



Mineral and Chemical Composition of Fly Ashes Deriving from Co-Combustion of Biomass with Coal and Its Application

Andrzej JAROSIŃSKI ¹⁾

¹⁾ Dr hab. inż.; Instytut Gospodarki Surowcami Mineralnymi I Energią PAN; ul. J. Wybickiego 7, 31-261 Kraków, Poland; e-mail: ajar@chemia.pk.edu.pl, tel.: +48 12 617-16-33

Summary

Improvement in the range of conventional raw materials balance for electricity production is possible through the use of renewable fuels. According to standard procedures co-combustion of biomass with coal is one of the simplest and cheapest solutions leading to an increase in the share of energy from renewable fuels. The main aim of this work was to determine the chemical and mineral composition of ash derived from biomass co-combustion with coal and its utilization. The assessment of composition and possibilities of ash utilization were based on the literature and own research. The presented data show that the chemical and mineral composition of ash depends on the used biomass and its amounts in initial fuel. In the work in conclusion the use of obtained ash under Polish conditions is recommended.

Keywords: fly ash, utilization

Introduction

Improvement in the range of conventional raw materials balance for electricity production is possible through the use of renewable fuels. Such solutions result of the conditions prevailing in the in the European Union as well as sustainable production and consumption of mineral resources, including energy resources. Furthermore, they must be met conditions in the range environmental protection. Substitution of fossil fuels is usually brought to the use of biomass for power generation processes and heat. According to Regulation of Minister of Management on 14 August 2008 (Dz.U. nr156,poz.969) biomass is a solid or liquid substances of plant and animal, biodegradable, deriving from the products, waste and residue from agricultural production and forestry as well as industry of their products processing, as well as other waste, which is biodegradable waste.

According to standard procedures co-combustion of biomass with coal is one of the simplest and cheapest solutions leading to an increase in the share of energy from renewable fuels. Co-combustion of these fuels have a number of advantages and drawbacks. The first include:

- possibilities of usage of large amounts of biomass,
- emission reducing of carbon dioxide, sulfur dioxide and NO_x compared to fossil fuels,
- diversification of energy sources,
- logistical issues related to the conditions of supply of biomass for energy producer,
- reducing the risk to the environment connected with obtaining fossil fuels,

– it is important that the combustion process and the distribution of thermal load of the heating surfaces.

The main disadvantages of co-combustion are due to technological criteria and the technical and economic. Among them are indicated:

- different characteristics of biomass in relation to physical and chemical properties of coal, calorific value, which is lower for biomass per unit volume. The values for biomass use in domestic conditions are at the level 6–20 MJ/kg,
- differences in contents of volatile matter in relation to their content in fossil fuels,
- significantly higher volatile matter content significantly affects the ignition conditions and the process of co-combustion,
- different softening and melting temperatures of ashes, which are connected with different chemical and mineral composition of biomass compared to coal.

The technical and economic criteria include the preparation of biomass technical possibility of using biomass along with coal into the furnace. The content of salts, particularly chlorides, promotes the formation of low melting eutectics, the presence of which stimulates the equipment corrosion processes.

Co-combustion of biomass with fossil fuels is generally carried out in the domestic conditions (Stelmach, Wasilewski, Haustein, Grabarczyk). Co-combustion is carried out in stoker-fired, dust or fluid boilers.

According to (Rozporządzenie Ministra Ochrony Środowiska, Zasobów Naturalnych i Leśnictwa z dnia 27 września 2001 r.) ashes deriving from the combustion of coal is classified into in group 10, subgroup 01 and type 02 (code -100102). Different properties of the fly ash from the combustion of coal and biomass resulted in the classification of thermal waste. Different properties of the fly ash from the combustion of coal and biomass resulted in the classification of waste thermal expansion of the following codes: 10 01 16 – fly ashes deriving from co-combustion and containing hazardous substance, 10 01 17 – fly ashes derived from co-combustion but that other than those mentioned in 10 01 16.

From domestic industrial practice results that the presence to co-combustion of coal is used woody biomass (sawdust, silvers, dusts, etc), biogas and waste deriving from animal and crop production i.e. bone meal, rape marc, coffee marc and etc.

It is estimated that the demand for domestic power industry will amount 8.3 million tones dry weight in 2020 year while in 2030 about 10,6 mln tones. Both the large mass arising from the ashes and the change in the characteristics of ash produced during biomass co-combustion with coal forces the search for methods of ashes utilization.

For these reasons, the issue of fly ash from co-combustion becomes the subject of widespread interest in research institutes and specialist companies.

The main aim of this study is to evaluate the chemical and mineral composition of ash from biomass co-firing with coal in terms of their use. The assessment was based on the literature and their own research, both ash from biomass combustion and co-combustion of biomass and coal.

Biomass and its characteristics

Renewable energy sources play an important role in the energetic politics of EU. According to the Directive of the European Parliament and of the Council 2009/28/EC in 2020 is expected to increase to 20% the share of renewable energy in the total energy consumption. For this purpose each country has different values depending on the level of development of the Member States of the European Union [20].

In Table 1 the share of renewable energy in primary energy in some EU countries is given while table 2 the acquisition of renewable energy in domestic conditions is presented.

Despite the fact that the figures refer to the period 2006–2008 shows a tendency to demand the kind of energy in Poland. The largest percentage of renewable energy in primary energy falls on Austria and the rate of increase is most pronounced in Germany. Poland compared to other countries of the European Union has a much smaller share of renewable energy in the national energy balance.

Table 1. The share of renewable energy in primary energy in some EU countries in years 2005-2008 [%] [21]

Tabela 1. Udział energii odnawialnej w całkowitym zużyciu energii w krajach UE w latach 2005-2008 [%] [21]

Country	2005	2006	2007	2008
Austria	75,5	73,8	75,5	78,2
Czech Republic	6,5	6,6	7,2	7,6
Finland	50,2	49,1	55,1	56,4
Germany	13,1	15,4	21,6	22,4
Poland	5,8	6,1	6,7	7,6

Table 2. Sources of renewable energy in Poland in years 2006-2008 [TJ]

Tabela 2. Źródła energii odnawialnej w Polsce w latach 2006-2008 [TJ]

Kind of renewable energy	2006	2007	2008
Solid biomass	192 097	197 150	198 401
Water energy	7 352	8 467	7 748
Liquid biomass energy	6 965	4 614	12 402
Biogas	2 613	2 708	5 515
Wind energy	922	1 878	3 012
Geothermal energy	535	439	531
Heat pump	33	68	605
Municipal waste	27	35	9
Solar energy	11	15	54

With expertise carried out by the European Centre for Energy shows that in comparison with other EU countries, Poland has a large technical potential of renewable energy sources. This amounts to around 2,514 PJ, which represents 60% of annual energy consumption in Poland. The analysis of data on energy production from renewable energy sources that will have the dominant role of solid biomass energy, wind power and biofuels. It will be up to 94%. It is estimated that as early as 2020 in our country, increase the use of renewable energy is 15% and in line with the obligations imposed on Poland the European Parliament and of the Council 2009/28/EC [24, 25].

Much of renewable energy will account for solid biomass. The essential advantage of the solid biomass for fossil fuels is the ability to scale the reload several years. When the combustion is no increase in carbon dioxide content in atmosphere unlike hydrocarbon fuel combustion of natural origin. The generated during biomass combustion carbon dioxide is assimilated by the next generation of trees. From this reason can speak of a zero emission carbon dioxide effect. Furthermore, wood is one of the fuel with zero emissions of sulfur compounds.

Rational use of energy from biomass is a key element of sustainable development and requires an

assessment of combustion or co-combustion of biomass, which is connected with physical and chemical properties. Due to the lack of appropriate standards of both national and European. Assessment of physical and chemical properties of biomass takes place in range of technology and the impact on the environment. For this purpose shall be energy balances for different boilers for biomass co-combustion processes of fossil fuel combustion in relation to combustion of standard fuel. In addition, compared to the total emission of pollutants into the atmosphere with respect to emissions in the combustion of fossil fuels. Table 3 gives some of the properties for various types of biomass.

These fuels is characterized by lower ash content and lower sulfur content in relation to its content of fine coal.

Characteristics ashes deriving from co-combustion

In purpose for comparison below contains the chemical compositions of the ashes of various fuels. In tables 4–9 chemical ashes composition deriving from combustion of some fuels are given.

In Fig. 1 X-ray diffraction of ash obtained during co-combustion coal with woody biomass is given. while

Table 3. Technical characteristics of certain types of biomass [Bogdańska]
Tabela 3. Charakterystyka techniczna niektórych typów biomasy [Bogdańska]

Kind of fuel	Calorific value [MJ/kg]	Ash content [%]	Carbon content [%]	Sulfur content [%]	Moisture content [%]
Pellets	16,5–18,5	0,5–1,2	50	ok. 0,02	8,0–12,0
Briquettes	17,5–19,5	0,2–2,0	50	ok. 0,03	10,0–12,0
silvers	10,0–18,0	0,6–5,0	50	ok. 0,03	30,0–60,0
Straw	14,0–16,0	0,5–5,0	46	0,05–0,15	10,0–20,0
Fine coal	20,0–24,0	18,0–25,0	68	ok. 1,2	do 12

Table 4. Chemical compositions of ashes derived from combustion of coal and lignite
Tabela 4. Skład chemiczny popiołów pochodzących ze spalania węgla kamiennego i brunatnego

Component	SiO ₂	Al ₂ O ₃	FeO	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	SO ₃
Coal [%]	50–57	25–30	3,5–8,0	0–1	2–4	1,5–3,0	2,5–3,0	0,2–2,0	0,5–1,2
Lignite [%]	43–60	19–34	3,0–6,0	1–7	4–6	0–2	0–2	0,5–1,0	0–5

Table 5. Average chemical composition of ashes deriving from classic and fluidal combustion (Fecko et. Al.)
Tabela 5. Średni skład chemiczny popiołów wynikający z klasycznego i fluidalnego spalania (Fecko et. Al.)

Ash	Chemical composition [%]										
	SiO ₂	Al ₂ O ₃	CaO	CaO *	MgO	TiO ₂	Fe ₂ O ₃	SO ₃	Na ₂ O	K ₂ O	Losses
Classic	52,2	28,0	3,1	0	1,4	2,4	9,7	0,6	0,5	1,6	5,9
Fluidal	42,3	19,4	18,2	2,6	2,5	1,6	5,8	5,3	0,4	1,7	10,7

* free lime

Table 6. Chemical composition and fuel properties of some biomasses in relation to traditional fuels (Lebecki 2010)

Tabela 6. Skład chemiczny i właściwości paliwa niektórych biomas w stosunku do tradycyjnych paliw (Lebecki 2010)

Parametr	Kind of biomass				Kind of fuel	
	wheat straw	willow	Waste paper	hybrid poplar	Coal	Lignite
Analysis of fuels, % dry matter						
Carbon (C)	17,71	16,07	7,42	12,49	77,00	43,44
Volatile matter	75,27	82,22	84,25	84,81	18,49	42,95
Ash	7,02	1,71	8,33	2,70	4,51	13,69
Elementary analysis, % dry matter						
Carbon	44,92	49,90	47,99	50,18	87,52	60,97
Hydrogen	5,46	5,90	6,63	6,06	4,26	4,07
Oxygen	41,77	41,80	36,84	40,43	1,55	18,50
Azotnitrogen	0,44	0,61	0,14	0,602	1,25	1,02
sulfur	0,16	0,07	0,07	0,02	0,75	1,81
Chlorine	0,23	<0,01	<0,01	0,01	0,16	0,04
Ash analysis, dry matter						
SiO ₂	55,32	2,35	28,10	5,90	37,24	20,93
Al ₂ O ₃	1,88	1,41	52,26	0,84	23,73	13,78
Fe ₂ O ₃	0,73	0,73	0,81	1,40	16,83	12,08
CaO	6,14	41,20	7,49	49,92	7,53	16,13
MgO	1,06	2,47	2,36	18,40	2,36	4,40
Na ₂ O	1,71	0,94	0,53	0,13	0,81	0,22
SO ₃	4,40	1,83	1,70	2,04	6,67	24,77
P ₂ O ₅	1,26	7,40	0,20	1,34	0,10	<0,01
TiO ₂	0,08	0,05	4,29	0,30	1,12	0,41
Calorific value (MJ/kg)	17,94	19,59	20,78	19,02	35,01	23,35

Table 7. Chemical composition and some physical properties ashes deriving from co-combustion (Łaskawiec et.al.)

Tabela 7. Skład chemiczny i niektóre właściwości fizyczne popiołów pochodzących ze współspalania (Łaskawiec et.al.)

Lo.	Properties	Results of investigations					
		power station A			power station B		
		Content of biomass In fuel (%)					
		0	12	±d* for α=0,05	0	20	±d* for α=0,05
1	Losses (%)	4,20	4,35	0,15	5,40	4,50	0,89
2	SiO ₂ (%)	48,55	48,58	0,39	49,72	48,13	1,32
3	Al ₂ O ₃ (%)	25,60	25,98	0,15	27,15	25,42	0,47
4	Fe ₂ O ₃ (%)	6,59	6,96	0,17	6,17	6,86	0,08
5	SO ₃ (%)	0,36	0,52	0,04	0,40	0,46	0,09
6	CaO (%)	4,58	4,50	0,07	2,92	4,60	0,54
7	CaO free (%)	0,10	0,35	0,04	2,13	26,34	0,39
8	MgO (%)	3,46	3,32	0,04	2,12	26,34	0,39
9	P ₂ O ₅ (mg/kg)	–	19,50	3,93	–	22,00	5,24
10	Density (g/cm ³)	2,12	2,12	0,01	1,93	1,94	0,04
11	Break up (forfeited through a sieve # 0,063) (%)	95,80	95,20	0,19	75,30	68,80	5,13
12	Water requirement (%)	26,70	31,30	–	31,90	27,60	1,01
13	Pozzolana activity, after 28 daysh	95,60	92,40	–	82,02	73,44	–
Concentration of natural radioactive elements							
14	f ₁	1,20	1,12	–	1,24	1,07	–
15	f ₁ (Bq/kg)	134,03	123,36	–	139,70	112,40	–

* Confidence interval (d) calculated for 9 samples

Table 8. Chemical composition of ash deriving from co-combustion biomass with coal

Tabela 8. Skład chemiczny popiołu wynikające ze współspalania biomasy z węglem

Content of component [%]											
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	TiO ₂	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	S	Losses	M*
53,10	21,08	8,63	0,83	0,70	2,96	0,78	3,14	0,49	0,18	9,15	5,97

Table 9. Chemical composition of sample deriving from co-combustion woody biomass with coal

Tabela 9. Skład chemiczny próbki pochodzącej ze współspalania biomasy drzewnej z węglem

Content of component [%]										
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	TiO ₂	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	S	
47,25	21,08	4,25	18,83	0,70	26,96	0,33	9,14	–	0,16	

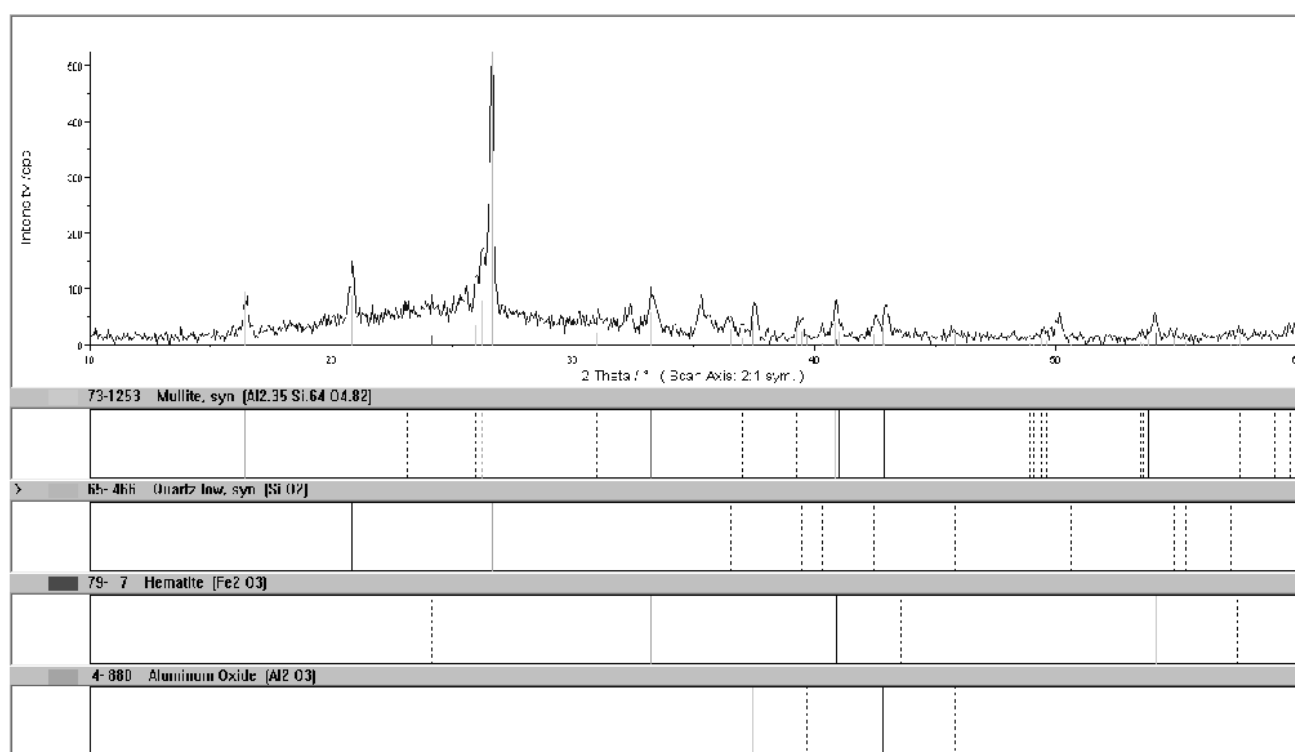


Fig. 1. X-ray diffraction pattern of ash corresponding chemical composition given in Table 8

Rys. 1. Rentgenogram dyfrakcyjny popiołu o składzie chemicznym podanym w tabeli 8

Similar mineral phases in samples deriving from co-combustion biomass with coal were confirmed by Łaskawiec.

In Fig. 2 is presented X-ray pattern of ash obtaining during co-combustion of biomass with coal. It was confirmed presence of quartz as main mineral phase. In smaller amounts of lime and hematite occurs in tested samples. Background of diffraction pattern indicates the presence of amorphous phase in tested samples. Chemical and mineral analysis indicates that amorphous phase form aluminosilicates.

The presented data show that ash from co-firing of biomass in an amount up to 15% do not differ

significantly from the composition of the ash from coal. In the samples deriving from co-combustion of biomass with coal is observed increase of content of lime and compounds of potassium and sodium. Furthermore, the chemical composition of samples includes phosphorus compounds. These compounds generally do not occur in the ash from the combustion of coal.

The effects of pollutants from the processing of fly ash for building materials include compounds of alkali elements. The soluble compounds of these elements promote the formation of efflorescence. The combustion products is detectable radioactive

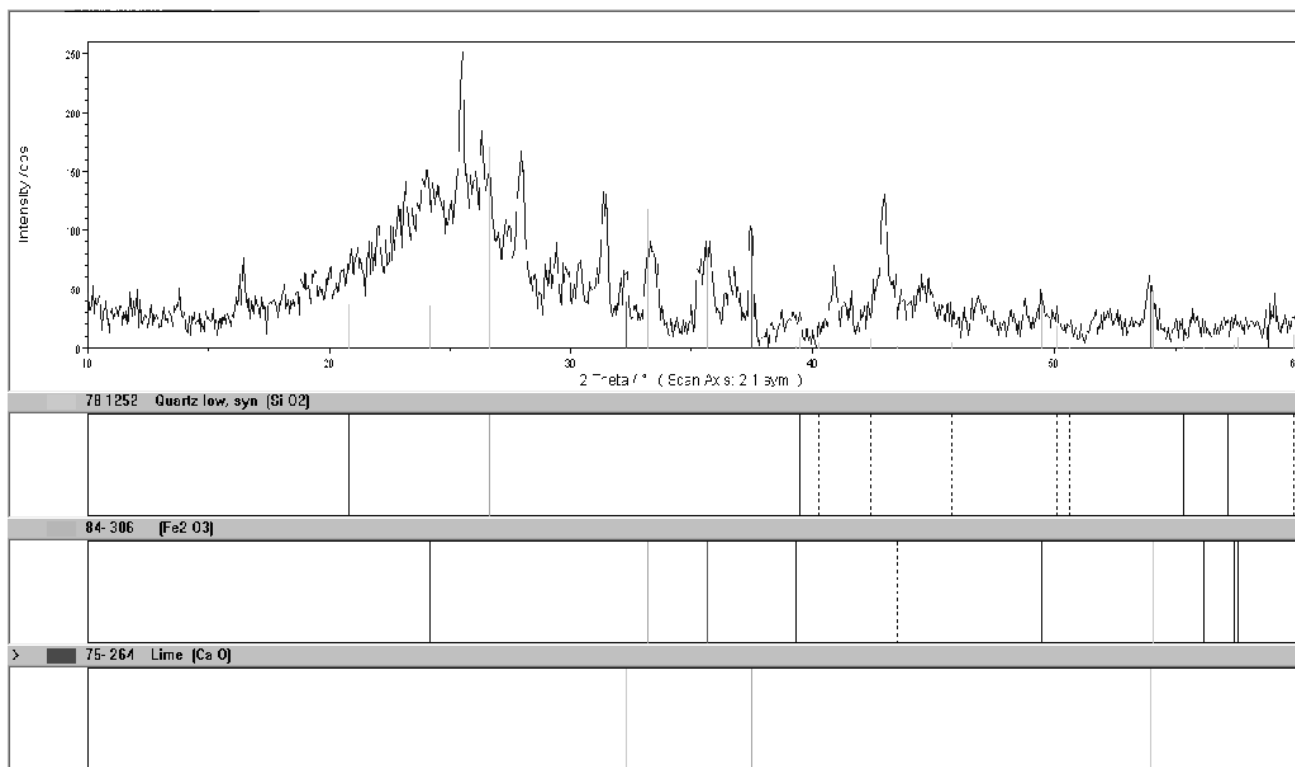


Fig. 2. X-ray diffraction pattern of ash corresponding chemical composition given in Table 9

Rys. 2. Rentgenogram dyfrakcyjny popiołu odpowiednim składzie chemicznym podanym w tabeli 9

elements: ^{40}K , ^{226}Ra and ^{232}Th . The content of these elements in the ash from the incineration is slightly lower in relation to their contents in ashes deriving from coal combustion. The coefficients f_1 and f_2 take appropriate values in the range 1,07–1,24 Bq/kg and 112–140 Bq/kg. Maximum permissible values for these indicators amount to $f_1 \leq 1$ Bq/kg, $f_2 \leq 200$ Bq/kg. These data confirm that the chemical composition and mineral ash depends on the type of coal burned, type of biomass, its participation in the fuel and power specifications. In summary it can be stated that the mineral composition of the ash is quite diverse and varied.

Utilization of ashes

In general, the use of fly ash is carried out in three directions (Dulewska):

- the use of fly ash as a substitute for natural resources (Secondary materials),
- in the work of reclamation, leveling and back-filling as materials in mining,
- the use of fly ash storage combination, for example, storage of tailings together with waste energy.

A necessary condition for the application of ash from co-incineration is meeting the relevant criteria: technological, technical and economic and ecological. In general, the ash from co-firing of biomass

with coal in an amount of 10–15% to meet the above requirements (no significant changes in the chemical and mineral composition) (Rajamma i in, Kosior-Kazberuk, Haustein, Grabarczyk). Such participation in the fuel does not adversely affect such properties as requirement of water, puzzalona activity and the like.

With the increase of phosphorus in the ashes have seen a reduction in the possibility of their use in the production of building materials

For example, the presence of these compounds inhibit the hydration of Portland cement and other binders.

The discrepancy between the period of greatest production of ash from co-firing of biomass and the period of demand for ash in the cement industry is a significant barrier inhibiting the intensity of management of the ashes (spring-summer period).

Another direction of the use of fly ash from co-combustion biomass with coal is a farming. Ashes contain a high content of ingredients typically fertilizer. Both potassium and phosphorus, essential macronutrient fertilizers and pH contributes to changes in soil structure and results in increased yields. The highly alkaline nature of the ash from co-incineration prefer them to de-acidification of soils.

The high pH of ash resulting chemical imbalance and reduce uptake by plants of some trace metals that are essential for normal metabolism.

Another direction of ash from co-incineration due to such features as:

- low sedimentation rate,
- pozzolanic properties, determining the binding capacity in excess hydraulic lime,
- hydrophobicity in the case of mineral oils.

The development of the mining industry is preferred above the ashes to backfill excavations.

Remarks

Ashes from the incineration of biomass are materials with slightly different physical and chemical properties compared to ash from coal combustion. On the basis of its own and literature data indicate that the quality of ash depends on many factors. Factors affecting these characteristics of discussed ashes are:

- kind and the amount and type of biomass fuel in the mixture,

- type boiler and auxiliary equipment,
- moisture content of the fuel mixture,
- the fineness of fuel,
- the residence time of fuel particles in the chamber,
- thermal load of the combustion chamber,

The differences in the properties of the ash are the greater the higher the content of the biomass fuel in the mixture. The increase in some components in the ash from co-combustion contributes to the reduction of its application.

In summary, the factors determining the development of ash from co-combustion of biomass are:

- physical and chemical properties of ashes,
- their effect on the technical properties of the produced materials,
- the effect on environment.

*Praca wykonana w ramach DS nr 61/12/12/0
Zadanie B.VI.2.*

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Podstawa prawna – Legal basis

1. Rozporządzenie Ministra Gospodarki z dnia 14 sierpnia 2008 r. w sprawie szczegółowego zakresu obowiązków uzyskania i przedstawienia do umorzenia świadectw pochodzenia, uiszczenia opłaty zastępczej, zakupu energii elektrycznej i ciepła wytworzonych w odnawialnych źródłach energii oraz obowiązku potwierdzania danych dotyczących ilości energii elektrycznej wytworzonej w odnawialnym źródle energii – Dz. U. Nr 156/2008 r., poz. 969, ze zm.
2. Dyrektywa Parlamentu Europejskiego i Rady 2009/28/WE z dnia 23 kwietnia 2009 r. w sprawie promowania stosowania energii ze źródeł odnawialnych zmieniająca i w następstwie uchylająca dyrektywy 2001/77/WE oraz 2003/30/WE, Dziennik Urzędowy Unii Europejskiej L 140 z 05.06.2009
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http://www.stat.gov.pl/cps/rde/xbcr/gus/PUBL_se_energia_zrodla_odnawialne_2009.pdf
4. Krajowy plan działania w zakresie energii ze źródeł odnawialnych
<http://www.mg.gov.pl/Bezpieczenstwo+gospodarcze/Energetyka/Odnawialne+zrodla+energii/Krajowy+plan+dzialan>
5. „Polityka Energetyczna Polski do 2030 roku.”
<http://www.mg.gov.pl/files/upload/8134/Polityka%20energetyczna%20ost.pdf>

Skład mineralny i chemiczny popiołów lotnych wynikające ze współspalania biomasy z węglem i jego zastosowanie

Poprawę w zakresie bilansu surowców konwencjonalnych można uzyskać poprzez stosowanie odnawialnych zasobów paliw do produkcji energii elektrycznej. Wśród producentów energii elektrycznej i ciepła wytwarzanych z odnawialnych źródeł energii, współspalanie biomasy z węglem według standardowych procedur zalicza się do najprostszyc i najtańszyc rozwiązań prowadzących do wzrostu energii z paliw odnawialnych. Zasadniczym celem pracy było określenie składu chemiczno-mineralnego popiołów lotnych pochodzących ze współspalania oraz jego wykorzystania. Oceny dokonano w oparciu o dane literaturowe i badania własne. Z przedstawionych danych wynika, że skład mineralno-chemiczny zależy od użytej biomasy i jej udziału w paliwie. W pracy wypowiedziano się na temat możliwości wykorzystania popiołów w warunkach krajowych.

Słowa kluczowe: popiół lotny, wykorzystanie