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ALICJA ULIASZ-BOCHEŃCZYK[1], EUGENIUSZ MOKRZYCKI[2]

The elemental composition of biomass ashes as a preliminary assessment of the recovery potential

Introduction

The commercial power industry in Poland is based on the use of solid, conventional fuels (Mokrzycki and Uliasz-Bocheńczyk 2009). However, the requirements for the use of renewable energy sources have increased the share of biomass use. The share of solid biofuels in energy from renewable sources was respectively: 82.07% (2012), 79.88% (2013), 76.14% (2014), 73.23% (2015), and 70.74% (2016).

The commercial energy industry in Poland consumed 57,714,283 GJ of biomass in 2016 (Emitor 2016).

Biomass is a very diverse fuel. The definition of biomass includes both energy plants and waste (the Act of February 20, 2015 on Renewable Energy Sources (Journal of Laws of 2015, item 478, as amended)).

Due to the wide scope of the term, various kinds of biomass were determined. Usually, biomass for energy purposes is divided into six groups (Vassilev et al. 2012):

1. Wood biomass (e.g.: trees (coniferous, deciduous, angiosperms, soft or hard), stems, bark, branches, leaves, shrubs, wood chips, pellets, briquettes, or sawdust).

✉ Corresponding Author: Alicja Uliasz-Bocheńczyk; e-mail: aub@agh.edu.pl

[1] AGH University of Science and Technology, Faculty of Mining and Geoengineering, Kraków, Poland; e-mail: aub@agh.edu.pl

[2] Mineral and Energy Economy Research Institute of the Polish Academy of Sciences, Kraków Poland; e-mail: eugeniusz.mokrzycki@min-pan.krakow.pl

2. Herbaceous and agriculture biomass:
   - Grasses and flowers (e.g.: alfalfa, bamboo, reed, miscanthus, a perennial ryegrass).
   - Straw (e.g.: barley, bean, corn, flax, mint, oats, rapeseed, rice, rye, sesame, sunflower, triticale, wheat).
   - Stalk (e.g.: bean, corn, cotton, sunflower, thistle, tobacco).
   - Fibers (e.g.: coconut, flax).
   - Shells and husks (e.g. almonds, cashew nuts, coffee, cotton, hazelnuts, millet, and sunflowers).
   - Seeds (e.g. apricots, cherries, olives, peaches, or plums).
   - Other residues (e.g. fruits, seeds, grains, cobs, feeds, pomaces, and pulps).
3. Marine or freshwater – biomass, macroalgae or microalgae, and multicellular or unicellular species (e.g.: green and red algae, diatoms, cilia, seaweed, or water hyacinth).
4. Biomass waste of animal origin (such as: bones, poultry litter, meat-and-bone meal, fertilizer).
5. The contaminated biomass and industrial biomass (e.g. municipal waste, wood from demolition, sewage sludge, paper pulp slurry, cardboard waste, chipboard, fiberboard, plywood, pallets and wooden boxes, railway sleepers).
6. Biomass mixtures.

The use of biomass results in an increase in the amount of waste from combustion, primarily in the form of fly ash (Uliasz-Bocheńczyk and Mokrzycki 2015; Uliasz-Bocheńczyk et al. 2015, 2016), a highly variable material, which is difficult to manage.

One of the key parameters determining the possible use of waste is the chemical composition. A high content of phosphorus may predispose them to be used in agriculture (Ciesielczuk et al. 2018), and limit their use in concrete production (Giergiczny 2009; Ban and Ramli 2011).

The article discusses the chemical composition of fly ashes from the combustion of biomass as one of the primary parameters in the assessment of the recovery potential. Depending on the elemental content, certain directions of use can be excluded. The analysis of elemental composition allow for a preliminary assessment of the potential for the use of the discussed ashes in various branches of economy.

1. The recovery of the ashes from the combustion of biomass

The most important applications of the analyzed fly ash from the combustion of biomass include (e.g. Cruz et al. 2017; Uliasz-Bocheńczyk and Mokrzycki 2015; Rajamma et al. 2015; Demis et al. 2014; Cuenca et al. 2013; Vassilev et al. 2013; Maschio et al. 2011; Ban and Ramli 2011; Pels and Sarabèr 2011; Ciesielczuk et al. 2011; Rajamma et al. 2009):

- use in the production of building materials,
- use in agriculture,
- use in road construction (road foundations and asphalt binders),

- chemical stabilization of municipal sewage sludge,
- use for wastewater treatment and as absorbents.

These ashes can also be used, among others (Vassilev et al. 2013b), for the production of: ceramics, membrane filters used in the food and petrochemical industries, glass and glaze, geopolymers, or zeolites.

However, the ashes from the combustion of biomass are most commonly used in the production of building materials and agriculture.

The use of fly ashes from the combustion of biomass in the production of building materials is limited mainly due to the high concentrations of potassium and chlorine, and thus the risk of efflorescences and corrosion due to leaching, and the variable content of heavy metals (Pels and Sarabèr 2011).

The high content of SiO_2 in ashes from biomass does not clearly indicate that they have pozzolanic properties (Demis et al. 2014).

When it comes to the chemical composition, Rajamma et al. (2009) has shown that fly ash from biomass combustion is similar to Class C fly according to standard EN 450. The authors stress, however, that due to the nature of the ashes from the combustion of biomass it is necessary to control the content of of chlorides, sulfates and alkali.

Fly ashes from biomass combustion contain biomass nutrients and therefore it is logical to use them in agriculture, "bringing" them back to their roots (Pels and Sarabèr 2011).

The use of ash from biomass combustion for agricultural purposes (Vassilev 2013b) primarily improves the soil balance thanks to the nutrients and essential components such as: C, O, H, Ca, K, and, less commonly, N, S, Mg, P, Cl, Na, Mn, Zn, Fe, B, Cu, or Mo, and by providing an alkaline pH (liming effect).

However, their usefulness depends on the type of biomass used as a fuel. Ashes from pure wood pellets contain mostly Ca and Mg, but ashes from agricultural waste can be rich in phosphorus and potassium. Sulfur is one of the important elements occurring in biomass ashes (Pels and Sarabèr 2011).

Significant amounts of manganese, zinc, and copper in the ashes from biomass combustion may be a reason for their limited use (Ciesielczuk et al. 2011).

Fly ash from biomass containing large amounts of potassium and phosphorus, e.g. from the combustion of forest waste, are the most likely to be used to improve the quality of the soil. Fly ashes from biomass mainly containing calcium and magnesium, e.g. from the combustion of bark, can be used as agents improving soil quality in order to balance the pH (Pels and Sarabèr 2011).

The factor limiting the use of ashes from biomass combustion as an agent improving soil quality is the presence of Cr (Cruz et al. 2017).

2. The elemental content of fly ash from the combustion of biomass

The chemical composition of fly ash from biomass is affected by many factors, including (Vassilev et al. 2012, 2013a, b, 2014; Gianoncelli et al. 2013):

- the origin of the biomass − the biomass type, mixing of various biomass types, age of plants, plant parts, use of fertilizers in crops, growth process and conditions of growth, harvest time, humidity, soil pollution, soil type, pH, preparation processes, weather, geographical location, e.g. the distance from the sea or the source of pollution, such as: highways, cities, factories, mines, and others,
- biomass combustion – fuel preparation, combustion technique and conditions, flue gas cleaning equipment,
- collection, transport, and storage of biomass.

Another factor affecting the chemical composition of ash from biomass combustion is a relatively low melting point (Gianoncelli et al. 2013).

Due to the large variability in the chemical composition of fly ash from biomass combustion, it was proposed to divide them into three groups (Livingston 2006; Bogush et al. 2018):

1. Ashes characterized by a high content of Si and K, low Ca content, with a low melting point – containing mainly ashes from the combustion of agricultural waste.
2. Ashes characterized by a low content of Si and K, with a high melting point – containing mainly ashes from the combustion of wood.
3. Ashes characterized by a high content of Ca and P, with a low melting point – containing mainly ashes from the combustion of animal waste.

Fly ashes from the combustion of biomass have a higher content of: Ag, B, Br, Ca, Cl, Cr, Cu, Ga, Hg, I, K, Mg, Mn, Mo, Na, P, Rb, Sr, Te, and Zn when compared to ashes resulting from the combustion of coal. Meanwhile, their content of: Al, As, Au, Ba, Be, Bi, Cd, Ce, Co, Cs, Dy, Er, Eu, F, Fe, Gd, Ge, Hf, Ho, In, Ir, La, Li, Lu, Nb, Nd, Ni, Os, Pd, Pr, Pt, S, Sb, Sc, Se, Si, Sm, Sn, Ta, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, and Zr is lower (Vassilev et al. 2013, 2014).

Tables 1−6 present elemental compositions of fly ashes from biomass combustion broken down by the most commonly used types of biomass.

Fly ashes from the combustion of straw (Table 1) are characterized by a high content of: potassium, calcium and chlorine, and the lack of silicon. Sulfur and silicon content has been confirmed only in one of the ashes (Bogush et al. 2018). The content of: As, Cd, Cr, Cu, Ni, Pb and Zn has been confirmed (Lanzerstorfer 2015; Bogush et al. 2018).

In addition, the mercury content has also been confirmed (Bogush et al. 2018).

A high variability in the chemical composition of ash from biomass combustion is particularly evident in the case of the use of various types of wood and forest waste (Table 2, 3, and 4).

Table 1. The elemental content of fly ash from the combustion of straw

Tabela 1. Zawartość pierwiastków w popiołach lotnych ze spalania słomy

Element	Fly ash from the combustion of:		
	straw	wheat straw	wheat straw, disintegrated bales
	Bogush et al. 2018	Lanzerstorfer 2015	
	%/ mg/kg	mg/kg	
Ca	13%	5.4	32.8
Mg	0.17%	0.4	7.7
P	2.2%	–	–
Na	0.051%	7.4	4.9
K	14.0%	570	407
Si	2.2%	–	–
Al	0.04%	1.4	0.01
Fe	0.021%	1.5	0.7
Mn	0.015%	0.1	0.04
As	1.3 mg/kg	7	10
Cd	3.3 mg/kg	3	8
Cr	12 mg/kg	22	7
Cu	43 mg/kg	<5	<5
Hg	–	0.3	0.4
Ni	1.8 mg/kg	<5	<5
Pb	28 mg/kg	<20	<20
Zn	490 mg/kg	0.238	0.325
Cl	22%	161.0	254.2
B	–	17	103
Ba	–	271	33
Bi	–	8	45
Co	–	<25	33
Mo	–	<5	46
Sb	–	<10	<10
Sr	–	55	25
V	–	<10	13
S	0.69%	–	–

Table 2. The elemental content of fly ashes from the combustion of wood

Tabela 2. Zawartość pierwiastków w popiołach lotnych ze spalania drewna

Element	Fly ash from the combustion of:											
	wood	wood waste with bark	coniferous wood		deciduous wood		deciduous	wood	wood	wood from forest waste; 80% coniferous wood, 20% deciduous wood	wood from forest waste; 80% spruce, 20% beech, oak, and birch	wood chips (mainly *Picea abies*)
			tree trunk	bark	tree trunk	bark						
	jukić et al. 2017	Kowalkowski and Olejarski 2011						Cuenca et al. 2013	Berra et al. 2015	Lanzerstorfer 2015		Maresca et al. 2017
	mg/kg	%						ppm	mg/kg			
1	2	3	4	5	6	7	8	9	10	11	12	13
Ca	–	13.2	22.4	28.5	19.5	27.1	8.09	–	–	59.3	231	104–263
Mg	–	1.47	4.3	2.8	3.6	2.2	0.90	–	–	4.7	30.0	10.2–22.9
P	–	2.93	12.4	9.8	20.4	12.2	4.48	–	–	–	–	40.0–60.3
Na	–	0.24	–	–	–	–	0.96	–	–	8.0	4.8	6.65–12.0
K	–	0.79	2.4	2.8	4.2	3.4	0.83	–	–	311	192	19.3–32.9
Si	–	0.56	2.3	1.2	2.1	1.1	1.00	–	–	–	–	45.6–124.0
Al	–	2.0	–	–	–	–	4.23	–	–	2.1	8.4	5.92–11.8
Fe	–	1.51	0.8	0.2	0.5	0.6	1.33	–	–	3.2	8.6	2.88–8.3
Mn	–	0.67	2.9	1.7	0.8	0.6	–	–	–	4.1	14.6	4.03–30.3
As	3.34	–	–	–	–	–	–	–	45	36	27	2.68–6.98

Table 2. cont.

Tabela 2. cd.

1	2	3	4	5	6	7	8	9	10	11	12	13
Cd	2.38	–	–	–	–	–	–	–	60	105	41	7.32–16.3
Cr	76.4	–	–	–	–	–	–	–	124	76	87	26.5–62.7
Cu	89.6	–	–	–	–	–	–	–	920	140	145	0.106–0.161
Hg	0.031	–	–	–	–	–	–	–	0.4	0.1	1.7	–
Ni	28.0	–	–	–	–	–	–	–	102	23	27	22.4–52.5
Pb	13.1	–	–	–	–	–	–	1.028	5,318	602	250	10.7–73.8
Zn	102	–	–	–	–	–	–	0.523	17,470	19.0	7.99	0.446–1.120
Cl	–	–	–	–	–	–	–	–	–	34.4	25.0	–
B	–	–	–	–	–	–	–	–	–	221	671	–
Ba	–	–	–	–	–	–	–	–	–	91	191	0.797–2.32
Bi	–	–	–	–	–	–	–	–	–	237	124	–
Co	–	–	–	–	–	–	–	–	–	39	<25	5.79–9.69
Mo	–	–	–	–	–	–	–	–	–	43	<5	1.46–4.29
Sb	–	–	–	–	–	–	–	–	–	12	<10	0.721–5.83
Sr	–	–	–	–	–	–	–	–	–	242	641	578–1 240
S	–	–	–	–	–	–	–	–	–	–	–	4.21–15.3
V	–	–	–	–	–	–	–	–	–	38	<10	6.75–18.2

Table 3. The elemental content of fly ash from the combustion of wood chips

Tabela 3. Zawartość pierwiastków w popiołach lotnych ze spalania zrębków

Element	Fly ash from the combustion of:						
	chestnut or poplar virgin wood chips	chestnut or poplar virgin wood chips	wood chips from forest residue > 90%; sawdust and bark < 10%	wood chips from forest residue, 90% softwood (spruce), 10% hardwood (beech, oak and birch)	beech wood chips	bark and wood chips	wood chips
	Berra et al. 2015		Lanzerstorfer 2015		Vassilev et al. 2014	Supancic et al. 2014	
	mg/kg				ppm	mg/kg	
Ca	–	–	158	125	–	155,000	48,200
Mg	–	–	12.7	11.6	–	11,700	5,740
P	–	–	–	–	1 786	5,340	2,440
Na	–	–	3.3	47.0	–	3,150	3,250
K	–	–	47.2	177	–	63,200	45,000
Si	–	–	–	–	–	215,000	377,000
Al.	–	–	19.1	7.2	–	19,300	17,300
Fe	–	–	13.2	10.4	–	8,020	2,730
Mn	–	–	8.4	6.8	10.595	5,090	1,210
As	18	15	19	62	4.5	1.6	1.9
Cd	9.0	7.6	19	77	4.9	4.5	0.2
Cr	101	18	92	70	24	20.1	21.1
Cu	175	48	11	156	98	70.1	44.2
Hg	0.2	0.3	0.8	4.2	–	–	–
Ni	41	50	31	4	36	34.1	8.0
Pb	177	39	352	892	38.7	20.7	18.5
Zn	2 274	636	3.67	15.4	–	198.0	420.0
Cl	6.2	236.7	–	–	–	166	2.0
B	–	–	263	292	10.257	–	–
Ba	–	–	484	136	1 786	–	–
Bi	–	–	95	167	–	–	–
Co	–	–	39	<25	4.2	6.7	2.0
Mo	–	–	24	<5	2.06	1.0	0.4
Sb	–	–	10	<10	0.71	–	–
Sr	–	–	284	283	324	–	–
V	–	–	36	<10	8.9	15.1	9.5
S	–	–	–	–	–	2,740	592

Table 4. The elemental content of fly ash from the combustion of forest waste, mg/kg

Tabela 4. Zawartość pierwiastków w popiołach lotnych ze spalania odpadów leśnych, mg/kg

Element	Fly ash from the combustion of:						
	forest residues (i.e., bark, wood chips, and branches) and agricultural residues (i.e., straw, rice husk, and cotton stalk) – cyclone	forest residues (i.e., bark, wood chips, and branches) and agricultural residues (i.e., straw, rice husk, and cotton stalk) – filter	wood chips from forest residue 1	wood chips from forest residue 2	wood chips from forest residue 3	forest wastes	90% wood chips from forest residue and 10% horse dung
	Li et al. 2012		Lanzerstorfer 2017b			Rajamma et al. 2009	Lanzerstorfer 2015
Ca	–	–	161	228	104	–	316
Mg	–	–	24.0	28.4	10.7	–	3.7
P	–	–				–	–
Na	–	–	2.7	2.3	39.4	–	5.1
K	–	–	138	81.2	143	–	118
Si	–	–	–	–	–	–	–
Al	–	–	–	–	–	–	1.3
Fe	1.988	8.136	8.3	8.5	11.2	–	1.9
Mn	5.02	7.144	13.8 g/kg	7.7 g/kg	7.7 g/kg	–	1.0
As	5.1	25.6	–	–	–	–	–
Cd	1.9	2.3	40	31	75	1.0	–
Cr	10.1	128.1	–	–	–	47	–
Cu	18.9	31.6	145	177	207	99	–
Hg	0.014	0.007	–	–	–	< 1	–
Ni	24.5	68.3	46	49	28	35	–
Pb	23.4	36.1	259	307	911	191	–
Zn	61.65	252	7.27	4.31	14.8	376	–
Ba	206.4	671.4	662	623	371	–	–
Co	6.4	11.5	–	–	–	–	–
Ti	982	179	–	–	–	–	–
Cl	–	–	–	–	–	–	52.3

The analysis is particularly difficult due to the fact that the authors of the studies present different results without explaining whether silicon is not present in the analyzed waste or simply was not determined. However, most of the results indicate the presence of: As, Cd, Cr, Cu, Ni, and Pb. Berra et al. (2015) paid particular attention to the significant contents of heavy metals such as: As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in the fly ashes from the combustion of chestnut or poplar wood chips or wood. The authors explained this fact by the sorption of heavy metals from soils containing phosphate fertilizers and sewage sludges. In addition, they paid attention to the high content of chlorine and alkalis, especially potassium.

The presence of heavy metals was also indicated by Cuenca et al. 2013, Rajamma et al. 2009 (Table 2 and 4). According to Jukić et al. (2017) (Table 2), the ashes from the combustion of wood have a high content of Zn and Cu and a low content of Cd and Hg. The analysis of different groups of ashes taking into account the type of biomass combusted (Tables 1–4), allows for drawing conclusions on their chemical compositions.

The presence of potassium has been found in the majority of the samples (Kowalkowski et al. 2011; Lanzerstorfer 2015, 2017; Maresca et al. 2017; Supancic et al. 2014).

The problem with the use of these ashes can be the presence of chlorine (Lanzerstorfer 2015; Berra et al. 2015; Supancic et al. 2014), and the lack of silicon (Maresca et al. 2017; Supancic et al. 2014; Kowalkowski et al. 2011) and aluminum (Lanzerstorfer 2015, 2017; Maresca et al. 2017; Supancic et al. 2014; Kowalkowski et al. 2011), which can limit their use as a component of cements and additive for concrete. The contents of potassium and phosphorus (Kowalkowski et al. 2011; Maresca et al. 2017; Supancic et al. 2014) are the reasons for their use in agriculture.

The ashes from the combustion of agricultural waste (Table 5) with a high content of Ca, K, and P, and containing no Si and Al (Romero et al. 2017) are likely to be used to improve the quality of soils. The high content of Ca, K, and P and the lack of Si and Al content does not exclude them from being used for the production of building materials.

Based on the results obtained by Vassilev et al. (2014) (Table 6), the ashes from the combustion of energy plants can be used for the production of both building materials and in agriculture.

The commercial power industry in Poland uses mostly forest biomass (sawdust, wood chips, wood pellets, forest chips) and biomass from agriculture (Salix viminalis chips, sunflower husk pellets, wheat straw pellets, hay pellets, wheat straw briquettes, hay briquettes, bran, grain residues, fruit pomace, orchard thinning, straw, hay, chips from fruit orchards, corn straw chaff) (www.tauron-wytwarzanie.pl/produkcja-energii/zielona-kopalnia; www.gkpge.pl/Biomasa/).

The analysis of ashes from the biomass combustion included the determination of the elemental composition using a MobiLab X5000 X-ray spectrometer.

The samples of five ashes, namely three from the combustion of forest biomass and agricultural biomass and two from the combustion of forest biomass in fluidized bed boilers in commercial generating units, were subjected to the analysis (Table 7).

Table 5. The elemental content of fly ash from the combustion of agricultural waste, mg/kg

Tabela 5. Zawartość pierwiastków w popiołach lotnych ze spalania odpadów rolniczych, mg/kg

Element	Fly ash from the combustion of							
	dry olive cake	wet olive cake mixed with olive leaves	wet olive cake mixed with bagasse	rice husks	corn cobs	plum pits	walnut shells	sunflower shells
	Romero et al. 2017			Vassilev et al. 2014				
	mg/kg			ppm				
Ca	52 ± 1	96 ± 1	69 ± 3	0.88	1.07	13.82	17.82	8.18
Mg	15 ± 0.9	14 ± 1	21 ± 1	0.26	0.84	1.11	1.50	5.26
P	4.2 ± 0.1	5.3 ± 0.3	6.9 ± 0.6	2 299	14.880	19.571	6 758	21.001
Na	2.8 ± 0.2	2.1 ± 0.1	12 ± 1	0.15	0.15	0.26	0.06	0.12
K	58 ± 3	35 ± 3	23 ± 2	3.02	27.79	5.93	26.69	30.29
Si	–	–	–	36.86	12.11	2.47	0.87	0.50
Al	–	–	–	0.48	0.30	0.60	0.18	0.05
Fe	6.3 ± 0.2	3.9 ± 0.4	10.8 ± 0.3	0.25	0.74	0.54	0.18	0.68
Mn	172 ± 5	218 ± 14	297 ± 12	1825	404	466	202	365
As	–	–	–	9.4	6.4	2.6	7.5	5.2
Cd	<0.2	<0.2	<0.2	8.2	5.1	3.5	5.9	4.4
Cr	–	–	–	348	750	160	167	1504
Cu	181 ± 5	214 ± 6	178 ± 5	76	139	636	477	331
Ni	30 ± 1	29 ± 2a	32 ± 2	107	286	64	60	574
Pb	67 ± 0.3	7 ± 1.1	5 ± 0.1	7.4	68.3	32.4	11.7	1.5
Zn	274 ± 4	156 ± 9	77 ± 3	103	1232	779	110	338
Ba	560 ± 17	228 ± 20	233 ± 14	101	47	136	113	46
Co	–	–	–	2.1	2.6	3.4	1.4	4.2
Cl	–	–	–	0.15	0.40	0.10	0.20	0.96
S	–	–	–	0.46	0.97	1.36	0.53	3.35
B	–	–	–	4 101	6 619	11.311	8 908	5 900
Mo	–	–	–	4.35	5.71	2.69	5.55	8.95
Sb	–	–	–	1.89	1.38	0.63	1.54	1.22
Sr	–	–	–	47	72	326	465	448
V	–	–	–	10.8	13.1	11.8	7.2	17.6

Table 6. The elemental content of fly ash from the combustion of energy plants

Tabela 6. Zawartość pierwiastków w popiołach lotnych ze spalania roślin energetycznych

Element	Fly ash from the combustion of:	
	switchgrass	miscanthus
	Vassilev et al. 2014	Lanzerstorfer 2017a
	ppm	mg/kg
Ca	4.30	–
Mg	1.98	–
P	8 320	–
Na	0.07	–
K	12.15	–
Si	23.01	–
Al	0.37	–
Fe	0.23	–
Mn	872	–
As	9.4	6
Cd	9.8	7
Cr	49	90
Cu	66	51
Ni	37	45
Pb	3.0	57
Zn	103	185
Cl	0.15	–
S	0.68	–
B	7 106	193
Ba	386	–
Mo	5.43	43
Sn	3.6	–
Sr	241	–
Co	1.3	16
V	10.5	101

Table 7. The elemental content of fly ash from the biomass combustion in the power industry in Poland, %

Tabela 7. Zawartość pierwiastków w popiołach lotnych ze spalania biomasy w energetyce zawodowej w Polsce, %

Element	Fly ash from the combustion				
	biomass from agriculture 1 + + forest biomass 1	biomass from agriculture 2 + + forest biomass 2	biomass from agriculture 3 + + forest biomass 3	forest biomass 1	forest biomass 2
Ca	16.178	15.8507	19.3788	13.7598	12.34
Mg	1.14	0.98	1.06	–	–
P	0.0467	0.5109	0.5315	0.2178	1.46
K	9.1297	33.6042	23.9118	3.3267	17.68
Si	8.292	1.2116	2.54	4.86	4.86
Al	0.55	–	–	–	–
Fe	2.9454	0.7770	2.3618	6.4590	2.04
Mn	0.3590	0.2128	0.5108	0.1894	0.24
Cr	0.026	0.0287	0.0394	0.0243	0.01
Cu	0.0246	0.0228	0.0255	0.0210	0.04
Ni	0.008	0.0088	0.0073	0.0106	–
Pb	0.0066	0.0044	0.0053	0.0061	0.10
Zn	0.039	0.0376	0.0613	0.0329	0.18
Cl	2.416	6.0783	5.1639	1.4892	1.07
S	0.894	1.4093	1.8081	1.1118	7.20
Bi	0.0021	0.0002	0.0023	0.0032	–
Sr	–	–	0.08	0.07	0.08
Zr	0.0149	0.0101	0.0128	0.0150	0.02
Co	0.0261	–	–	0.0474	–
V	0.0664	–	–	0.0754	–
Ti	0.185	0.2756	0.1615	0.3161	0.11
Rb	–	–	0.02	0.01	0.02
Ba	–	–	0.05	0.06	0.08
W	–	–	–	–	0.01

The ashes are characterized by a high content of Ca and K, which confirms the results obtained by García et al. (2015), Maeda et al. (2017), and Lanzerstorfer (2017). The high content of Ca is associated primarily with the type of boiler used for biomass combustion (fluidized bed boilers). The ashes contained no Cd, As, and Na.

Meanwhile, these discussed fly ashes contain Si and Fe. The Mn, Cr, Cu, Ni, Pb, Zn, Cl, and S content was found only in ashes from the combustion of agricultural biomass + forest biomass 1.

The high content of chlorine, potassium, and sulfur may limit their use in the production of building materials (Rajamma et al. 2009; Pels and Sarabèr 2011).

In the case of the discussed ashes, special attention should be paid to a high content of Ca, K, and Cl and a low Na content, which is associated with the type of biomass but also can be associated with the type of fertilizers (García et al. 2015; Maeda et al. 2017).

The knowledge of the chemical composition will allow a preliminary assessment of the recovery opportunities. For example, the lack of Si and a high content of Cl, K, and S may limit the use of fly ash as an additive to concrete type II according to PN-EN 450-1:2012 standard *fly ash for concrete — part 1: Definitions, specifications and conformity criteria* (Giergiczny 2009).

Conclusions

Waste from biomass combustion is a raw material with a very diverse composition, even in the case of using only one type of biomass. The analysis of literature data is particularly difficult due to the fact that most publications do not precisely specify the type of biomass e.g. wood. Presently, most publications lack data on combustion technology itself, which has a significant impact on the chemical composition of waste. The content of individual elements is highly variable and ranges from 0 to several dozen percent. These differences make it difficult to draw conclusions for the whole group of the discussed waste (fly ash from the combustion of biomass).

Vassilev et al. (2014) paid attention to the problems related to the recovery of ashes from biomass combustion resulting from the presence of some trace elements in biomass and ashes itself. This is due to their high concentrations in the ashes, as well as the possibility of leaching.

The lack of accurate data on the type of biomass burned is the reason why each waste should be analyzed individually. Generalization is particularly difficult because fuel is usually a mixture of different types of biomass.

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THE ELEMENTAL COMPOSITION OF BIOMASS ASHES AS A PRELIMINARY ASSESSMENT OF THE RECOVERY POTENTIAL

Keywords

recovery, elemental composition, biomass ash, fly ash

Abstract

The use of biomass in the energy industry is the consequence of ongoing efforts to replace Energy from fossil fuels with energy from renewable sources. However, due to the diversity of the biomass, its use as a solid fuel generates waste with diverse and unstable chemical composition. Waste from biomass combustion is a raw material with a very diverse composition, even in the case of using only one type of biomass. The content of individual elements in fly ash from the combustion of biomass ranges from zero to tens of percent. This makes it difficult to determine the optimal recovery methods. The ashes from the combustion of biomass are most commonly used in the production of building materials and agriculture. This article presents the elemental composition of the most commonly used biomass fuels. The results of the analysis of elemental composition of fly ashes from the combustion of forest and agricultural biomass in fluidized bed boilers used in the commercial power industry were presented. These ashes are characterized by a high content of calcium (12.3–19.4%), silicon (1.2–8.3%), potassium (0.05–1.46%), chlorine (1.1–6.1%), and iron (0.8–6.5%). The discussed ashes contained no sodium. Aluminum was found only in one of the five ashes. Manganese, chromium, copper, nickel, lead, zinc, sulfur, bismuth, titanium and zirconium were found in all of the examined ashes. The analysis of elemental composition may allow for a preliminary assessment of the recovery potential of a given ash.

CHARAKTERYSTYKA PIERWIASTKOWYCH SKŁADÓW CHEMICZNYCH POPIOŁÓW ZE SPALANIA BIOMASY JAKO WSTĘPNA OCENA KIERUNKU ODZYSKU

Słowa kluczowe

popioły ze spalania biomasy, skład pierwiastkowy, odzysk, popioły lotne

Streszczenie

Stosowanie biomasy w energetyce jest działaniem w ramach zastępowania paliw kopalnych pozyskiwaniem energii ze źródeł odnawialnych. Jednak jej stosowanie jako paliwa stałego ze względu na różnorodność stosowanej biomasy powoduje powstawanie odpadów o bardzo zróżnicowanym i niestabilnym składzie chemicznym. Odpady ze spalania biomasy są surowcem o bardzo zróżnicowanym składzie nawet w przypadku spalania biomasy jednego rodzaju. Zawartość poszczególnych pierwiastków w popiołach lotnych ze spalania biomasy waha się od zera do kilkudziesięciu procent. To zróżnicowanie powoduje, że trudno znaleźć dla nich metody odzysku. Najczęściej rozpatrywane kierunki stosowania popiołów ze spalania biomasy to produkcja materiałów budowlanych i rolnictwo.

W artykule przedstawiono wyniki badań pierwiastkowych składów chemicznych z podziałem na najczęściej stosowane paliwa z biomasy. Zaprezentowane zostały wyniki dotyczące pierwiastkowych składów chemicznych popiołów lotnych ze spalania biomasy leśnej i rolniczej w kotłach fluidalnych w energetyce zawodowej. Popioły te charakteryzują się wysoką zawartością: wapnia (12,3–19,4%), krzemu (1,2–8,3%), potasu (0,05–1,46%), chloru (1,1–6,1%), żelaza (0,8–6,5%). Nie stwierdzono w nich obecności sodu. Tylko w jednym z 5 popiołów stwierdzono obecność glinu. We wszystkich badanych popiołach stwierdzono obecność: manganu, chromu, miedzi, niklu, ołowiu, cynku, siarki, bizmutu, cyrkonu, tytanu. Analiza pierwiastkowych składów chemicznych może pozwolić na wstępne określenie kierunku odzysku dla danego popiołu.