Pollution Prevention and Control

The Preliminary Studies of the Phase and Chemical Composition of Ashes Formed in the Co-combustion of Hard Coal and Wood Biomass in an Individual Domestic Furnace (Poland)

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Abstract

This work presents the analysis results of ashes formed in the combustion of hard coal and wood biomass (birch) in an individual domestic furnace (upper combustion boiler) in Poland. The ash was sampled from under the grate (grain size from 100 μm to a 2 cm) and from the upper chamber at the chimney (max. grain size 20 μm). A mineral composition was determined in ash samples by an X-ray diffraction method and a powder method and the phase compo**s**ition was determined by means of the scanning electron microscope. The samples of hard coal and wood biomass ashes were analysed in terms of the content of potentially toxic elements (PTE): Pb, Cd, Cu, Ba, As, Zn, Ni, Mn by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) .

Keywords

ard coal, Wood biomass, Individual domestic furnace, Minerals phase, Trace elements

Introduction

A dominant impact on the size and structure of the air pollution emission in Poland is exerted by commercial energy and hard coal combustion in individual domestic furnaces. The emission and ashes from individual domestic furnaces constitutes 35.8% (share in total emissions) at the national level [1]. This results from the fact that individual domestic furnaces do not have any devices for fumes de-dusting. Solid combustion products in the form of coarse and fine dusts, which are discharged at municipal landfills, also constitute a serious problem. Individual heating consumes more than 10 mln tonnes of hard coal annually (approximately 14% of the national consumption). It is estimated that 1 tonne of hard coal produces about 0.4 tonne waste (ashes) [2]. During the heating season, ashes emitted by individual domestic furnaces and related PTE contribute to air pollution, causing adverse effect on the environment and human health.

The chemical and phase composition of ashes formed in the co-combustion of hard coal and biomass in individual domestic furnaces differs basically from ashes formed of commercial energy plants (power plants, heat and power stations) [3-6]. A dominant component in ashes formed during the combustion of hard coal in commercial energy plants is SiO_2 [7-9]. According to Vassilev et al. [10] fluidised ashes from the co-combustion with biomass may include more elements, such as: Ag, Au, Cd, Cr, Cu, Mn, Ni and Zn compared to the ashes from coal combustion. However, this is not a rule because the trace elements content is mostly influenced by such parameters as: the physical and chemical properties of hard coal, the chemical composition of biomass and combustion technology.

It is estimated that approximately 480 mln tonnes of ash from the combustion and co-combustion of biomass may be generated worldwide annually, assuming that the biomass combusted amounts to 7 billion tonnes/year [11-13]. The ash content is usually lower in biomass than in hard coal; yet, this is not a rule.

In individual domestic furnaces, the process of hard coal combustion takes place in lower temperatures due to the insufficient quantity of oxygen. This process leads to the formation of ashes with a different chemical and mineral composition and variable PTE content [14]. Wood combustion is an important source of organic and in-organic solid particles emitted to the environment [15-17].

The aim of the present work was to study the concentrations of potentially toxic elements of the ash generated from the combustion of hard coal and wood biomass. To establish what phase mineral are present in ash from individual domestic furnaces.

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Methodology

Sample collection and preparation

Coal ash, hard coal and biomass samples come from individual domestic furnaces using Upper Silesia Basin coals (Poland) as a fuel for central heating purposes, one located in the Rybnik town (sample codes A1–A9, B1-B2 and C - unburned coal in Table 1). A total of 12 samples were taken.

The city of Rybnik is the centre of a metropolitan area, the Rybnik Coal Region (Figure 1). Geographical co-ordinates defining the Rybnik town location are $50^0 5'$ northern latitude and $18^0 33'$ of eastern longitude.

Ash was sampled in November, December and January of 2018/2019. The biomass burned in the furnace was softwood (birch). The percentage of wood biomass in the combustion process is 35%. Wood usually is not available in a dried state and it is characteristic for varied humidity which ranges from 15% to 60% (the Author's own research) depending on the seasoning duration. The hard coal net calorific value is 23 GJ/t. This is energy coal of a walnut size (commercial assortment). The net calorific value of birch wood is about 17 GJ/t [18].

Hard coal was a combusted in the boilers of the Zębiec SWK-21. The SWK boiler with the upper combustion of solid fuels ensures the efficient heating of any type of building: from a garage, a house and utility buildings to commercial spaces. Indicative thermal power in depedence from stove 21 kW and admissible pressure was 0.15 MPa. Temperature of combustion gas in boilers was from 300^0C to 400^0C. The hard coal combusted in the individual domestic furnace comes from the coal mines belonging to the Upper Silesian Coal Basin (USCB). Its calorific value is low (19 MJ/kg) (data from the Rydułtowy-Anna coal mine).

The grain - size analysis was performed with the application of a laser particle size meter, type Analysette 22 Micro Tec plus (University of Silesia, Faculty of Natural Sciences).

X-ray powder diffraction

The mineral composition of the samples was analyzed with the X-ray diffractometry (XRD) method ussing an - X'Pert Pro MPD PW3040/60 diffractometer, utilizing Co-K α radiation with a graphite monochromator. The lamp electric voltage was 40 kV with current intensity of 40 mA. Impulse time counting in the method was 100 s and the rate of a tape movement was 0.01/min. The estimated concentrations (%) of the analyzed amorphous phase are given using the X'PERT computer program.

Scanning electron microscopy

Qualitative phase analysis of ashes and biomass was carried out with the method of scanning electron microscopy equipped with EDAX EDS using PHILIPS XL 30 under the following analytical conditions acceleration voltage 15-20 keV, beam current intensity 20 nA.

Chemical analysis

The content of the potentially toxic elements was analysed at Activation Laboratories Ltd.**'s Global Headquarters (**Ancaster, Ontario, Kanada) by means of inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy (ICP-MS) methods using the Perkin Elmer SCIEX ELAN 6000 and Varian 735 ES (ICP-OES). ICP-OES and ICP-MS analyses by 4-acid (hydrochloric, nitric, perchloric and hydrofluoric) digestion are "near total" digestions.One blank is analyzed per work order. International certified reference materials USGS GXR-1, GXR-2, GXR-4 and GXR-6 are analyzed at the beginning and end of each batch of samples.

Results

In ashes from hard coal and wood biomass combustion, the share of large fraction (> 100 μm) amounts to 52.21–78.42%, and that of fine fraction (< 6 μm) is at the level of 17.25–25.24% (samples A1-A5). The average values in ash samples are given in Table 2. The percentage fractions of the grain fraction were calculated for the upper grain size limit.

Mineral composition of wood biomass ash

The wood biomass ashes (B1-B2) show different mineral composition and variable content of respective components. Calcite (25.6%-69%), quartz (2.1%-17%) and fairchildite (2.3%-8.6%) are the main mineral components in ash from wooden biomass. Monetite, arcanite, apatite, periclase, sylvine, portlandite and lime constitute from 1.8% to 5.5%. A high share of an amorphic substance was found in the tested wood biomass ashes (55.7% - 62.4%). Samples of ashes difractogram s show hight background and a hump, characteristic for amorphous substance, with maximum at 20^0-27^0 2Θ and 40^0-50^0 2Θ. The chemical and phase differences among the specified natural and anthropogenic biomass groups and sub-groups are significant and they are related to diverse biomass source and origin [19].

Mineral composition of hard coal and wood biomass ash

The fine ash samples (A6-A9) constitute from 25.6% to 30.8% of the total ash mass obtained after the combustion of hard coal with wood biomass. The main mineral components identified in the analyzed ashes (A1-A9) are anhydrite, hematite, magnetite, mullite, pyrite, galena, gypsum, quartz, calcite, feldspars, kaolinite. Fairchildite and monetite occure in to the non-combusted coal substance. The amorphic substance (aluminosilicates and carbonates) in the examined ash samples constitutes from 56.7% to 63.7%.

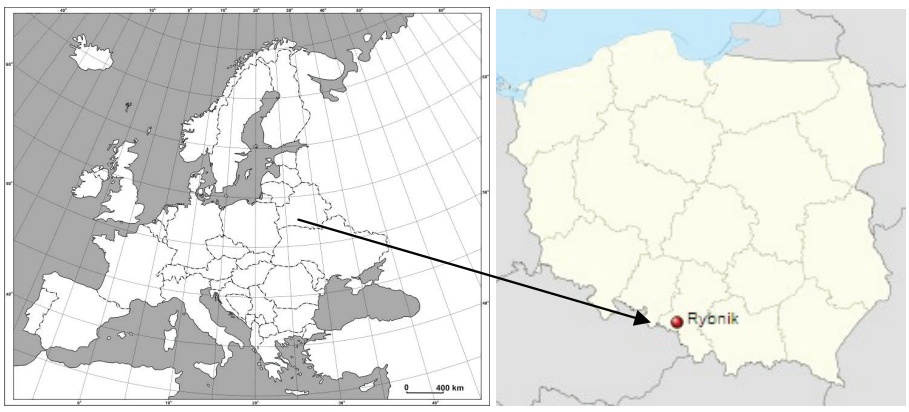


Figure1: Location of sampling for testing (https://www.google.com/search=Poland)

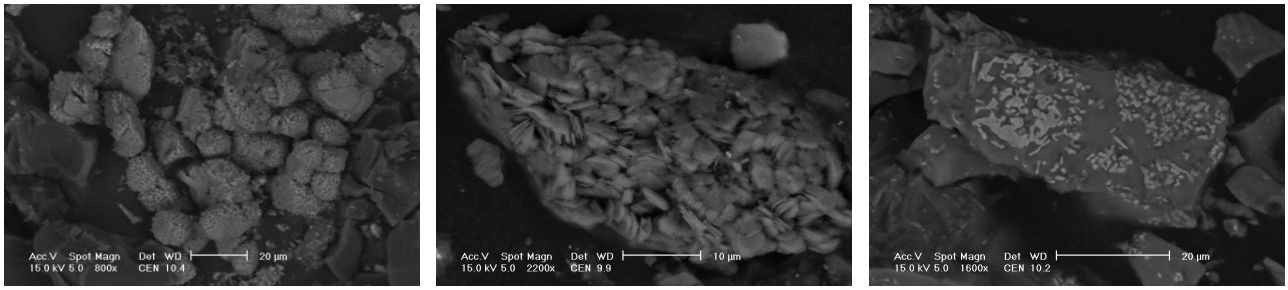
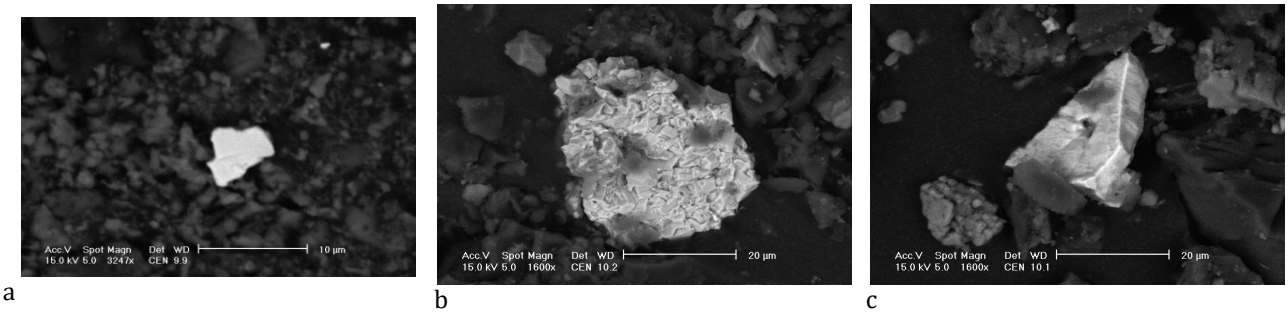


Figure 2: Aluminosilicate phases in hard coal and wood biomass ashes



a b c

Figure 3: Sulphide forms - Pb (a), Zn (c) and substance with a composition of chalcopyrite (b) in hard coal and wood biomass ashes

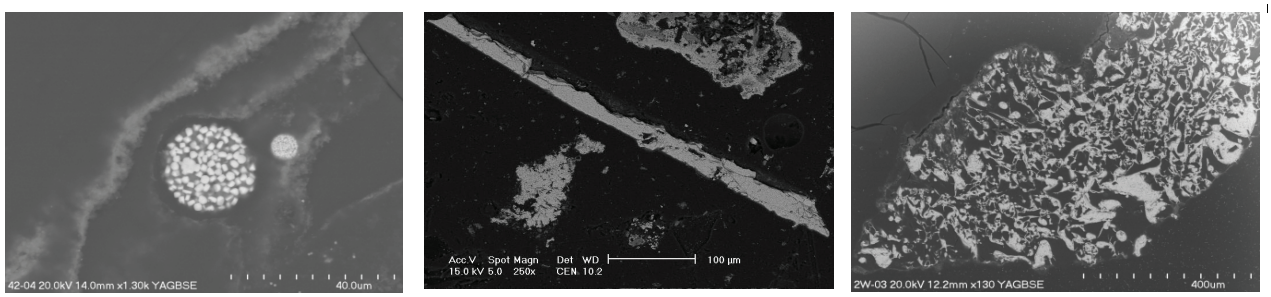


Figure 4: Pyrite forms in hard coal and wood biomass ashes

SEM analysis

The examination by means of scanning electron microscope with EDS enabled us to characterize both the chemical composition of single ash grains and their morphology.

In the ashes obtained from hard coal combustion mainly aluminosilicate forms with smooth surfaces and spherical shapes were observed. Sizes of aluminosilicate spheres were from 5µm to 200µm (Figure 2), and following elements were adsorbed and their surface: calcium, potassium, magnesium, iron, barium, zinc and manganese. They are on the surface of the ash particles (EDS spectrum). One could also notice aluminiosilicate substance, which appeared in the form of irregular forms, which had porous surface and size up to 100µm.

The next group consisted of sulphides of lead, zinc and copper (Figure 3 a-c). The substance PbS was present in the investigated samples sharp-edged forms, which had smooth surface and their size was not bigger than 5µm. The substance ZnS was represented probably by sphalerite, which built units and their size was about 20µm.

In the ashes one could also notice single grains of pyrite (Figure 4), which built longitudinal forms (their length was about 600µm) and aggregate concentrations, which size was from 20 to 300µm.

Forms of iron oxides are shown in Figure 5. Their forms are mostly oval, bar- like or spherical. Particle sizes are up to 20µm. The unburned carbonaceous substance contains inclusions of a monetite and fairchildite composition (Figure 6a). Quartz often occurs in unburned plant and carbonaceous substance (Figure 6c).

Ash has typical chemical composition for ash from combustion wood biomass [20,21]. Also, metals might be adsorbed on the surface of biomass ash particles and new formed phases [22].

Chemical analysis

The concentrations of potentially toxic elements determined in the analyzed samples (A1-A9; B1-B2; C) are shown in Table 3.

Elements such as Pb, Zn Ba and Mn concentrations in ash from wood biomass are characteristic for the highest variability. The concentrations of these elements are comparable to or lower than the ashes generated in the co-combustion of hard coal and biomass. Fly ashes from the combustion of biomass have a higher content of PTE when compared to ashes resulting from the combustion of coal [10,19,23,24]. Concentrations of metals in wood ash varies in wide ranges: Cd 1-41 mg/kg, Cu 13-8793 mg/kg, Ni 3-510 mg/kg, Pb 3-1900 mg/kg, Zn 0.01-1.21%, and Mn 0.17-2.37% [21,25].

The ashes formed in the co-combustion of hard coal and wood biomass are enriched in Pb and Zn compared to the ashes formed

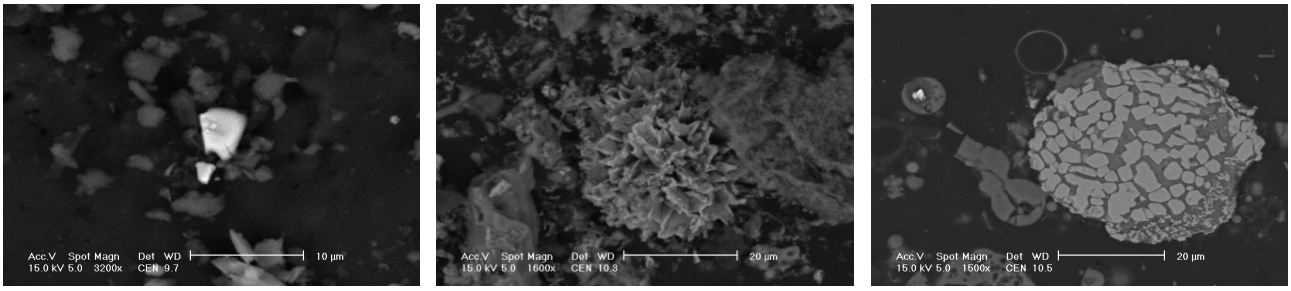


Figure 5: Forms of iron oxides in hard coal and wood biomass ashes

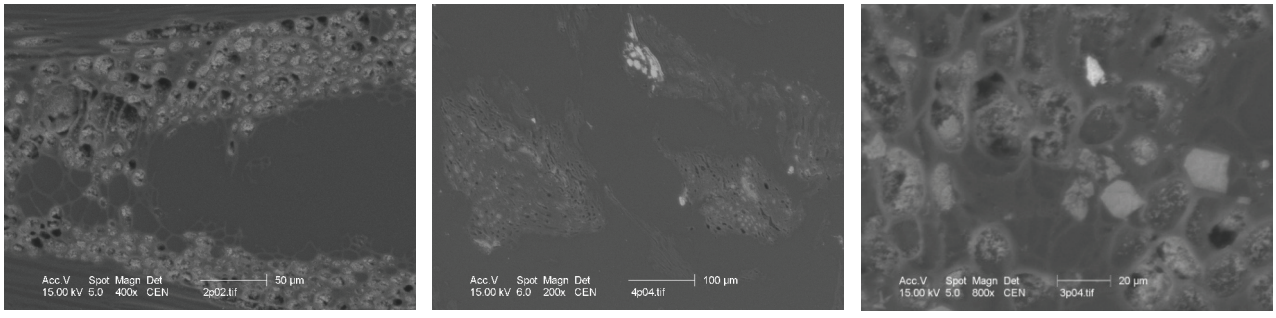


Figure 6: Substance with a composition of monetite and fairchildite (a, b - bright particles) and quartz (c) in coal and wood biomass ashes

Sample code	Sample type	Source
A1	Ash from co-firing of hard coal and biomass (under the grate)	Individual domestic furnace (Rybnik town)
A2		
A3		
A4		
A5		
A6	Ash from co-firing of hard coal and biomass (by the chimney)	
A7		
A8		
A9		
B1	Ash from burning birch (fresh)	Individual domestic furnace (Rybnik town)
B2	Ash from burning birch (seasoned)	
C	Unburned coal	Rydułtowy-Anna coal mine

Table 1: Samples description

Source	Ash particle diameter - upper limit (µm)					
	6.0	20.0	50.0	100.	200.0	250.0
Ash from co-firing of hard coal and biomass (under the grate)	21.38	2.00	3.83	61.9	7.52	3.37
Ash from co-firing of hard coal and biomass (by the chimney)	79.16	20.84		-	-	-

Table 2: Average content of grain fractions (%) in the samples of ashes

Sample	Pb	Cd	Cu	Ba	As	Zn	Ni	Mn
MDL	0.5	0.01	0.2	1	0.1	0.2	0.1	1
A1	387	0.6	86	355	11	778	71	870
A2	370	1.4	77	482	8	660	80	680
A3	363	2.2	78	311	6	748	87	712
A4	371	1.4	75	296	10	790	98	825
A5	388	1.1	78	321	11	665	81	805
Average	375.8	1.3	78.8	353	9.2	728.2	83.4	778.4
SD	9.95	0.574	3.763	67.352	1.939	86.783	8.902	71.219
A6	421	2.3	10	755	14	880	32	1885
A7	476	2.1	11	874	16	821	31	1850
A8	520	1.8	31	890	18	790	26	1980
A9	551	2.2	23	787	14	855	28	1750
Average	492	2.1	18.6	826.5	15.5	836.5	29.3	1866.3
SD	48.893	0.216	8.728	59.922	1.654	34.045	2.387	61.023
B1	1149	7.1	8	3750	34	1235	41	4655
B2	285	4.7	2	2677	14	144	71	13336
Average	717	5.9	5	3213.5	24	689.5	56	8995.5
SD	432	1.691	3	536.499	10	545.75	15	4340.49
C	12	0.7	23	165	4	67	23	582

Table 3: Concentrations of PTE (mg/kg) in ashes from hard coal and wood biomass combustion. Sample C is an unburned coal

MDL - Method detection limits (ppm)
SD - Standard deviation

in the combustion of hard coal only [14]. The concentrations of PTE in the fine fraction of ash samples (A5-A9) are higher than in the ashes of large fraction (A1-A5). Generally, fine ash fractions are more enriched with trace elements due to their large development area.

A slightly higher Mn concentration was determined in the fine ash fraction (A5-A9). The enrichment of ashes formed in the co-combustion of coal and biomass in Pb, Ba, Zn, Mn results from the content of these elements in the wood biomass (Table 3 - samples B1, B2). The results indicate that a wood quality affects the PTE content. The seasoned birch contains considerably lower concentrations of the potentially toxic elements concentrations than the fresh birch wood (except for Ni and Mn).

Conclusion

Calcite, quartz and fairchildite are the main mineral components of ashes from the combustion of wood biomass (birch) in an individual domestic furnace. These ashes are enriched Pb, Mn, Ba and Zn.

The mineral composition of ashes formed in the co-combustion of hard coal and wood biomass is dominated by anhydrite, iron oxides, quartz, mullite, Pb, Zn and Cu sulphides, mixture of fairchildite and monetite. The amount of fairchildite and monetite is lower in ashes from co-firing of hard coal and biomass. These ashes include higher concentrations of Pb, Mn, Ba and Zn compared to the ashes from wood biomass. This results from the wood quality because fresh birch is characteristic for higher PTE concentrations.

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