Comparison of fly ash from co-combustion of coal/solid recovered fuel (SRF) and coal/refuse derived fuel (RDF).

A Ściubidło1, I Majchrzak-Kucęba1 and M Niedzielska2

1Institute of Advanced Energy Technologies, Czestochowa University of Technology, 73 Dabrowskiego Street, 42-201 Czestochowa, Poland, e-mail:*asciubidlo@is.pcz.pl
2 Fortum Power and Heat Polska Sp. z o. o., Poland

Abstract: 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 alternative fuel SRF/coal and RDF/coal. The major objectives of this paper is to present the detail characteristics of ash by using the advanced instrumental techniques (XRF, XRD, SEM, BET, TGA).

1. Introduction

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, 12 485,4 thousand Mg of municipal waste was collected in Poland in 2018 [1]

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 [2-5].

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. [6-8]. 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.

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. [9-12] The most important factor that influences this process is the composition of alternative fuels. It is worth to mentioned, that the using SRF, RDF 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 CO2 emissions [13-15]

In Europe, there are some power plants where the SRF and RDF are used as an alternative fuel. 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 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 of RDF and SRF fly ashes. The morphological studies and the thermal behaviour of ashes were performed.

2. Experimental

2.1. Materials
Fly ash samples examined in this study included three fly ashes from co-combustion of solid recovered fuel (SRF) (samples 1-2) and co-combustion of refuse-derived fuel (RDF) (samples 3). The coal used for the co-combustion of SRF experiments was a lignite coal. The co-combustion of studied fuel blends were carried out at 0.1 MWth fluidized bed combustor (at the Institute of Advanced Power Technologies of the Czestochowa University of Technology). In this study, coal + 10 % SRF and coal + 20 % SRF fuels were tested. During combustion experiments, the fluidized bed temperature was about 850 °C. The fly ashes from co-combustion RDF and hard coal were collected from combined-heat-and-power (CHP) plant in Zabrze. The fuel used was a mixture of 40% RDF and coal.

2.2. 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 (SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O, SO₃, MnO₂, TiO₂, P₂O₅). 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: CuKα1=1,5406 Å). 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. Nitrogen adsorption/desorption was conducted using the Micrometrics ASAP 2010 (Micrometrics Instrument Corporation, Norcross, GA, USA) apparatus. A Mastersizer 2000 Particle Size Analyzer was used to measure the particle size distribution of the fly ash samples. 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.

3. Results and Discussion

The chemical composition of studied ashes is presented Table 1.

Table 1. The main elements of the ashes in the form of oxides, % (XRF method).

| Ash          | SiO₂ | Al₂O₃ | CaO | Fe₂O₃ | MgO | P₂O₅ | K₂O | Na₂O | TiO₂ | MnO | SO₃ |
|--------------|------|-------|-----|-------|-----|------|-----|------|------|-----|-----|
| FA10% SRF*   | 39.97| 27.89 | 3.59| 9.99  | 2.16| 0.10 | 1.56| 0.35 | 1.67 | 0.04| 3.93|
| FA20% SRF*   | 37.02| 25.1  | 3.85| 9.99  | 2.45| 0.17 | 1.46| 0.35 | 1.56 | 0.05| 4.34|
| FA40% RDF    | 26.81| 19.17 | 16.90| 4.38 | 2.33| 0.39 | 0.42| 0.58 | 0.91 | 0.08| -   |

* - CFB boiler combustion

The concentration of the main oxides is different, because of different origin of studied fuels. The chemical position reported in Table 1 shows that fly ashes in mainly composed of silicon (SiO₂), aluminium (Al₂O₃) and iron (Fe₂O₃). In addition, the RDF ash is rich in calcium (CaO). The concentration of potassium and sodium are not high and comparable, this can suggest that slagging of these ashes should not to appear.

3.1. Thermogravimetric experiments

Figure 1 presents the TG and DTG curves during heating the studied ashes under the nitrogen atmosphere. TG results show that thermal conversion up to 1000 °C of studied ashes have different course. For 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.

![Figure 1. TG and DTG curves for studied ashes.](image)

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 is 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.

For 40% RDF ash the mass loss goes into three stages from c.a. 340°C to 840 °C. The weight loss is observed between c.a. 340 to 420 °C. The second weight loss is observed between c.a. 420°C to 680 °C with maximum weight loss rate at 590 °C, which was indicated to the oxidation of coal. The next weight loss between 700°C to 900 °C was the result of the oxidation of carbon by the iron oxides. 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 (Fe₃O₄) and between 480°C –1000 °C was oxidation of the bulk 2Fe₂O₄ → 3Fe₂O₃. 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). CaSO₄ is decomposed only at temperatures higher than 1000 °C. In a case of hematite in temperature 400°C -500°C shows some weight loss and oxide undergoing decomposition and dehydration of hematite [16].

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

### 3.2. BET specific surface area

Table 2 shows the specific surface area (BET) of studied ashes. The specific surface area (S_{B.E.T}) of studied ashes is in the range from 17.92 m²/g to 6.88 m²/g for SRF ashes.

| No sample | BET Surface area S_{BET} m²/g |
|-----------|-----------------------------|
| 10 % SRF  | 17.92                       |
| 20 % SRF  | 14.87                       |
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 alternative fuels in fuel mixture. Figure 2 shows the N$_2$ adsorption isotherm at 77K for studied ashes.

![N$_2$ adsorption isotherm for studied ashes.](image)

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.

### 3.3. 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 3.
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.

3.4. Mineralogical composition

The mineralogical characteristics of the fly ashes were analysed by XRD (Figure 4). 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 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.

Figure 3. SEM photographs of the studied ashes: a) 10% SRF, b) 20% SRF c) 40% RDF.

Figure 4. X-ray diffraction analysis, where: q–quartz (SiO₂), p–Fe₂O₃, a–anhydrite (CaSO₄), g–magnetite (Fe₃O₄), r–forsterite (Mg₂SiO₄), i–illite (K₀.6-0.85Al₂(Si,Al)₄O₁₀(OH)₂), s–calcium silicate CaSiO₃, h–hematite (α-Fe₂O₃), v–muscovite (KAl(Si,Al)₄O₁₀(OH)₂), m–mullite (Al₆Si₂O₁₃),
4. Conclusion
In the work were presented a detail analysis of ashes obtained during co-combustion of coal/SRF and coal/RDF 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 and RDF 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. 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$_2$O$_3$) and iron (Fe$_2$O$_3$). It was well observed, that the chemical composition of ashes from co-combustion of blends reflects the amount of SRF/RDF addition.

Acknowledgements.
The research was supported by The National Science Centre in Poland, based on the decision DEC-2011/03/B/ST8/05916. The part of research was financed by statutory funds no. BSPB-406-301/11. Publication supported financially under Contract No. 944/P-DUN/2019 from funds of MNiSW intended for dissemination of science (DUN)

References
1. https://stat.gov.pl/obszary-tematyczne/srodowisko-energia/srodowisko/ochrona-srodowiska-2018,1,19.html
2. Rada, EC. and Andreottoala, G. 2012. RDF/SRF which perspective for its future in EU. Waste Management 32(6), pp. 1059–1060.
3. Bessi et al. 2016 – Bessi, C., Lombardi, L., Meoni, R. Canovai, A. and Corti, A. 2016. Solid recovered fuel: An experiment on classification and potential applications. Waste Management 47, pp.184–194.
4. Medic-Pejic et al. 2016 - Medic-Pejic, L., Fernandez-Anez, N. Rubio-Arrieta, L. and Garcia-Torrent, J. Thermal behaviour of organic solid recovered fuels (SRF). International Journal Hydrogen Energy 41, pp.16556–16565.
5. Iacovidou et al. 2018 – Iacovidou, E., Hahladakis, J. Deans, I. Velis, C. and Purnell, P. 2018. Technical properties of biomass and solid recovered fuel (SRF) co-fired with coal: Impact on multi-dimensional resource recovery value. Waste Management 73, pp. 535-545.
6. Schwarzböck et al. 2016 – Schwarzböck, T., Aschenbrenner, P. Rechberger, H. Brandstätter, C. and Fellner, J. 2016. Effects of sample preparation on the accuracy of biomass content determination for refuse-derived fuels. Fuel Processing Technology 153, pp. 101-110.
7. Nam-Chol, O. and Kim, W-G. 2017. Investigation of characterization of municipal solid waste for refuse-derived fuel, a case study. Energy Source A: Recovery Utilization and Environmental Effects 39(15), pp. 1671–1678.
8. Wagland et al. 2011 – Wagland, ST., Kilgallon, P. Coveney, R. Garg, A. Smith, R. Longhurst, PJ. Pollard, SJT. and Simms, N. 2011. Comparison of coal/solid recovered fuel (SRF) with coal/refuse derived fuel (RDF) in a fluidised bed reactor. Waste Management 31, pp. 1176–1183.
9. Psomopoulos, CS. and Themelis, NJ. 2015. The combustion of as-received and pre-processed (RDF/SRF) municipal solid wastes as fuel for the power sector, Energy Source A: Recovery Utilization and Environmental Effects 37(16), pp. 1813–1820.
10. Vainio et al. 2016 – Vainio, E., Kimmune, H. Laurén, T. Brink, A. Yrjas, P. DeMartini, N. and Hupa, M. 2016. Low-temperature corrosion in co-combustion of biomass and solid recovered fuels. Fuel 184, pp. 957–965.
11. Schubidlo, A, Nowak W. Co-combustion of solid recovered fuel (SRF) and coal and its impact on fly ash quality, Mineral Resources Management 2018 Volume 34 Issue 2 Pages 117–136 DOI: 10.24425/118651
12. Fu et al. 2008 – Fu, X., Li, Q. Zhai, J. Sheng, G. and Li, F. 2008. The physical–chemical characterization of mechanically-treated CFBC fly ash. *Cement Concrete Composites* 30(3), pp. 220–226.

13. Zhang et al. 2012 – Zhang, Z., Qian, J. You, C. and Hu, Ch. 2012. Use of circulating fluidized bed combustion fly ash and slag in autoclaved brick. *Construction and Buildings Materials* 35, pp. 109–116.

14. Kobyashi, N., Itaya, Y., Piao, G., Mori, S., Kondo, M., Hamai, M. & Yamaguchi, M. 2005. The behavior of flue gas from RDF combustion in a fluidized bed. Powder Technology 151: 87-95.

15. Zhao, S., Li, H.B., Yan, C.F. & Zhao, Z.L. 2005. NOx formation of RDF combustion in a fluidized bed reactor. *Journal of Fuel Chemistry and Technology* 33: 633-636.

16. Földvári, M., 2011. *Handbook of thermogravimetric system of minerals and its use in geological practice*. Geological Institute of Hungary. Budapest, 180 pp.