

Short Communication

Co-Combustion of Coal and Biomass – Chemical Properties of Ash

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Abstract

This article describes the chemical properties of the resulting ash from co-combustion of hard coal with biomass. Biomass consisted of sunflower husks, bran grains, and forest biomass. To test the fly ash we sampled from different types of boilers: pulverized, fluidized, and in the case of pulverized boilers ash samples with and without desulfurization products were tested. The results were compared with the properties of ash without co-combustion, which were obtained in the same type of boilers. Chemical and mineralogical compositions were determined and thermal analysis was carried out as well. Studies showed no effect of co-combustion biomass with coal on the tested properties of obtained ash.

Keywords: fly ash, co-combustion, biomass

Introduction

Management of the ash from coal combustion depends mainly on their physical-chemical properties, but also on economic factors. Among individual properties the major role is played by those that determine the impact of ash on the environment, human health, or life, and determine its suitability for utilization (including the content of useful components, geotechnical properties). The requirements related to the ash are concluded in the governing standards and they concern a specific use, among other European norms, ASTM standards. In these regulations a huge pressure is put on the waste chemical composition tests, heavy metals, and chemical pollutant leaching.

In many countries obtaining electricity/heat from biomass by eg. co-combustion has become popular because the other kind of waste is formed – co-combustion fly ash. Directions and possible use of ash depends on their properties; therefore, it is the subject of many studies [1-5].

Physical-chemical properties of ash from the combustion of coal or biomass depends on the type of burned coal, the type of burned biomass, preparation and storage of fuel, and combustion and exhaust gas purification technologies [6, 7]. The main mineral components of ash from coal combustion are silica-alumina glaze, quartz, alumina, iron oxide, mullite, calcium, and coal, which is defined as content of unburned substance (loss on ignition). In addition, they include many trace elements such as: Ba, Cl, Cr, Cu, F, Mn, P, Pb, Ti, Zn, Zr, and V [8, 9]. On the other hand, ash from biomass combustion is characterized with much higher diversity in terms of physical-chemical properties due to many types of biomass [6, 10-12]. By comparing the characteristics of ash from coal used in power generation and biomass, it should be noted that the elemental composition is equal, taking into consideration the quality. Differences can be found in shares of individual elements and chemical compounds [13].

The main aim of the research is to identify the physico-chemical properties of fly ash from co-combustion of coal and biomass, which is necessary to determine the direction of its economic use.

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This article presents the results of research on chemical composition, content of trace elements, and phase composition and thermal change of ash from co-combustion. They were also compared with the results of research on properties of ash from coal combustion.

Materials and Experimental Methods

The samples of tested ash originated from Polish thermal power plants, which co-combust hard coal with biomass in two types of boilers: pulverized (P) and fluidized (F). In addition to the type of boiler, the flue gas desulfurization method was also included (ash without (-) and with products from desulfurization (S)) and types of biomass that participated in the fuel ranging from 7 to 17%. In order to determine the impact of biomass on the properties of fly ash, the ash from coal combustion was examined in pulverized and fluidized beds.

Ash sample to chemical composition was obtained using a microwave oven and digested with an acidic solution of HNO_3/HCl . The solution was diluted with distilled water and analyzed by inductively coupled plasma spectrometry/atomic emission spectroscopy (ICP-AES) by means of a PLASMA 40 apparatus and inductively coupled plasma mass spectrometry (ICP-MS) with the use of a PERKIN ELMER ELAN 6100 apparatus.

Crystalline phases were detected by x-ray diffraction (XRD) and the microscopic method (SEM) equipped with the EDS system. Furthermore, gravimetric and differential thermal analysis (TG/DTA) were carried out.

Results and Discussion

The chemical composition of tested fly ash is shown in table 1. They include mainly: SiO_2 (59 – 73% mass), Al_2O_3 (3-14% mass.), CaO (3-13% mass), and Fe_2O_3 (2-6% mass). Variations of contents of components in individual samples are a result of different combustion and purification methods. In ash from pulverized beds the content of SiO_2 amounted to more than 69%, while in a fluidized bed it amounted to approximately 60%. In ash from fluidized beds there is much more Al_2O_3 compared to ash from pulverized beds. These results confirm studies in literature [8]. A distinct impact on the chemical composition of the ash is the method of exhaust purification. Some of the ash contain exhaust desulfurization products like unreacted reagents, which are shown by higher contents of CaO and SO_3 in ash PS, PSB, F, and FB in comparison to other ash.

Comparison of the chemical composition of the ash from the combustion of the coal and ash from co-combustion in the same type of boiler or in installations with the same method of exhaust purification (P1-2 with PB1-3, PS with PSB, and F with FB) shows no significant differences in the chemical composition of ash. The main cause is very low content of the substance in the unburned biomass (0.5-10%) in relation to that in coal (about 25%), and also amounts of co-fired biomass in fuel which equaled from 7 to 17%.

The contents of individual components in the ash from the combustion and co-combustion are shown in Table 1. These data do not differ from each other significantly. No specific changes are observed in the contents of the individual components resulting from the fact that biomass is co-fired.

The results of the qualitative analysis are shown on the x-ray diffraction patterns (Fig. 1). Variation in chemical composition of the different types of ash were reflected in the diversity of their mineralogical composition. Ash from pulverized beds without exhaust desulfurization products (samples P1, P2, PB1, PB2, PB3) is characterized by similar mineralogical composition (Fig. 1a). Most of all they contain two crystalline phases: quartz (29-52%) and mullite (10-69%). In the samples there were also significant amounts of hematite (samples P1, P2, PB1, PB2) and small amounts of periclase (sample P2 and PB1). In the case of ash samples containing exhaust desulfurization products (PS and PSB), we may meet mullite and quartz, silicate minerals: microcline, kyanite, indialite, and minerals containing Ca: lime, portlandite, and calcite (Fig. 1b). In the mineralogical composition of ash from fluidized beds (samples F and FB) the dominating part was taken by silicate minerals: quartz, kyanite, and muscovite, as well as minerals containing Fe: hematite, pyrrhotite (Fig. 1c). They also contained minerals related to the process of exhaust desulfurization in a fluidized bed (lime, anhydrite, magnesium calcite). Additionally, the FB sample contained large amounts of corundum (being a product of the low-temperature decomposition of clay minerals). X-ray analysis did not reveal the relationship between mineralogical composition of the fly ash and biomass content in fuel.

TG/DTA analysis of fly ash samples allowed for the quantitative and qualitative determination of physical processes and chemical reactions occurring under the influence of heating the samples. Thermal analysis enabled the possibility to compute the amount of organic matter left in ash and calcium compounds. As thermal analysis revealed in fly ash from pulverized beds (samples P1, P2, PB1), organic matter in the form of coal and biomass residues occurred (from 2.4% to 10.3%). Total calcination losses for all ash samples ranged between 2.5-10.7%. The analysis of fly ash samples from hard coal that contained exhaust desulfurization products (PS and PSB) allows us to conclude organic matter content, respectively 2.7 and 6.1%, whose ash also contained calcium compounds like $\text{Ca}(\text{OH})_2$, CaCO_3 , and CaSO_4 originating from the exhaust desulfurization process. Total calcination losses of these samples equaled 5.5 and 7.0%, respectively. As thermal analysis revealed, fly ash from fluidized beds (samples F and FS) contained 14.1 and 3.9% of organic matter and significant amounts of calcium compounds from exhaust desulfurization in fluidized beds. On the basis of thermal analysis results, we found relationships between chemical reaction and physical processes occurring under the influence of fly ash temperature and burning technology or exhaust desulfurization products content in the sample of fly ash. A dependence between processes and biomass content in fuel was not observed.

Table 1. Ash chemical composition and trace element content.

	Fly ash								
	P1	P2	PB1	PB2	PB3	PS	PSB	F	FB
Feed fuel	Hard coal 100%	Hard coal 100%	Hard coal 93%/sunflower husks 7%	Hard coal 89%/bran corn 11%	Hard coal 90%/bark, woody chips 10%	Hard coal 100%	Hard coal 90%/bark, woody chips 10%	Hard coal 100%	Hard coal 83%/sunflower husks 11%, bark, woody chips 6%
Chemical composition [% mass]									
SiO ₂	70.25	74.53	71.77	73.08	70.9	69.2	69.88	59.16	59.36
Al ₂ O ₃	6.98	6.94	5.41	8.01	8.62	3.39	3.25	14.39	14.2
Fe ₂ O ₃	5.99	3.82	4.15	3.55	6.48	3.04	2.16	4.48	4.02
CaO	5.11	2.91	4.81	2.99	5.31	12.09	13.35	7.4	9.39
MgO	2.67	1.59	2.77	1.9	2.85	1.36	1.28	3.7	2.48
SO ₃	0.71	0.46	0.3	0.31	0.41	8.47	3.26	4.22	4.93
Na ₂ O	0.44	0.75	0.53	0.29	0.83	0.21	0.24	0.63	1.65
K ₂ O	0.76	0.58	0.86	1.31	0.82	0.36	0.35	1.82	1.7
TiO ₂	0.18	0.16	0.05	0.04	0.05	0.08	0.09	0.08	0.09
P ₂ O ₅	1.03	0.8	2.16	1.56	1.66	0.45	0.97	2.87	0.83
Trace element content [mg/kg]									
As	79.1	21.6	11	15.4	33.3	27.1	23.1	14.4	10.8
Ba	902.1	478.3	612.3	973.5	723.5	387.6	553.5	948	413.1
Cd	2.3	0.7	0.5	0.4	1	1	0.7	0.6	1.3
Co	23.6	16.8	15.3	18	23.4	10.3	11.7	24.4	17.4
Cr	129.9	75.5	78.5	75.2	129.4	55.3	49.5	80.5	70.9
Cu	182.8	59.8	87.8	56.7	81	93.1	36.5	119.5	96.9
Hg	0.3	0.1	0.1	0.1	0.3	0.2	0.2	0.2	0.2
Li	75.5	57.6	73.1	79.9	124.6	36.9	43.3	107	120.8
Mn	1093.4	562.1	734.9	683.8	1121.3	537.9	332.7	853.6	966
Mo	8.4	5.5	0.4	12.6	0.1	3.2	4.8	1.8	0.4
Ni	87.2	48.9	52.8	55.1	79	37.5	39.8	66.8	46
Pb	317.5	72.2	51.5	30.1	69	121.8	27.4	54	138.5
Sr	390.1	278.7	362.4	274.2	349.2	210.7	269	583.2	251.4
Zn	1365.9	209	143.7	146.7	248.5	604	105.9	198.7	377.5

Conclusions

This article describes the chemical properties of fly ash originating from co-combustion of coal and biomass. Their chemical and mineralogical compositions were studied as well as thermal analysis. The main components of ash from co-combustion were SiO₂, Al₂O₃, CaO, Fe₂O₃, and SO₃ in the case of ash with exhaust desulfurization products and

from fluidized beds. These are typical components for ash coming from coal combustion. Along with the above-mentioned elements, the content of trace elements (in decreasing order of significance) such as: Mn, Ba, Sr, Zn, Cr, Cu, Pb, Ni and others is in comparable quantities for the ash from the combustion of coal itself. There also were not any significant differences in the phase composition of tested ash in comparison to ash without co-combustion. The main

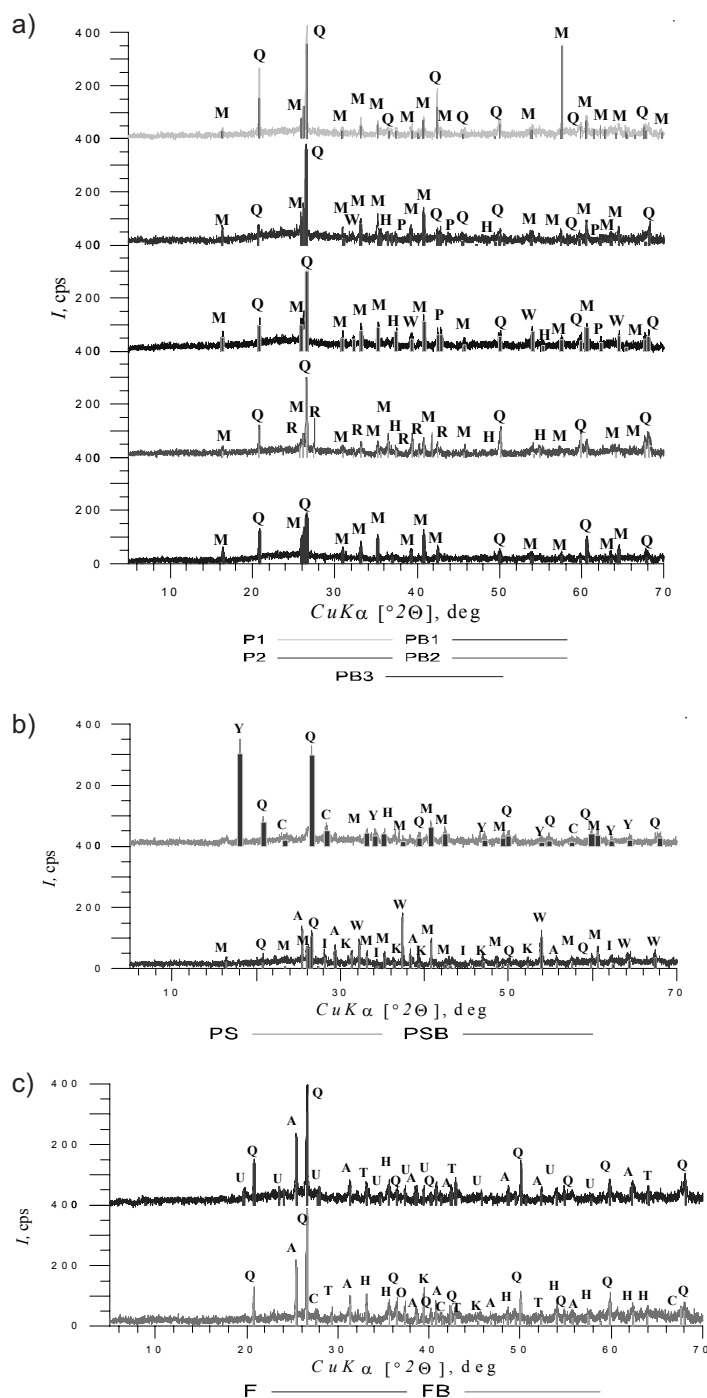


Fig. 1. X-ray diffraction patterns of fly ash a) from pulverized bed, b) with products of exhaust desulfurization originating in a pulverized bed, and c) from fluidized bed.

C – Kyanite $\text{Al}_2\text{Si}_4\text{O}_{10}$, U – Muscovite $\text{KAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$, Q – Quartz SiO_2 , O – Corundum Al_2O_3 , H – Hematite Fe_2O_3 , T – Pyrrhotite FeS , A – Anhydrite CaSO_4 , K – Calcite CaCO_3 , M – Mullite $\text{Al}_6\text{Si}_2\text{O}_{13}$, P – Periclase MgO , W – Lime CaO , R – Microcline $(\text{K},\text{Na})[\text{AlSi}_3\text{O}_8]$, Y – Portlandite $\text{Ca}(\text{OH})_2$, I – Indialite $\text{Mg}_2\text{Al}_3[\text{AlSi}_5\text{O}_{18}]$

phases of ash from co-combustion were quartz, hematite, aluminosilicates and, in smaller quantities, anhydrite and lime. TG/DTA analysis showed differences resulting from technology of combustion or the presence of exhaust desulfurization products in ash, which were not caused by biomass participation. The analysis of the results of our studies showed no significant differences in the properties of the ash resulting from the co-combustion of biomass and coal

compared to ash from combustion of coal itself. This is due to the low participation of biomass in fuel as well as the small ash content in biomass.

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