. (2003). Utilization of industrial waste products as adsorbents for the removal of dyes, *Journal of Hazardous Materials*, 101, pp. 31–42, DOI: 10.1016/ S0304-3894(03)00146-8.
- Janos, P., Buchtova, H. & Ryznarova, M. (2003). Sorption of dyes from aqueous solutions onto fly ash, *Water Research*, 37, pp. 4938–4944, DOI: 10.1016/j.watres.2003.08.011.
- Jarosiński, A. (2013). Mineral and Chemical Composition of Fly Ashes Deriving from Co-Combustion of Biomass with Coal and Its Application, *Inżynieria Mineralna – Journal of the Polish Mineral Engineering Society*, 14, pp.141–148.

- Journal of Laws of 2016 item 1277, enclosure 3. Regulation of the Minister of Economy of 16 July 2015 on regarding issuing permission to store waste on landfills. (in Polish)
- Mirowski, T., Mokrzycki, E. & Uliasz-Bocheńczyk, A. (2018). *Energetyczne wykorzystanie biomasy*, Wydawnictwo IGSMiE PAN, Kraków. (in Polish)
- Parzentny, H.R. & Róg, L. (2007). Potentially hazardous trace elements in ash from combustion of coals in limnic series (Upper Carboniferous) of the Upper Silesian Coal Basin (USCB), *Górnictwo i Geologia*, 2(3), pp. 81–91. (in Polish)
- Plewa, F., Popczyk, M. & Pierzyna P. (2013). Możliwości wykorzystania wybranych odpadów energetycznych z udziałem środka wiążącego do podsadzki zestalanej w podziemiu kopalń, *Polityka energetyczna – Energy Policy Journal*, 16(4), pp. 257–270. (in Polish)
- Polowczyk, I., Bastrzyk, A., Sawiński, W., Koźlecki, T., Rudnicki, P., Sadowski, Z. & Sokołowski, A. (2010). Właściwości sorpcyjne popiołów ze spalania węgla, *Inżynieria i Aparatura Chemiczna*, 49(1), pp. 93–94. (in Polish)
- PN-G-04534:1999 Solid fuels. Determination of chlorine content. Polish Standard, 1999. (in Polish)
- PN-82/G-04543 Hard coal and lignite. Determination of fluorine content. Polish Standard, 1982. (in Polish)
- PN-EN 15400:2011 Solid recovered fuels Determination of calorific value. Polish Standard, 2011.
- PN-EN 15402:2011 Solid recovered fuels Determination of the content of volatile matter. Polish Standard, 2011.
- PN-EN 15403:2011 Solid recovered fuels Determination of ash content. Polish Standard, 2011.
- PN-EN 15407:2011 Solid recovered fuels Methods for the determination of carbon (C), hydrogen (H), and nitrogen (N) content. Polish Standard, 2011.
- PN-EN 15408:2011 Solid recovered fuels Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content. Polish Standard, 2011.
- PN-EN 15414-3:2011 Solid recovered fuels Determination of moisture content using the oven dry method – Part 3: Moisture in general analysis sample. Polish Standard, 2011.
- PN-EN ISO 17828:2016 Solid biofuels Determination of bulk density. Polish Standard, 2016.
- PN-ISO 589:2006 Hard Coal. Determination of total moisture content. Polish Standard, 2006.
- PN-ISO 1171:2002 Solid mineral fuels. Determination of ash content. Polish Standard, 2002.
- Q/LP/32/B:2016 Solid fuels. Determination of mercury content. Technical Procedure IChPW, 2016. (in Polish)
- Q/LP/33/A:2011 Solid combustion by-products. Determination of mercury content. Technical Procedure IChPW, 2011. (in Polish)
- Q/LP/37/A:2011 Biomass. Determination of bulk density. Technical Procedure IChPW, 2011. (in Polish)
- Q/LP/40/A:2011 Solid post-combustion waste products. Determination of combustible fraction using automatic analyzer. Technical Procedure IChPW, 2011. (in Polish)
- Q/LP/54/A:2016 Wastes and solid recovered fuels. Determination of total mercury content. Technical Procedure IChPW, 2016. (in Polish)
- Q/LP/55/B:2016 Solid fuels. Determination of the chemical composition of ash by the ICP-OES technique. Technical Procedure IChPW, 2016. (in Polish)
- Q/LP/57/B:2016 Solid fuels. Determination of trace elements using ICP-OES. Technical Procedure IChPW, 2016. (in Polish)
- Q/LP/62/B:2016 Solid post-combustion waste products. Determination of the chemical composition of ash using ICP-OES. Technical Procedure IChPW, 2016. (in Polish)



- Q/LP/63/A:2012 Solid post-combustion waste products. Determination of trace elements using ICP-OES. Technical Procedure IChPW, 2012. (in Polish)
- Q/LP/65/B:2016 Wastes and solid recovered fuels. Determination of chemical composition of ash using ICP-OES. Technical Procedure IChPW, 2016. (in Polish)
- Q/LP/66/A:2014 Wastes and solid recovered wastes. Determination of trace elements using ICP-OES. Technical Procedure IChPW, 2014. (in Polish)
- Saraber, A. (2012). Co-combustion and its impact on fly ash quality; pilot-scale experiments, *Fuel Processing Technology*, 104, pp. 105–114, DOI: 10.1016/j.fuproc.2012.04.033.
- Sarbak, Z. & Kramer-Wachowiak, M. (2012) Wykorzystanie popiołów lotnych jako adsorbentów metali ciężkich, *Przemysł Chemiczny*, 91(2), pp. 189–192. (in Polish)
- Sobolewski, A., Wasielewski, R., Dreszer, K. & Stelmach, S. (2006). Technologie otrzymywania i kierunki zastosowań paliw alternatywnych otrzymywanych z odpadów, *Przemysł Chemiczny*, 8–9, pp.1080–1084. (in Polish)
- Stelmach, S. & Wasielewski R. (2008). Co-combustion of dried sewage sludge and coal in a pulverized coal boiler, *Journal of Material Cycles and Waste Management*, 10, pp. 110–115, DOI: 10.1007/s10163-007-0206-9.
- Szarek, Ł. & Wojtkowska, M. (2018). Properties of fly ash from thermal treatment of municipal sewage sludge in terms of EN 450-1, Archives of Environmental Protection, 44(1), pp. 63–69.
- Styszko, K. & Drobniak, A. (2015). Analiza możliwości adsorpcji wybranych ksenobiotyków z roztworów wodnych na popiele lotnym, *Ochrona Środowiska*, 37(1), pp. 25–31. (in Polish)
- Ściubidło, A. (2016). Synthesis of sorbents for exhaust gases purification n.d. Advanced CO₂ Capture Technologies for Clean Coal Energy Generation. In: Majchrzak-Kucęba, I. & Wawrzyńczak, D. (Eds) *Monographs No 320*, Czestochowa University of Technology, Częstochowa pp. 63–5. (in Polish)
- Sciubidio, A. & Nowak W. (2012). Novel sorbents for flue gas purification, *Journal of Power Technology*, 92, pp. 115–126.
- Ściubidło, A. & Nowak, W. (2018). Co-combustion of solid recovered fuel (SRF) and coal and its impact on fly ash quality, *Mineral Resources Management*, 34(2), pp. 117–136, DOI: 10.24425/118651. (in Polish)
- Suarez-Ruiz, I. & Valentim, B. (2015) Atlas of Fly Ash Occurrences: Identification and Petrographic Classification of Fly Ash Components Working Group. Commission III–ICCP. *ISBN:* 978-84-608-1416-0. 203 pp. Available at. http://www.iccop.org/ documents/atlas-of-fly-ash-occurrences.pdf (accessed 13 March 2017).
- Thiel, S. & Thomé-Kozmiensky, K.J. (2012). Co-combustion of solid recovered fuels in coal-fired power plants, *Waste Management & Research*, 30(4), pp. 392–403, DOI: 10.1177/0734242X11427946.

- Uliasz-Bocheńczyk, A., Mazurkiewicz, M. & Mokrzycki, E. (2015). Fly ash from energy production – a waste, byproduct and raw material, Gospodarka Surowcami Mineralnymi – Mineral Resources Management, 31(4), pp.139–150, DOI: 10.1515/ gospo-2015-0042. (in Polish)
- Uliasz-Bocheńczyk, A., Pawluk, A. & Sierka, J. (2015). Wymywalność zanieczyszczeń z popiołów lotnych ze spalania biomasy, Gospodarka Surowcami Mineralnymi – Mineral Resources Management, 31(3), pp.145–156, DOI: 10.1515/gospo-2015-32. (in Polish)
- Wang, S., Yashveersingh, B., Choueib, A., Ng, E., Wu, H. & Zhu Z. (2005). Technical Note. Role of unburnt carbon in adsorption of dyes on fly ash, *Journal of Chemical Technology and Biotechnology*, 80, pp. 1204–1209, DOI: 10.1002/jctb.1299.
- Wang, S., Ma, Q. & Zhu, Z. (2008). Characteristic of coal fly ash and adsorption application, *Fuel*, 87 (15–16), pp. 3469–3473, DOI: 10.1016/j.fuel.2008.05.022.
- Wasielewski, R. & Bałazińska, M. (2018). Odzysk energii z odpadów w aspekcie kwalifikacji wytworzonej energii elektrycznej i ciepła jako pochodzących z odnawialnego źródła energii oraz uczestnictwa w systemie handlu uprawnieniami do emisji gazów cieplarnianych, *Polityka Energetyczna – Energy Policy Journal*, 21(1), pp. 129–142. (in Polish)
- Wasielewski, R., Głód, K. & Telenga-Kopyczyńska, J. (2018). Energy and emission aspects of co-combustion solid recovered fuel with coal in a stoker boiler, *E3S Web of Conferences, Air Protection in Theory and Practice,* 28, 01037, DOI:10.1051/ e3sconf/20182801037.
- Wasielewski, R. & Sobolewski, A. (2015). Uwarunkowania i perspektywy wykorzystania paliw z odpadów do generowania energii elektrycznej i ciepła, *Przemysł Chemiczny*, 4, pp.1000–1005, DOI:10.15199/62.2015.4.3. (in Polish)
- Wójcik, M., Stachowicz, F. & Masłoń, A. (2017). Możliwość wykorzystania popiołów lotnych w celu poprawy odwadniania osadów ściekowych, *Journal of Civil Engineering, Environmental* and Architecture, 34(64), pp. 377–393, DOI: 10.7862/rb.2017.35. (in Polish)
- Wu, H., Glarborg, P., Frandsen, F., Dam-Johansen, K., Jensen, P.A. & Sander, B. (2009). Co-combustion of coal and SRF in an entrained flow reactor: a preliminary study. In 4th European Combustion Meeting Technical University of Denmark, Department of Chemical Engineering.
- Wu, H., Glarborg, P., Jappe Frandsen, F., Dam-Johansen, K., Jensen, P.A. & Sander, B. (2013). Trace elements in co-combustion of solid recovered fuel and coal, *Fuel Processing Technology*, 105, pp. 212–221, DOI: 10.1016/j.fuproc.2011.05.007.
- Żygadło, M. (2018). Wybrane elementy problematyki współspalania paliw alternatywnych, *Ochrona Środowiska*, 40(2), pp. 39–44. (in Polish)