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Co-combustion of solid recovered fuel (SRF) and coal and its impact on fly ash quality

Introduction

Increasing the energy consumption and the climate change are two of world's most critical problems, and now receive the highest priority for research, economy and innovation. The EU budget is assigned directly addressing the need for renewable and sustainable energy solutions, and indicates to mitigate climate change, including the reduction of emissions, the introduction of renewable and alternative energy sources, low carbon technologies, energy conservation in buildings and additionally, the wastes recycling and its effective application.

According to the Regulation of the Polish Minister of Economy (1/1/2016) the landfill deposition of municipal waste with the higher heating value (HHV) than 6 MJ/kg is prohibited. Implementation of the requirements of this regulation is currently one of the biggest challenges for municipal waste management in Poland. Based on the statistical data, 10,863 thousand Mg of municipal waste was collected in Poland in 2015, out of which 8326.1 thousand Mg was collected as residual/mixed waste, 243,2 thousand Mg paper and cardboard, 424.1 thousand Mg glass, 303.2 thousand Mg plastics, 19.2 thousand Mg metals, 1.7 thousand Mg textiles, 1.2 thousand Mg hazardous, 262.4 thousand Mg bulky and 657 thousand Mg biodegradable. Only 13.24% of wastes were thermally converted (Council of Ministers 2016).

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The application of waste derived fuels for energy production seems to be good option taking into account the environmental protection and the reduction of disposal. More waste fractions are characterized by high calorific value, that is why can be used as an alternative fuel. The use of waste as an energy source is an integral part of waste management and National Smart Specializations. The waste derived fuels from various types of wastes such as municipal solid wastes (MSW), industrial wastes or commercial wastes are commonly called refuse-derived fuel (RDF) and solid recovered fuel (SRF), depending on the fuel's characteristics (Rada and Andreottola 2012; Bessi et al. 2016; Medic-Pejic et al. 2016; Iacovidou et al. 2018).

RDF is generated from domestic wastes, which includes biodegradable materials as well as plastics. Non-combustible materials such as glass and metals are removed and the residual material is then removed. Whereas, solid recovered fuel (SRF) is produced from non-hazardous wastes including paper, wood, textiles and plastic with a calorific value up to 30 MJ/kg (depending on composition), and carbon and hydrogen contents c.a. 50 and 7%, respectively. The net calorific value, chlorine and mercury contents of SRF are the main requirements which are classifying the SRF and they are described in SRF standard EN15359. (PN-EN 15359:2012; Schwarzböck et al. 2016; Nam-Chol et al. 2017).

Refuse derived fuel is used in combined heat and power facilities, many of them in Europe. With a moisture content of less than 15% solid recovered fuel has a high calorific value and is used in facilities such as cement kilns.

The additional parameters are organic element contents, sulphur, bromine and major (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) and trace (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo) elements.

The SRF contains mineral matter, generally in proportions substantially different from those found in coal. Moreover, the nature and mineralogical origin of SRF ash is more diverse and more difficult to classify. Mineral compounds in coal deposits are mainly in the form of silicates (up to 50% wt.), carbonates (up to 20% wt.), sulphides (up to 20% wt.) and sulphates. The main chemical composition of coal fly ash are SiO_2 (30−50% wt.), Al_2O_3 (15−30% wt.), Fe_2O_3 (2−22% wt.), CaO (1.5−15% wt.), MgO (1−8% wt.), SO_3 (1−5% wt.), P_2O_5 (0.2−1.5% wt.) and K_2O + Na_2O (1−5% wt.) (Adrian et al. 1986; Vassilev and Vassileva 2005; Blissett and Rowson 2012). Whereas the chemical composition of SRF is varied, strongly depends on the origin (Dunnu et al. 2010).

Nowadays, the addition of alternative fuels (like SRF and RDF) in co-combustion has increased. Several authors have been studied the co-combustion of coal and SRF e.g. (Wu et al. 2011; Iacovidou et.al. 2018; Wasielewski et al. 2018). The most important factor that influences this process is the composition of alternative fuels. It is worth to mentioned, that the using SRF instead of coal in co-combustion process helps to preserve natural resources and limiting the use of fossil fuels and reducing the impact on the environment through lower CO_2 emissions (Wagland et al. 2011; Psomopoulos and Themelis 2015; Vainio et al. 2016).

In Europe, there are some power plants where the SRF is used as an alternative fuel. The co-combustion of coal and SRF in CFB technology seems to be successfully carried out (Fu et al. 2008; Czakiert et al. 2012; Zhang et al. 2012).

In Poland, there is a new combined-heat-and-power (CHP) plant in Zabrze, where varied solid fuels can be combusted. The fuel mixtures consist of RDF and coal, and biomass and coal are combusted. The amount of alternative fuel (RDF) can be up to 50% of the total fuel mixture. The power plant will have a production capacity of 220 MW, including 145 MW of heat and 75 MW of electricity, and its annual production is estimated to be approximately 730 and 550 GWh of heat and electricity respectively.

Thus, the main aim of this paper is to study the co-combustion process of coal and SRF (with different amount) in a fluidised bed combustor. The ashes obtained from coal + SRF fuel mixtures were studied to compare the influence of percentage amount of SRF on ash properties. The morphological studies and the thermal behaviour of ashes were performed.

Studies of these ashes presented above were also carried out to ascertain their applicability to zeolite synthesis. Synthesis zeolites from fly ash is one of the effective, economical and simple methods of fly ash utilization. Due to the chemical composition -high content of SiO_2 and Al_2O_3 – fly ash is suitable starting material for the synthesis of zeolites (White and Case 1990; Hansen et al. 1997; Henmi 1997). CFA and zeolite consist mainly of Al and Si (Querol et al. 2002) and the major difference between them is the crystalline structure. CFA is composed mostly of amorphous structure, whereas zeolite has a well-defined crystalline structure. Due to these similarities in the composition between CFA and zeolite, CFA is potential candidate for conversion to zeolite (Zhao et al. 1997). The main element of fly ash-aluminosilicates, is converted to zeolitic crystals by alkali hydrothermal reaction.

Natural zeolites have restricted pore sizes and channels, whereas fly ash based-zeolites possess a variety of pore structures and are economically viable sorbent minerals for removing contaminants from water and gases. These synthesized zeolites can be used as sorbents and ion exchangers for removing ions and dangerous molecules from wastewater and radioactive waste as well as adsorbents for gases containing atmospheric pollution (Breck 1974; Singer and Berkgaut 1995; Hui et al. 2005).

1. Experimental

1.1. Materials

The coal used for the combustion experiments was a lignite coal from Turow, Poland. For experimental purposes, the coal was sieved to provide a particle size between 5 and 13 mm. Fuel SRF was also grinded and homogenised. The SRF comes from an alternative fuels plant in Germany. The chemical composition of coal and SRF is presented in the Table 1.

The carbon and hydrogen contents of coal and SFR are similar. Necessary, the SRF characterizes very high content of sulphur, what can be negative aspect of SRF combustion, taking into account the sulphur compounds emissions. The coal contains higher the moisture and ash contents that SRF but lower content of volatile matter. The calorific value of coal

Table 1.   Chemical analysis of coal and SRF

Tabela 1.   Analiza chemiczna węgla i SRF

Element	Coal	SRF
Elementary analysis (% dry basis)		
C (%)	45.28	43.81
H (%)	4.50	5.60
N (%)	0.42	1.51
S (%)	1.60	6.49
Proximate analysis		
Moisture (%)	6.23	4.6
Ash (%) (db)	22.44	12.15
VM/Volatile matter (%) (daf)	39.87	68.39
CV/ calorific value (MJ/kg)	17.52	16.22

Daf – dry-ash-free-basis; db – dr basis.

and SFR are similar. The four fuel blends were prepared: coal + 1% SRF, coal + 5% SRF, coal + 10% SRF coal + 20% SRF.

1.2. Co-combustion process in CFB

The co-combustion of studied fuel blends were carried out at 0.1 MWth fluidized bed combustor (Fig. 1) at the Institute of Advanced Power Technologies of the Częstochowa University of Technology.

The unit consists of a 0.1 m inner diameter and approximately 5.0 m tall combustion chamber, connected to a 0.25 m inner diameter hot cyclone. Solids separated in the cyclone return to the combustion chamber via a 0.075 m inner diameter downcomer and a non-mechanical loopseal. The unit is provided with three heaters around the combustion chamber. These heaters are used to heat the unit to (or beyond) the ignition point of the fuel being used. Primary gas (PG) is supplied through a ceramic grid at the bottom of the combustion chamber. This gas can be preheated with the help of two heaters (HE and PGH) installed in series. Secondary gas (SG) can be supplied optionally through a common-rail fitted with three nozzles at the level of 0.55 m above the grid. Fuel is fed continuously by a screw feeder located on a return leg, between the combustion chamber and the loopseal. Bed material can be fed by an additional screw feeder at the bottom of the combustion chamber. A single fabric baghouse filter, installed downstream of the cyclone, is used for ultimate flue gas

particulate cleanup. The baghouse can be bypassed if necessary. The flue gas leaving the baghouse (or bypassing the baghouse) is vented with the help of an induced draft (ID) fan to the atmosphere, through a stack. The test rig is equipped with a developed data acquisition system for temperature (T) and pressure (P) measurements, as well as a number of ports for flue gas (FG), bottom ash (BA), fly ash (FA), and circulating material (CM) sampling.

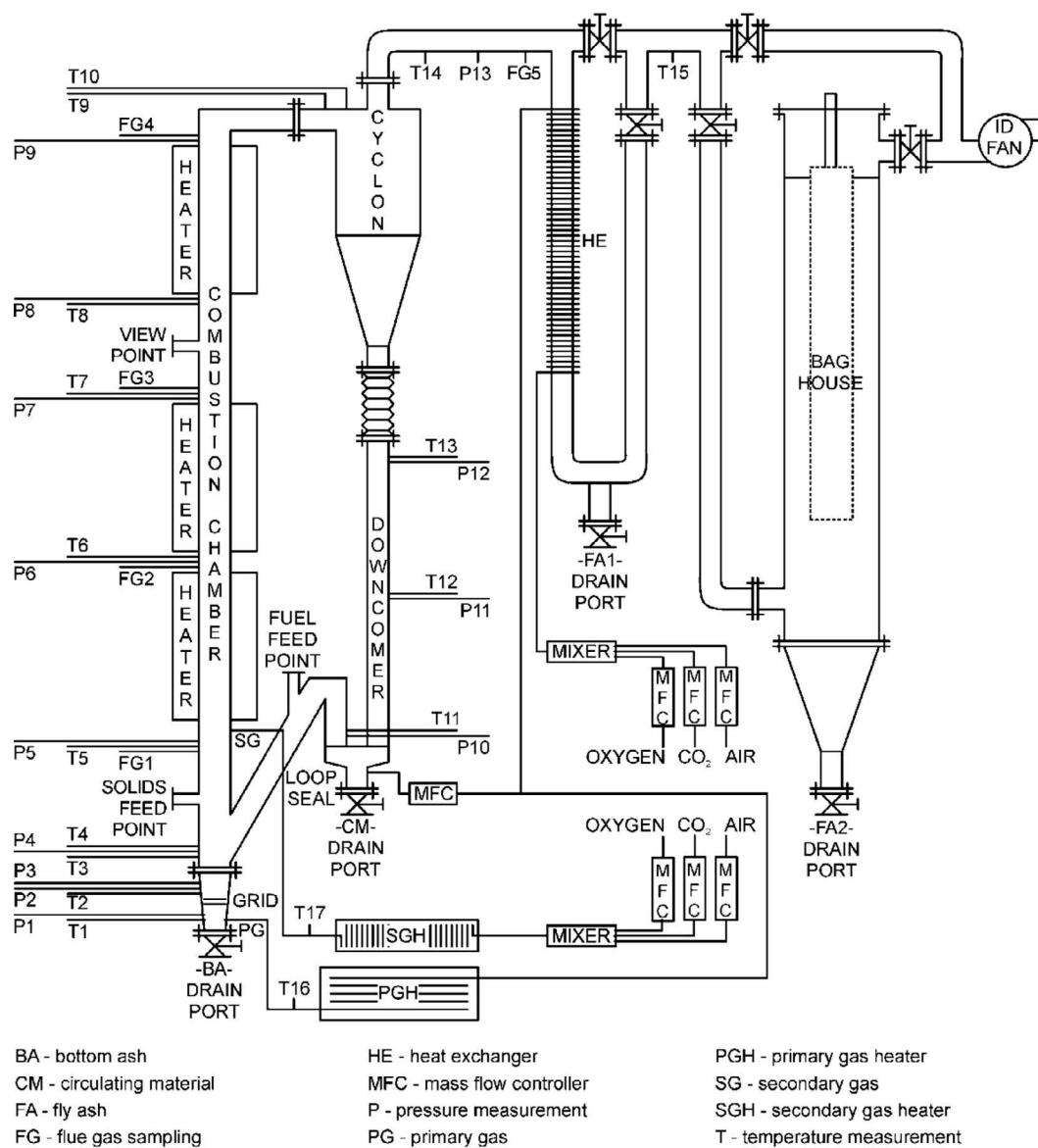| BA - bottom ash | HE - heat exchanger | PGH - primary gas heater |
CM - circulating material	MFC - mass flow controller	SG - secondary gas
FA - fly ash	P - pressure measurement	SGH - secondary gas heater
FG - flue gas sampling	PG - primary gas	T - temperature measurement

Fig. 1. Schematic diagram of fluidized bed combustor (0.1 MWth)

Rys. 1. Schemat stanowiska doświadczalnego z cyrkulacyjną warstwą fluidalną (0,1 MWt)

In this study, coal + 1% SRF, coal + 5% SRF, coal + 10% SRF and coal + 20% SRF fuels were tested. During combustion experiments, the fluidized bed temperature was about 850°C. The fly ash samples were collected from a CFB. Various experimental methods for the physical and chemical characterization of ashes are required. The most important parameter determining the character of ash is the chemical composition and thermal behaviour. The detail chemical composition of the obtained ashes is presented in Table 2 and 3.

1.3. Instrumental methods

The samples of fly ashes were collected and prepared according to the standards BN-81-0623-01 (for slag, ash, and slag-ash mixtures). The investigation of the chemical composition included a determination of a basic chemical composition (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, SO_3, MnO_2, TiO_2, P_2O_5) of ash was performed by using X-ray fluorescence (XRF). A Minipal4 wavelength dispersive XRF spectrometer was used for this purpose. The XRF was calibrated over a range of glass compositions using standard reference materials. The major elements of the ashes were given as wt%. oxides.

An identification of crystalline phases present in the fly ashes, along with defining their relative amounts in the samples was carried out by means of the X-ray method on the D8 Advance (Bruker) powder diffractometer, equipped with a monochromatic device Ge (the length of radiation: $CuK_{\alpha 1} = 1.5406$ Å). Diffraction patterns were identified in a room temperature, in the range of 6–60° of 2 theta angle, with a 0.05° step. Relative amounts of crystalline components in the ashes samples were determined by means of an internal model method. Model diffraction patterns were received in the same measurement conditions as in the case of the selected samples.

Morphology investigation and sample textures were conducted using of the scanning microscope type Tesla BS-301- Satellite, equipped with spectrometer of energy dispersion (EDX), which allowed to determine the chemical composition of the selected samples of materials. Preparations for SEM microscope were obtained by means of a deposition of surfaces of the investigated materials with a thin film of Au−Pd in a vacuum deposition apparatus, followed by taking digital photos from the SEM microscope's detector of different fragments of those surfaces and with different magnification levels (5000, 15 000 and 50 000 times).

Nitrogen adsorption/desorption was conducted using the Micrometrics ASAP 2010 (Micrometrics Instrument Corporation, Norcross, GA, USA) apparatus. Before the nitrogen adsorption, the samples (200 mg) were subject to degasification in the temperature of 573 K for 3 hours. The apparatus was used to measure the low-temperature (–196°C) nitrogen adsorption/desorption isotherm, on the basis of which such parameters were measured as: the specific surface area, the total volume of the pores, the average pores diameter, distribution of pores volumes in the function of their diameter as well as the distribution of the specific surface area in the function of the pores diameters. Several conclusions on the structure of

Table 2.   The main elements of the ashes in the form of oxides, % (XRF method)

Tabela 2.   Skład pierwiastkowy popiołów w postaci tlenkowej (metoda XRF)

Ash	SiO$_2$	Al$_2$O$_3$	CaO	Fe$_2$O$_3$	MgO	P$_2$O$_5$	K$_2$O	Na$_2$O	TiO$_2$	MnO	SO$_3$
Coal	46.30	30.95	1.96	4.99	1.54	0.12	1.21	0.40	2.40	0.03	1.60
SRF	23.90	7.90	31.55	3.14	2.99	1.72	1.07	0.35	2.45	0.18	6.50
Coal*	41.02	29.03	1.89	4.83	1.37	0.10	1.13	0.35	2.00	0.03	1.39
Coal + 1% SRF*	40.98	29.07	3.29	10.23	1.97	0.07	1.57	0.39	1.67	0.03	3.04
Coal + 5% SRF*	40.73	29.05	3.58	9.28	2.01	0.08	1.57	0.39	1.67	0.03	3.75
Coal + 10% SRF*	39.97	27.89	3.59	9.99	2.16	0.10	1.56	0.35	1.67	0.04	3.93
Coal + 20% SRF*	37.02	25.10	3.85	9.99	2.45	0.17	1.46	0.35	1.56	0.05	4.34

* CFB boiler combustion.

Table 3.   Content of minor elements in studied ashes, ppm

Tabela 3.   Zawartość śladowych pierwiastków w popiołach, ppm

Ash	Cd	Co	Cr	Cu	Hg	Ni	Pb	Sb	V	Zn
Coal	0.62	18.59	141.27	60.20	–	115.45	34.07	7.61	250.23	112.87
SRF	0.49	12.26	556.81	650.97	0.09	52.00	196.35	3.58	77.74	1 955.78
Coal*	0.64	18.01	142.02	61.00	–	112.00	33.25	7.01	248.04	113.00
Coal + 1% SRF*	0.69	28.00	167.20	106.40	0.09	134.85	51.77	5.56	249.07	242.56
Coal + 5% SRF*	0.58	24.39	169.69	107.48	0.11	124.46	54.20	5.30	196.54	288.81
Coal + 10% SRF*	0.55	24.22	174.54	199.43	0.14	118.81	57.12	5.22	164.08	299.81
Coal + 20% SRF*	0.55	23.33	195.91	127.82	0.19	116.98	58.61	5.18	154.09	302.91

* CFB boiler combustion.

the investigated compound were made on the basis of the qualitative analysis of the received adsorption-and-desorption isotherms.

A Mastersizer 2000 Particle Size Analyzer was used to measure the particle size distribution of the fly ash samples. Water was used as a carrier agent since it was found to be capable of dispersing and wetting the particles. An ultrasound sonicator bath was used to disperse the particles.

Thermal analysis can provide important information about the thermal behaviour of the sample (phase transition, decomposition, etc.). TGA/DSC1 thermal analyzer (produced by Mettler Toledo was used in this study. The fly ash was heated in a platinum crucible under the atmospheric pressure and in a neutral atmosphere (N_2), with a flow ratio of a reaction gas equal to 50 cm^3/min, and in a range of temperatures between 20–1000°C, with the heating rate equal to 20°C/min. In order to ensure an accuracy of mass measurements, received TG curves were corrected (i.e. reduced) by a so-called blank test (i.e. TG curve of an appropriate inerrant sample, registered in particular measurement conditions). For a temperature calibration model substances, with known temperatures of phase conversion, were used.

2. Results and discussion

The ash, mineral part of the fuel, plays significant role in thermal processes. The formation of ash deposits influencing on the heating surface limiting the heat transfer and accelerating the corrosion process. Consequently, the combustion efficiency is decreased by the slagging, fouling and bed agglomeration phenomena (Magdziarz et al. 2016).

Thus, the chemical composition of studied ashes obtained after co-combustion of coal and SRF is presented Table 2 and 3.

To comparison the chemical composition of coal and SRF are presented, too. The concertation of the main oxides is different, because of different origin of studied fuels. The chemical position reported in Table 2 shows that coal ash in mainly composed of silicon (SiO_2), aluminium (Al_2O_3) and iron (Fe_2O_3). Whereas the SRF ash is rich in calcium (CaO), what could be usefulness for SO_2 capture. The concertation of potassium and sodium are not high and comparable, this can suggest that slagging of these ashes should not to appear. It is well observed, that the chemical composition of ashes from co-combustion of blends reflects the amount of SRF addition. The amount of the major oxides in studied ashes is listed from the highest to the lower values: SiO_2, Al_2O_3, Fe_2O_3, CaO, SO_3, MgO, TiO_2, K_2O. The concentration of trace elements in the ashes is presented in Table 3.

Analysing coal and SRF ashes the content of trace elements is different. The coal ash characterises the high concentration of V, Cr, Zn, Pb, the Hg was not detected. For SRF ash the concertation of Zn, Cu, Cr, Pb, Ni as well as Hg was detected. Additionally, the sum of trace elements in SRF ash is much higher than in coal ash.

Considering the chemical composition of studied ashes, they can be utilize as a zeolites and porous materials, due to the high content of SiO_2 and Al_2O_3 in these ashes (Wang et al. 2009; Vainikka et al. 2011; Zhoua et al. 2016).

The parameter which determines ash usefulness as a zeolite is the Si/Al ratio. The SiO_2/Al_2O_3 content of ashes, being optimal for zeolites A is c.a. 2, what reflects to all studied all ashes. The SiO_2/Al_2O_3 content of ash, being optimal for zeolites X in the range of 2.2–3.3 and for zeolites Y in the range of 3.1–6.0. Unfortunately, this ratio was too low to synthesis zeolites X and Y. Trace elements such as TiO_2, MnO, K_2O, Na_2O, and MgO along with anions – sulfate, carbonate appear to promote nucleation and crystallization of zeolite. Iron oxides may decrease the quality of the product by incorporating themselves into the zeolite matrix giving the product a brownish shade (Rayalu et al. 2001). In addition, these cations may favorite one type of zeolite over another, therefore it is important to choose the specific zeolite that can be converted from a specific CFA (Bukhari et al. 2015).

2.1. Thermogravimetric experiments

Figure 2 presents the TG and DTG curves during heating the studied ashes under the nitrogen atmosphere. TG (thermogravimetry) curve presents the weight loss of studied
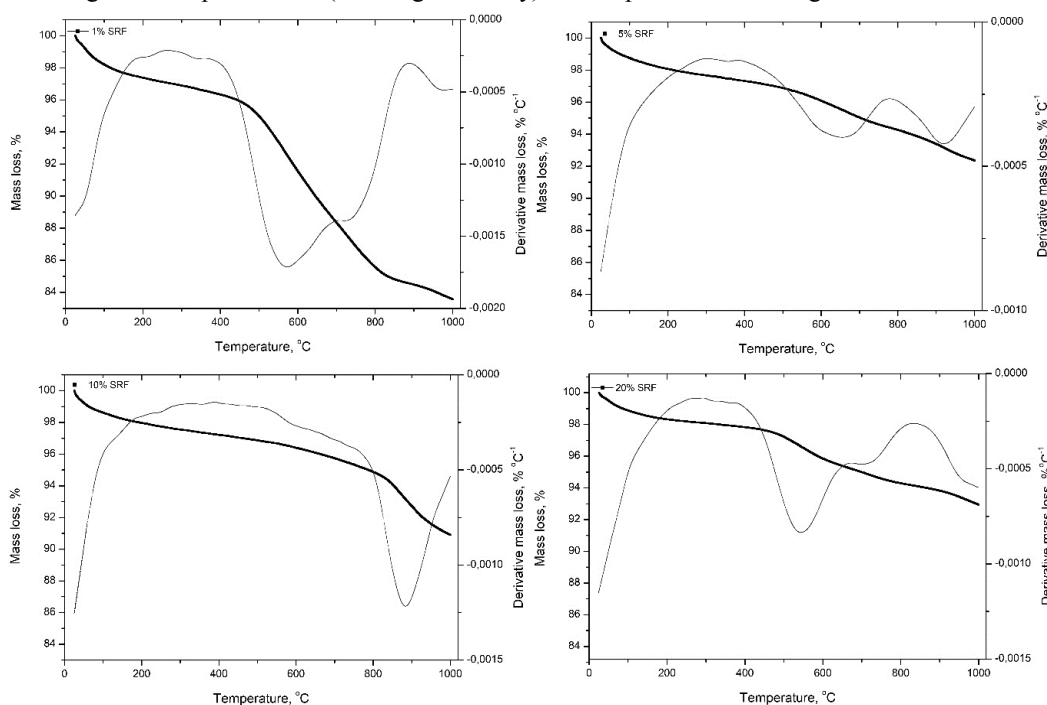

Fig. 2. TG and DTG curves for studied ashes

Rys. 2. Krzywe TG i DTG popiołów

samples in contrast to the initial mass under increasing temperature, and DTG (differential thermogravimetry) is based on the rate of weight loss with the increasing temperature.

TG results show that thermal conversion up to 1000°C of studied ashes have different course. For coal + 1% SRF ash the mass loss goes into two stages from c.a. 350°C to 883°C. The first step from 25°C to 352°C corresponds to removal of moisture and light volatiles with a total loss of about 3.36%. The significant weight loss is observed between c.a. 352°C to 670°C with the total loss of 6.66% with maximum weight loss rate at 585°C, which was indicated to the oxidation of coal. The second weight loss between 670°C to 883°C was the result of the oxidation of carbon by the iron oxides with the total loss of 4.69%. The residue at c.a. 1000°C was about 83,57% of the original sample weight.

The addition of SRF is observed for the coal + 5% SRF where the thermal behaviour of the ash is quite different, the mass loss rate is much smaller than for previous one. The two stages can be define, too. The first weight loss is observed between c.a. 350°C to 780°C with total loss of about 3.10% and the second weight loss between 780°C to 990°C with total degradation of 2.04%. The first weight loss was followed by the active pyrolysis and oxidation and the second was the result of the oxidation of carbon by the iron oxides. The residue at c.a. 1000°C was about 92.36% of the original sample weight.

For coal + 10% SRF ash the mass loss above 200°C goes different than for other ash samples. Up to 750°C the thermal decomposition takes place with nearly the same rate. Above 750°C the mass loss is significant and maximum weight loss is observed at 883°C. This weight loss was the result of the oxidation of carbon by the iron oxides. The residue at c.a. 1000°C is about 90. 9% of the original sample weight.

The major addition of SRF (20%) to coal influences on its ash thermal behaviour. The significant mass loss is observed in the temperature range 400°C and 600°C. Above 600°C the mass loss in nearly constant. The weight loss is observed between c.a. 352 to 670°C with the total loss of 2.74% with maximum weight loss rate at 544°C, which was indicated to the oxidation of coal. The second weight loss between 670°C to 777°C was the result of the oxidation of carbon by the iron oxides with the total loss of 0.83%. The residue at c.a. 1000°C was about 83.57% of the original sample weight.

Due to several overlapping peaks, the minerals are difficult to identify. The most of the effects detected on the TGA diagrams are related to the loss of humidity between room temperature and approximately 300°C. Thermal reactions between 275–450°C was oxidation of the surface (Fe_3O_4) and between 480–1000°C was oxidation of the bulk $2Fe_3O_4 \rightarrow 3Fe_2O_3$. Between 100°C and 200°C: escape of adsorbed and interlayer water. About 550°C was dehydroxylation of illite and at ca. 900°C was destruction of the lattice and formation of spinel (illite). $CaSO_4$ is decomposed only at temperatures higher than 1000°C. In a case of hematite in temperature 400–500°C shows some weight loss and oxide undergoing decomposition and dehydration of hematite (Földvári 2011).

Concluding, the weight losses of studied ashes with the increase of temperature take place due to moisture loss and the decomposition of some minerals.

2.2. BET specific surface area

Low-temperature nitrogen adsorption was used for the characterization of porous materials. Table 3 shows the specific surface area (BET) of studied ashes.

The specific surface area (S_{BET}) of studied ashes is in the range from 14.87 m^2/g to 29.80 m^2/g. The addition of SRF to the combustion process caused the ash generation with the lower specific surface area.

The ash adsorption capacity is a major property for the beneficial utilization of ash. The adsorption capacity of fly ash mainly indicates from amount of carbon content but also from other properties such as the particle size, surface chemistry, and positioning of carbon in the fly ash particle. The values of sorption capacity of studied ashes decrease with the share of SRF in fuel mixture. Figure 3 shows the N_2 adsorption isotherm at 77 K for studied ashes.

Table 4. The BET specific surface areas of the fly ash samples

Tabela 4. Powierzchnia właściwa BET popiołów lotnych

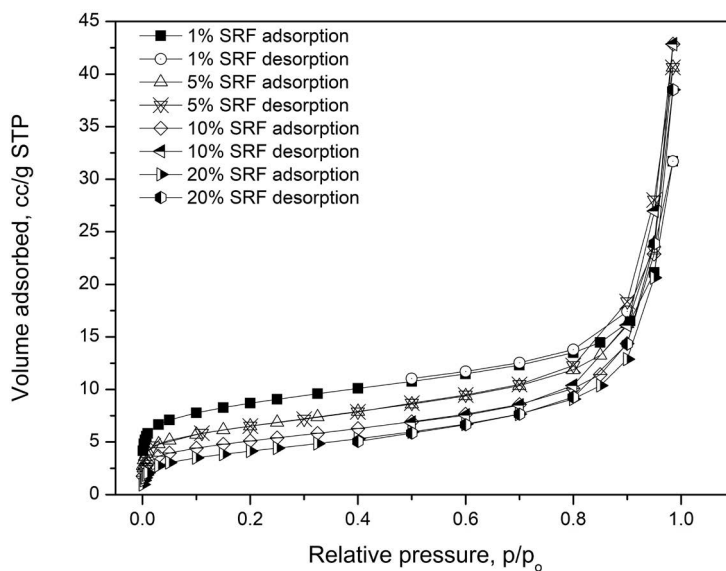| Ash	BET Surface area S_{BET} m^2/g
Coal + 1% SRF	29.8028
Coal + 5% SRF	22.7251
Coal + 10% SRF	17.9218
Coal + 20% SRF	14.8691

Fig. 3. N_2 adsorption isotherm for studied ashes

Rys. 3. Izotermy adsorpcji N_2 popiołów

The N_2 adsorption isotherm is the graph between the amounts of adsorbate adsorbed on the surface of adsorbent and pressure at constant temperature.

N_2 adsorption isotherms for all ashes were classified according to IUPAC regulations as isotherms of type II. This type of isotherms is typical for macro-pores materials, and is connected to situations in which low relative partial pressures of an adsorptive on a surface of an adsorbent result in occurrence of some monomolecular mini-layer of the adsorbed substance (N_2), whereas in the case of high relative partial pressures some multi-molecular layer of adsorbent on the surface of adsorbent is created. In the isotherms of the fly ashes were observed that the loop of hysteresis (type H3), begins with relative low pressures that prove a low content of micropores in that structure. The loop of H3 hysteresis is typical for adsorbents with pores formed in the shape of gaps.

2.3. Particle size distribution

The particle size analysis by Laser Scattering Analyzer for all studied ashes was carried out. A three-point specification including D10, D50, and D90 particle size values offer appropriate information for presenting the particle size span width of fly ashes. D50 is the diameter that splits the distribution with half above and half below this diameter. The D90 and D10 represent the coarsest and finest parts of the distribution, respectively.

The distribution of grains of the fly ashes is asymmetric distribution. The volume weighted percentiles D10, D50, D90 of fly ashes were reported in Table 5 and the cumulative curve of all fly ashes was shown in Fig. 4b.

Table 5.   Particle size distribution of fly ashes

Tabela 5.   Rozkład uziarnienia popiołów lotnych

Ash	D_{10}, μm	D_{50}, μm	D_{90}, μm
Coal + 1% SRF	3.00	15.30	47.93
Coal + 5% SRF	3.67	18.87	43.62
Coal + 10% SRF	3.47	18.57	45.70
Coal + 20% SRF	3.30	17.71	44.26

90% of the particles for studied ashes had diameters smaller than 47.93 μm, 43.62 μm, 45.70 μm, and 44.26 μm, respectively. The data for the D50 values for the fly ashes were less than 15.30 μm, 18.78 μm, 18.57 μm and 17.71 μm. Ten percent for fly ashes had diameters smaller than 3.00 μm, 3.67 μm, 3.47 μm and 3.30 μm, respectively.
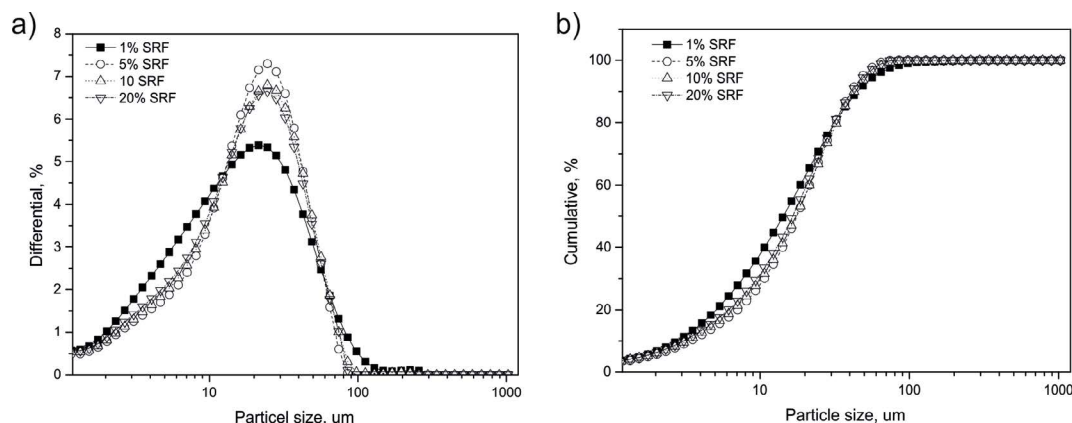
a)

b)

Fig. 4. a) Differential particle size distribution of fly ashes;
b) Cumulative particle size distribution of fly ashes

Rys. 4. a) Krzywa różniczkowa rozkładu wielkości cząstek;
b) Krzywa kumulacyjna rozkładu wielkości cząstek

The differential particle size distributions of fly ashes (Fig. 4a) were in a range from 0.51 to 85,31 microns for ash no. 2 and 4, from 0.514 to 224,41 microns for ash no. 3 and from 0.514 to 295.00 microns or ash no. 1. The ashes had similar distribution of the grains volumes. The distribution of grains of the fly ashes is asymmetric Gauss distribution.

2.4. Texture analysis

In order to determine the morphology and the porous structure, the samples of fly ashes were subjected to an analysis of SEM-EDX scanning microscopy. The results were presented in Figure 5.

The morphology of the co-combustion ashes were quite similar to each other. The dominant particles of all ashes were contained mainly coarse and angular, flaky, drossy, and irregular particles with a broad particle size range.

The morphology of a fly ash particle was controlled by combustion temperature and cooling rate. The multi-mineral, subangular particles of fly ash often were consisted of a core of quartz or aluminosilicate that were reacted with calcium to produce a calcium-rich aluminosilicate followed by calcium and iron oxides. In all fly ashes were also observed irregularly shaped unburned carbon particles.

The grains of CFB ashes had irregular shapes because in the temperature of the CFB boiler, mineral substances accompanying the coal were not subject to partial melting. Due to low temperature in CFB boiler, in the CFB ashes mullite was not present.
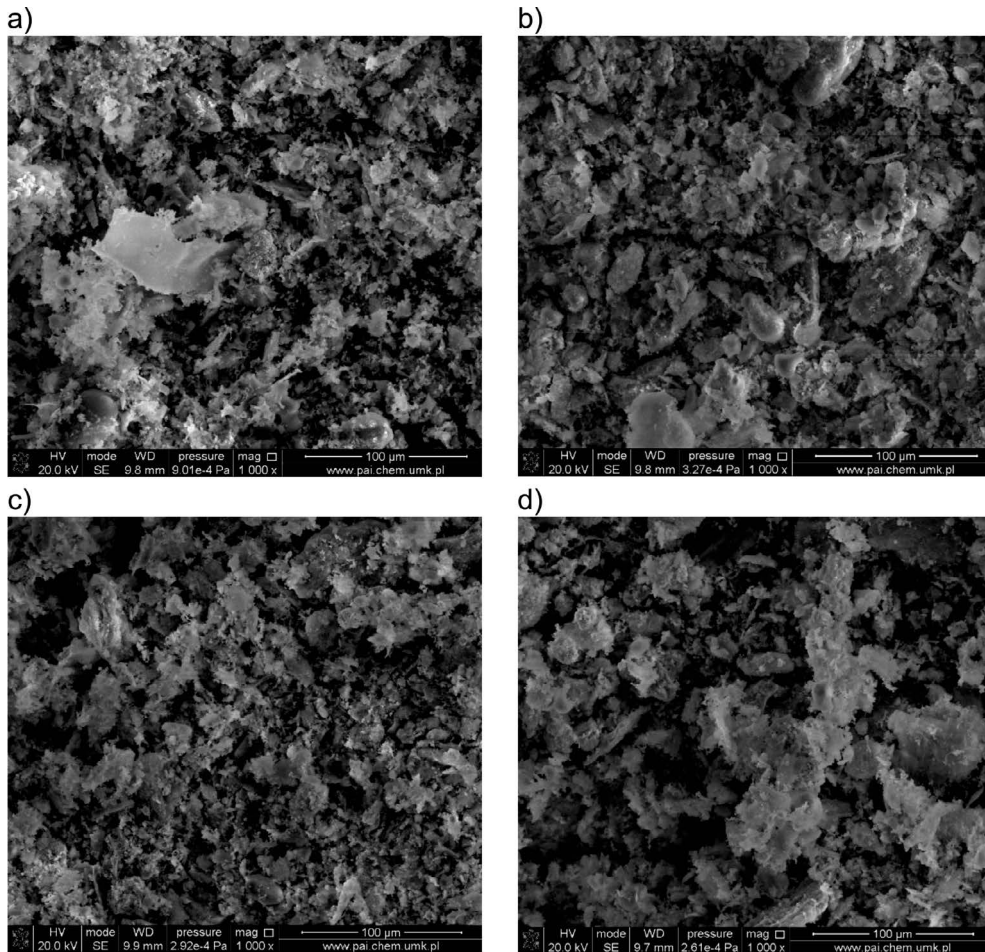
a)

b)

c)

d)

Fig. 5. SEM photographs of the studied ashes
a) coal + 1% SRF; b) coal + 5% SRF; c) coal + 10% SRF; d) coal + 20% SRF

Rys. 5. Zdjęcia SEM popiołów
a) węgiel + 1% SRF; b) węgiel + 5% SRF; c) węgiel + 10% SRF; d) węgiel + 20% SRF

2.5. Mineralogical composition

The mineralogical characteristics of the fly ashes were analysed by XRD (Fig. 6). Quartz, anhydrite and illite were identified in all studied ashes. These minerals are usually present in coal fly ashes.

In addition, magnetite and iron oxide were also present. In the fly ash several peaks were present that could not be related to specific XRD-patterns of minerals. The presence of the
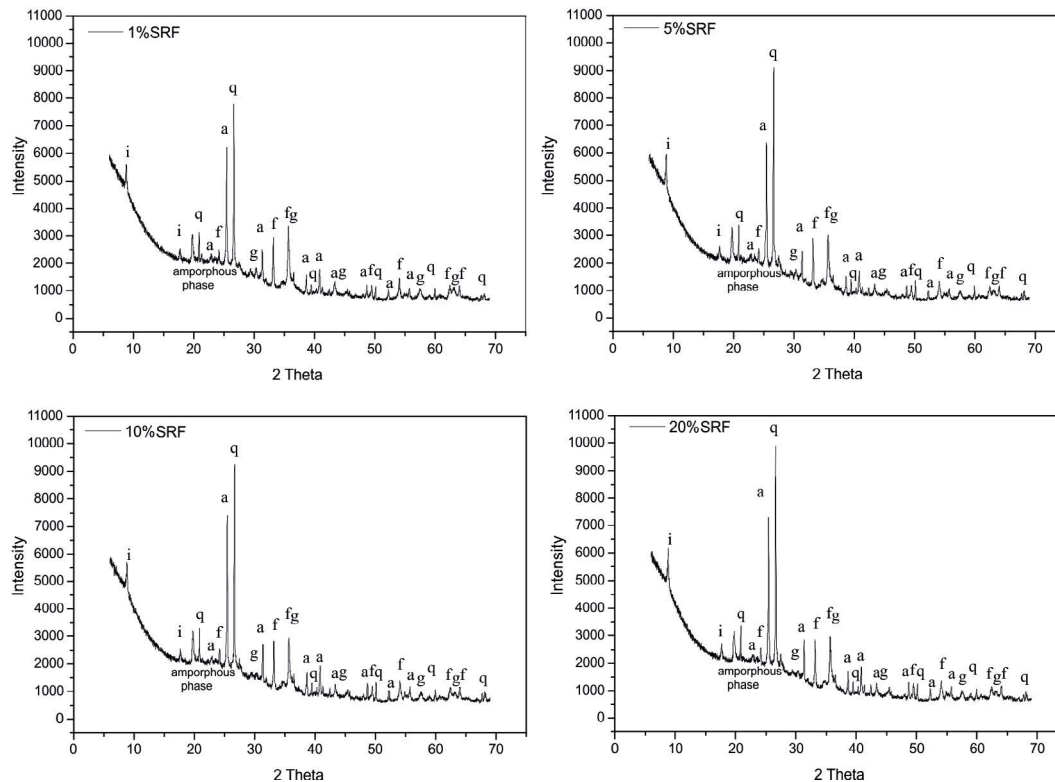
Fig. 6. X-ray diffraction analysis
q − quartz (SiO$_2$), f − Fe$_2$O$_3$, a − anhydrite (CaSO$_4$), g − magnetite (Fe$_3$O$_4$), r − forsterite (Mg$_2$SiO$_4$),
i − illite (K$_{0.6-0.85}$Al$_2$(Si,Al)$_4$O$_{10}$(OH)$_2$)

Rys. 6. Dyfraktogramy XRD
q − kwarc (SiO$_2$), f − Fe$_2$O$_3$, a − anhydryt (CaSO$_4$), g − magnetyt (Fe$_3$O$_4$), r − forsteryt (Mg$_2$SiO$_4$),
i − illit (K$_{0,6-0,85}$Al$_2$(Si,Al)$_4$O$_{10}$(OH)$_2$)

background in the diffraction pattern points to amorphous phases, which was represented a wide peak from 15° to 35° 2Θ. The position of the background is influenced by the composition of the amorphous phase.

Conclusions

In the work were presented a detail analysis of ashes obtained during co-combustion of coal and SRF using a number of instrumental techniques including XRF, XRD, SEM-EDS. The values of sorption capacity of studied ashes decreased with the share of SRF in fuel mixture. The morphology of the co-combustion ashes were quite similar to each other.

The dominant particles of all ashes were contained mainly coarse and angular, flaky and irregular particles with a broad particle size range. In all fly ashes were also observed irregularly shaped unburned carbon particles.

Due to low temperature in CFB boiler, in the CFB ashes mullite was not present. Quartz, anhydrite and illite were identified in all studied ashes. In addition, magnetite and iron oxide were also present. The presence of the background in the diffraction pattern points to amorphous phases. The research shows that coal ash in mainly composed of silicon (SiO_2), aluminium (Al_2O_3) and iron (Fe_2O_3). Whereas the SRF ash is rich in calcium (CaO). The concertation of potassium and sodium are not high and comparable, this can suggest that slagging of these ashes should not to appear. It was well observed, that the chemical composition of ashes from co-combustion of blends reflects the amount of SRF addition.

The amount of the major oxides in studied ashes is listed from the highest to the lower values: SiO_2, Al_2O_3, Fe_2O_3, CaO, SO_3, MgO, TiO_2, K_2O. The coal ash characterises the high concentration of V, Cr, Zn, Pb, the Hg was not detected. For SRF ash the concertation of Zn, Cu, Cr, Pb, Ni as well as Hg was detected. Additionally, the sum of trace elements in SRF ash is much higher than in coal ash.

The high silica content of fly ash makes it a potential useful source for the synthesis of nanoporous materials, such as zeolites. Synthesis of these materials from fly ash is one of the methods of fly ash utilization and it is economical, effective, safe and simple. The parameter which determines ash usefulness as a zeolite is the Si/Al ratio. Thus all SRF-fly ash samples with the SiO_2/Al_2O_3 ratio ca. 2.0 can be converted to zeolite A. The efficiency of fly ash conversion is also dependent on the contents of non-reactive phases (mainly hematite, magnetite, lime) and resistant aluminum–silicate phases, such as mullite and quartz, and the grain size distribution. The Al- and Si-bearing phases are dissolved during different stages of the zeolitization in the order glass > quartz > mullite. Due to the SiO_2/Al_2O_3 content and high content of SiO_2 and no mullite in SRF – fly ash, fly ashes can be used to synthesis zeolite A.

The results of study were confirmed that SRF can be successfully combusted with coal in CFB technology and can play role as an alternative fuel and the fly ashes obtained from coal + SRF fuel mixtures can be used to synthesis zeolites.

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CO-COMBUSTION OF SOLID RECOVERED FUEL (SRF) AND COAL AND ITS IMPACT ON FLY ASH QUALITY

Abstract

Due to the fact that the landfill deposition of municipal waste with the higher heating value (HHV) than 6 MJ/kg in Poland is prohibited, the application of waste derived fuels for energy production seems to be good option. There is a new combined-heat-and-power (CHP) plant in Zabrze, where varied solid fuels can be combusted. The formation of ashes originating from the combustion of alternative fuels causes a need to find ways for their practical application and demands the knowledge about their properties. Therefore, the present work is devoted to studying the co-combustion of solid recovered fuel (SRF) and coal, its impact on fly ash quality and the potential application of ashes to synthesis zeolites.

The major objectives of this paper is to present the detail characteristics of ash generated during this process by using the advanced instrumental techniques (XRF, XRD, SEM, BET, TGA).

The co-combustion were carried out at 0.1 MWth fluidized bed combustor. The amount of SRF in fuel mixture was 1, 5, 10 and 20%, respectively. The focus is on the comparison the ashes depending

on the fuel mixture composition. Generally, the ashes characterise high amounts of SiO_2, Al_2O_3 and Fe_2O_3. It is well observed, that the chemical composition of ashes from co-combustion of blends reflects the amount of SRF addition. Considering the chemical composition of studied ashes, they can be utilize as a zeolites A. The main conclusions is that SRF can be successfully combusted with coal in CFB technology and the fly ashes obtained from coal + SRF fuel mixtures can be used to synthesis zeolites.

K e y w o r d s : SRF, co-combustion, fly ash, CFB

WSPÓŁSPALANIE STAŁEGO PALIWA WTÓRNEGO (SRF) WĘGLEM I JEGO WPŁYW NA JAKOŚĆ POPIOŁU LOTNEGO

S t r e s z c z e n i e

Mając na uwadze, iż składowanie odpadów komunalnych o wyższej wartości opałowej (HHV) niż 6 MJ /kg w Polsce jest zabronione, dobrym rozwiązaniem jest zastosowanie paliw odpadowych do produkcji energii. W Zabrzu budowana jest nowa elektrociepłownia (CHP), w której można będzie spalać różne paliwa stałe. Powstawanie popiołów pochodzących ze spalania paliw alternatywnych powoduje potrzebę znalezienia sposobów ich praktycznego zastosowania, a to wymaga poznania ich właściwości. Dlatego niniejsza praca skupia się na badaniu współspalania stałego paliwa wtórnego (SRF) z węglem, jego wpływie na jakość otrzymanych popiołów lotnych oraz możliwości wykorzystania popiołów do syntezy zeolitów.

Głównym celem tego artykułu jest określenie właściwości popiołu lotnego powstającego podczas tego procesu za pomocą zaawansowanych technik instrumentalnych (XRF, XRD, SEM, BET, TGA). Współspalanie przeprowadzono na stanowisku doświadczalnym z cyrkulacyjną warstwą fluidalną o mocy 0,1 MWt. Ilość SRF w mieszaninie paliw wynosiła 1, 5, 10 i 20%. W pracy zwrócono uwagę na porównanie właściwości popiołów w zależności od składu mieszanki paliwowej. Zasadniczo otrzymane popioły charakteryzują się dużą ilością SiO_2, Al_2O_3 i Fe_2O_3, a zawartość potasu i sodu nie jest wysoka i jest porównywalna. Zauważono, że skład chemiczny popiołów ze współspalania odzwierciedla ilość dodanego SRF. Biorąc pod uwagę skład chemiczny badanych popiołów można je wykorzystać do syntezy zeolitu A. Podsumowując, SRF może być z powodzeniem współspalany z węglem w CFB, a otrzymane popioły lotne mogą być użyte do syntezy zeolitów.

S ł o w a   k l u c z o w e : SRF, współspalanie, popiół lotny, CFB