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M. FRÖHLICHOVÁ*[#], R. FINDORÁK*, J. LEGEMZA*, M. DŽUPKOVÁ***THE FUSION CHARACTERISTICS OF ASHES FROM LIGNIN AND THE COKE BREEZE**

In this paper are presented results of study fusion characteristics of the biomass ashes from the hydrolyzed lignin and the ashes from the coke breeze. The hydrolyzed lignin ashes were compared with the coke breeze ashes i.e. with a fossil fuel. These ashes were prepared in muffle furnace at the temperature of 550°C (hydrolyzed lignin) and 850°C (coke breeze).

Biomass (the hydrolyzed lignin) represents the new fuels for sintering process and an attractive way to decrease CO₂ emissions from the energy production. The characterization methods were the following: standard fuel characterization analyses, chemical and mineralogical composition of the ashes and phase analyses of the ashes of biomass and the coke breeze. These ashes were prepared by the same method.

Characterisation of the ashes samples was conducted by means of X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Quantitative analysis of the crystalline and amorphous phases in each of the ash samples were carried out using the Rietveld method. The dominant phase of the ash from the coke breeze was mullite (Al₆Si₂O₁₃). SiO₂ is the dominant phase of the ash from the hydrolyzed lignin.

Keywords: biomass, ash, fuel, mineral phases, iron ore sinter

1. Introduction

The energy we use today originates predominantly in the fossil fuels, which are still being formed, but their current consumption is many times higher than their production. The fact that they are not replenished as quickly as we consume them means that they are going to be depleted in the near future. For this reason, fossil fuels are considered as non-renewable. We are energy-dependent, but we need energy sources that are inexhaustible - renewable resources that are capable of ensuring sustainable development of the society [1].

However, the limitation of the fuel sources is not the only threat faced by humanity. The burning of the fossil fuels leads to serious damage to the environment. Renewable resources compared to the fossil fuels are much cleaner for the environment.

For this reason, technologies that do not harm the environment are being sought more and more intensely and there is beginning a transition to other than fossil energy sources. One of the renewable energy sources is biomass, which hides a huge amount of energy that we can use both for heat generation and for electricity production. The use of biomass as a renewable energy source is a strategy that is seen as a partial solution for achieving CO₂ emission reduction. Recently there has been a significant increase in the use of biomass in the processing industry, including the production of a pig iron.

The future of the pig iron production in blast-furnace agglomerates is contingent on lowering the average consumption of the coke and the fuels, increasing the quality of production and minimizing ecologically harmful impact to the environment.

Blast furnace production is directly dependent on the agglomeration process, which provides us with the production of an iron ore agglomerate that forms the basis of the blast furnace charge. The agglomeration process is based on the burning of the coke breeze present in the agglomeration charge. The coke breeze is an undersize fraction obtained as a by-product from the metallurgical coke production and is currently the most suitable and the most used fuel. But we have to realize that the stock of the coking coal is declining and we must not forget its negative impact on the environment [2].

Based on the fact that biomass use is a strategy that is considered to be a partial solution to the CO₂ emission reduction, it is necessary to analyze the current knowledge in this field of research and to answer the question of its applicability in the agglomeration process. The decisive parameter about the suitability of biomass as a fuel for the agglomeration process is its energy properties. The most important of biomass energy features include moisture, calorific value, combustion heat, ash content, fuel combustible composition, volume specific weight (density), bulk density. Moisture is a typical biomass property and significantly affects the combustion process, reduces com-

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bustion heat and combustion efficiency. Negative effect on the calorific value has also ash, as it forms an incombustible residue without energy effect.

Ash is one of the three basic components of the fuel that arises from the process of combustion in the reaction of minerals with oxygen. It consists predominantly of the oxides of the elements of these minerals that are contained in the biomass (CaO, MgO, Fe₂O₃, Al₂O₃, SiO₂, P₂O₅, K₂O, Na₂O). Its content is given by own chemical structure of the different types of biomass and the contamination of the soil from which it has drew its nutrients during its growth. Generally, biomass contains incomparably less ash than the fossil fuels. A smaller amount of ash is a guarantee of a lower particulate content in combustion gases resulting from biomass burning, which plays an important role in the agglomeration process.

There is a problem associated with ash that affects the combustion process, and hence its sintering, which is that after exceeding a certain temperature, i.e. the ash flow temperature, the ash is melting and leaking to the grate of the agglomeration device. The baked ash clogs the grate and thus breaks down the gas dynamics of the agglomeration charge sintering process, which is a serious problem [3-6]. There is currently enough information about the ashes of the fossil fuels, but less information about the ash from biomass as an alternative fuel in the metallurgical industry and precisely this issue is the topic of this contribution.

Ash is the general term used to describe an inorganic matter in the fuel. In biomass fuels, the ash content may originate from the biomass itself. An ashing temperature for biomass fuels is 550°C, lower than the typical ashing temperature for coals, which is 850°C. The reason is that the biomass ash contains several volatile elements, which may not be present in the laboratory produced ash if it is combusted in high enough temperatures. Thus, high temperatures for ash mean a non-representative ash sample, both in terms of quantity and quality. It is also fairly obvious that ash collected from real-life application is different in some extent in composition from the fuel ash prepared in the laboratory [7-8].

The presence of ash forming elements of biomass is the result of chemical processes, intake of minerals from the soil and method of transporting biomass. Some of these elements are necessary for plant growth. Constituent parts of ash biomass are divided into macronutrients (potassium, calcium, magnesium, phosphorus and sulphur) and micronutrients (iron, manganese and chlorine) [9]. In this paper are presented results of the study of hydrolyzed lignin ashes and its comparison with the coke breeze ashes. The ashes were studied by AFT (ash fusion temperatures test), XRF and XRD methods.

2. Experimental and material

The coke was shipped from the agglomeration plant. It is a undersize fraction that is obtained from the production of the metallurgical coke. A fraction below 5 mm does not meet the requirements for the blast furnace iron production fuel. This fraction is classified as the agglomeration coke and is currently the most suitable and the most used fuel for agglomerate production. The agglomerate forms the basic metal-bearing charge of the blast-furnace production.

Biomass is a technical hydrolyzed lignin (lignin) [10]. Lignin is a by-product of ethanol production by distillation of wood. This industrial ethanol production has turned out to be highly energy intensive and has been stopped; only huge waste of wood heaps remained. Whether it is possible to consider it as the alternative fuel to the fossil fuels are going to show a detailed analysis of this material which is the subject of this contribution.

Lignin is a loose polydisperse substance with a pronounced fibrous structure of particles. Regarding natural substances, its physical and thermal characteristics are closest to a milling peat [10]. Chemical analysis and energy contents of the coke breeze and lignin are given in the Table 1.

The lignin was subjected to an experimental study for its use as a partial replacement of the agglomeration coke for the production of a iron ore agglomerate. The samples were ashed on the basis of standard STN EN 14775, 2009: Solid biofuels. Determination of ash content [11]. The ashes were tested to determine melting temperature and chemical composition of ash. Lignin was also subjected to X-ray phase analysis to determine from what phases is compounded the input raw material. From the phase analysis, it is clear that 90 % of the lignin consists of amorphous phase, which can not be determined by the XRD method and 10% of the crystalline phase corresponding to SiO₂.

2.1. Analysis methods

The fusion temperatures of the ashes were measured according to standard, ISO 540, (2008): Hard coal and coke: Determination of ash fusibility [12]. The morfological characteristics and element component of the ashes were analysed by means of SEM (Scanning Electron Microscope) fitted with EDS (Energy Disperse Spectroscopy). Chemical analysis of the ash samples was determined using XRF spectrometer. The minerals species and the transformation characteristics were also detected using XRD (Xray diffraction spectroscopy).

TABLE 1

Chemical analysis and energy contents of the fuels

Fuel	Proximate analysis, [wt.%]				Ultimate analysis, [wt.%]					Calorific value [MJ/kg]
	H ₂ O (W)	Ash (A)	Volatile (CV)	Fixed carbon (C _{FIX})	C	H	O	N	S	
Coke breeze	5.5	12.10	1.50	80.9	97.15	0.34	0.69	1.48	0.34	28.16
Lignin	8.6	3.4	67.90	20.1	65.11	5.95	28.57	0.20	0.17	23.14

2.2. The measurement of the ash fusion temperature

The ash fusion test is a traditional standard test used to describe the melting behaviour of the coal ashes by measuring four characteristic temperatures, namely a initial deformation temperature (DT), a softening temperature (ST), a hemispherical temperature (HT) and a fluid temperature (FT) [12]. The determination of these temperatures, in spite of the well defined standards, does in many cases not exclude subjective assessment. Furthermore this approach has been shown to be unable to distinguish similar samples, especially when it refers to the biomass samples.

2.3. Chemical analysis of the ash samples

An XRF analysis was used for elemental determinations. The XRF, X-ray fluorescence analysis is in practice the most used method of sub-valence electron atomic spectroscopy, which is finds broad application especially for the analysis of solid samples. The XRF analyzes the surface layer of the sample and this method is based on secondary X-ray radiation monitoring and its output is a line spectrum in which the number of pulses per second is displayed for the respective wavelengths or the corresponding energies.

The XRF analysis is used for qualitative (semiquantitative and in special cases, quantitative) chemical composition analysis. The advantage of this analysis is the possibility to analyze powder materials, but there is a prerequisite to select a sample with a homogeneous chemical composition throughout the volume. In addition to solid materials, it is possible to analyze liquid samples, i.e. solutions of investigated substances. The measurement method is non-destructive. In this case, the samples were analyzed in a powdery state. The major elements in the analyzed ashes were determined using the XRF spectrometer ARL 9900S.

2.4. Scanning electron microscopy

The morphological characteristics and element component of the ashes were also analyzed by means of SEM fitted with EDS analyser FEI PHILIPS QUANTA400 with EBSD detector.

2.5. X-ray diffraction (XRD) analysis

In order to get the X-ray powder diffraction pattern of the investigated sample the SEIFERT XRD 3003/PTS diffractometer was used. The parameters of measurement are in the Table 2.

The X-ray diffraction method was used for the determination of phase composition content. The diffraction pattern was analyzed by DIFFRAC.EVA software with the database PDF2 and by program TOPAS that uses the Rietveld system to evaluate the percentages of the crystalline mineral phases and the

The measurement conditions of X-ray

Generator	35 kV, 40 mA
X-ray radiation	Co-line focus
Filter	Fe
Scan step	0.02 theta
Range of measuring	15-130° 2theta
Input slits	3 mm, 2 mm
PSD Detector	Meteor1D

proportion of non crystalline phases in the ashes from lignin and the ashes from the coke breeze.

3. Results and discussion

3.1. Fusion temperature

The fusion temperatures of the ashes from the coke breeze and lignin are shown in the Table 3. The ash fusion temperatures were determined by observing the shapes of the ash cones during heating. Four characteristic temperatures including the deformation temperature, the softening temperature, the hemisphere temperature and the flow temperature were determined [12-13].

As can be seen from the Table 3, the initial (deformation) temperature of the lignin ash is lower by about 82°C compared to the ST temperature of the coke ash. Conversely, the lignin ash flow temperature (FT) is by 58°C higher than that of the coke ash. The melting process of both compared ashes is smooth with a slightly increasing temperature up to the flow temperature. A significant increase in temperature occurs in the range of melting and flowing temperatures, which corresponds to 305°C for lignin ash. The difference between the coke ash melting point and the flow temperature 91°C, which is about 3.5 times less than for the lignin ash. The ash of lignin, compared to the ash coke, has a lower melting point by 135°C and a higher flow temperature by 58°C. The obtained flow temperatures of the compared ashes are very close. The chemical composition of ash is the determining factor that affects the melting temperature, the Table 3. The basic components are Al₂O₃, SiO₂, Fe₂O₃, CaO, MgO, K₂O and Na₂O oxides, which determine the melt formation and hence the melting temperature of each ash type. As can be seen from Table 3, the melting temperature of lignin ash is lower than the melting temperature of coke breeze ash by 156°C. SiO₂ and especially Al₂O₃ increase the melting temperature while Fe₂O₃, CaO, MgO and also K₂O and Na₂O reduce it. The chemical analysis shows that the SiO₂/Al₂O₃ ratio for the lignin ash corresponds to 7.91 and for the coke ash to 1.66. The sum of the alkali bases in the lignin ash is 3.37 and in the coke breeze ash 3.86 %, indicating a small difference.

Despite the significantly higher ratio of SiO₂/Al₂O₃ in the lignin ash, its melting temperature is lower. Based on this findings, it can be stated that the more significant influence on melting temperatures has Al₂O₃ than SiO₂.

TABLE 3

The measurement conditions of X-ray

Sample	Temperature (°C)			
	DT – Deformation temperature	ST – Sphere temperature	HT – Hemisphere temperature	FT – Flow temperature
Lignin	1141	1162	1185	1490
Coke breeze	1223	1289	1341	1432

3.2. Chemical analysis of the ash samples

The influence of the chemical composition of an individual ash types on their melting temperature can be explained on the basis of the ternary diagram $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ (Fig. 1). In the ashes, as products of the fuel combustion, there are primary and secondary mineralogical phases that have major impact on the physical properties of the ashes. The presence of primary phases is determined by the type of fuel and their interactivity. The occurrence of secondary phases is contingent on many conditions, especially the temperature of the combustion process and the chemical composition of ash. By standard combustion of coke and lignin have been obtained the ashes, which chemical compositions are expressed as oxides in the Table 4.

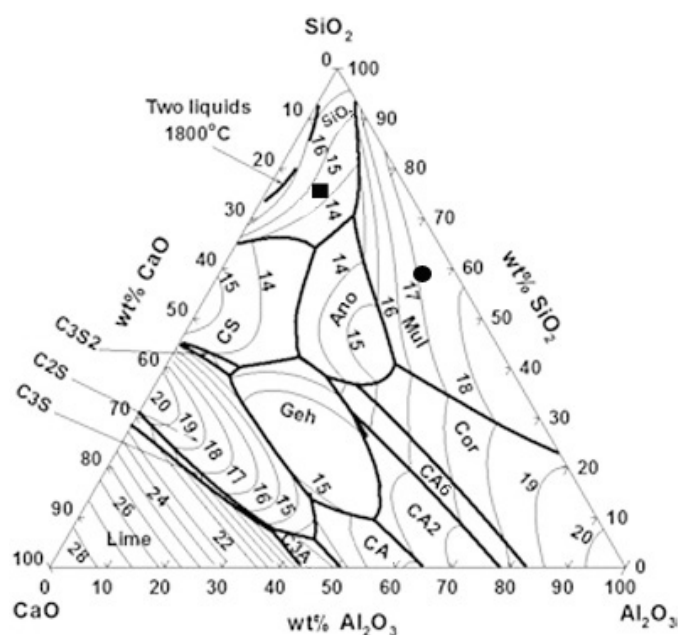


Fig. 1. The $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ phase diagram with plotted simplified composition of the ashes obtained by the laboratory combustion of coke and lignin

According to analysis of the chemical composition, the elements occurring in these ashes can be divided in principle into two groups. A group of elements facilitating the melting (Fe, K, Na) and therefore decreasing the melting points of the whole system in which they occur, and to a group of dominant elements (Si, Al, Ca), with the possibility of creating high melting phases increasing the melting points. If both ash compositions are recalculated, maintaining the ratios, for this dominant group, it is possible to predict their different behaviour during heating on the basis of the ternary diagram $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$, (Fig. 1).

As can be seen from Fig. 1, the basic ash systems are diametrically different. While the ash of lignin falls into a high-silica system, the coke ash into a mullitic. From there also arises their different behaviour in the presence of the melt elements. Considering the chemical composition, the Table 4, it can be stated that the sum, the content of the elements considered classical melt elements (P, K, Na), differs only by 0.64% in the individual systems, i.e., they should act in the same way. But on a high-silica system, where one of the modifier forms prevails, these predominantly alkaline elements have a more pronounced effect on the formation of a low melting eutectics and therefore the DT, ST and HT temperatures are substantially lower than in the multicomponent system where the interaction of the melt elements is hampered by the mullite structure. Iron in the high silicon system also acts as a flux, but compared to its relatively low content (4.35%), it does not have the same efficacy on this system as the alkalis. Not even in the mullitic system, although an higher levels (14.59%) of iron does not have a more pronounced effect on the monitored temperatures. An anomaly in flow temperatures (FT), when for a high-silica as higher temperature (by about 60°C) was determined than for the coke ash, can be attributed to the definition of FT temperature measurement and the silicon melt viscosity. The viscosity of the silicon melt (glass) at such low temperatures is considerable and probably higher than that of the mullitic composition melt viscosity, despite the presence of the melt elements.

3.3. Scanning electron microscopy

This technique gives the location of elements in the region being scanned, allowing the distribution of each element to be evaluated in the ash samples. The chemical composition of the particulates was determined from the analysis of the energy dispersive spectra (EDS) produced by X-rays generated from the particles by the electron beam. Morphology, texture and chemistry

TABLE 4

Chemical composition (wt%) of the ash samples as determined by XRF analysis

Sample	Content of ash [%]	Chemical composition, [wt %]							
		SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	CaO	MgO	K_2O	Na_2O
Lignin	3.4	63.99	8.09	4.35	0.3	13.53	1.35	1.40	1.97
Coke breeze	12.1	43.48	26.19	14.59	0.28	4.60	1.83	2.85	1.01

of the coke ash and the lignin ash were analysed by scanning methodology (SEM).

The element composition of the ashes from lignin and the coke breeze are shown in the Table 5, 6. SEM images ash from lignin are shown in Fig. 2. and ash from coke breeze in Fig. 3. As shown in both cases (Fig. 2, 3) are dispersed, angular particles.

The particles of the coke breeze ash were much larger compared to the ash samples of lignin.

The EDS analysis showed that there were no significant differences in content proportions of Na, Mg, Fe in both ashes. The EDS analysis showed that ash from lignin contained more Si, Ca, K and less Al. Each detected element was in both cases

TABLE 5

Element composition of the ashes from lignin

Element, Wt %	C	O	Na	Mg	Al	Si	K	Ca	Fe
1	16.06	22.07	01.03	00.76	05.20	28.38	01.38	18.82	06.31
2	06.74	31.25	00.23	00.35	00.57	49.09	00.68	08.69	01.73
3	9.84	22.20	00.44	01.41	07.24	23.22	00.47	31.77	02.37

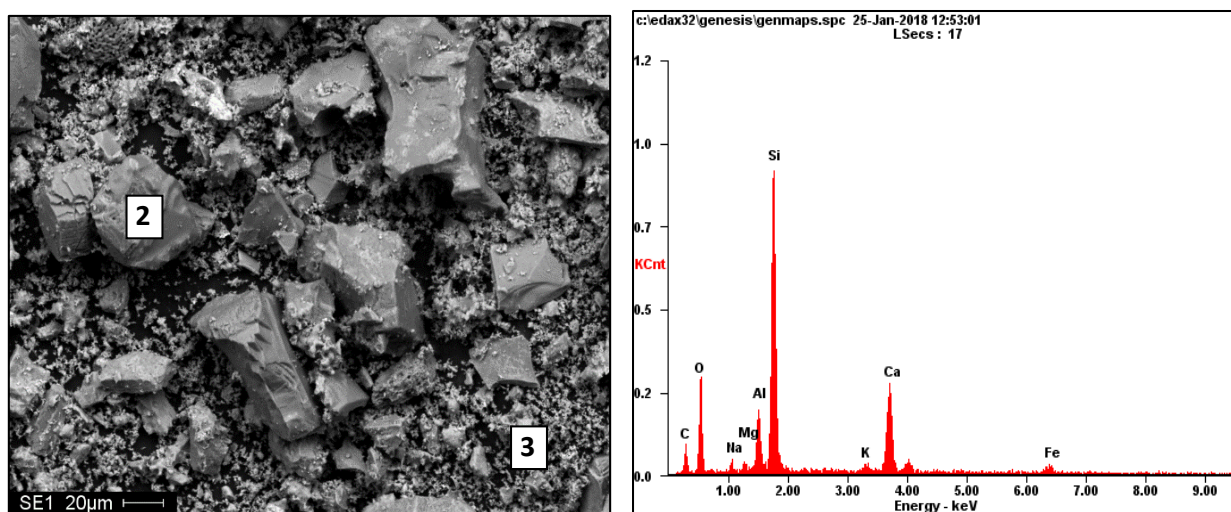


Fig. 2. SEM and EDX analyses of the ash from lignin. 1 – surface analysis

TABLE 6

The element composition of the ashes from the coke breeze

Element, Wt %	C	O	Na	Mg	Al	Si	K	Ca	Fe
1	21.66	25.05	00.45	00.89	14.80	23.30	03.46	03.08	06.54
2	06.40	29.15	00.73	01.04	17.70	37.62	03.43	01.54	02.37
3	06.15	24.25	00.66	01.06	24.74	31.27	03.67	02.18	04.26

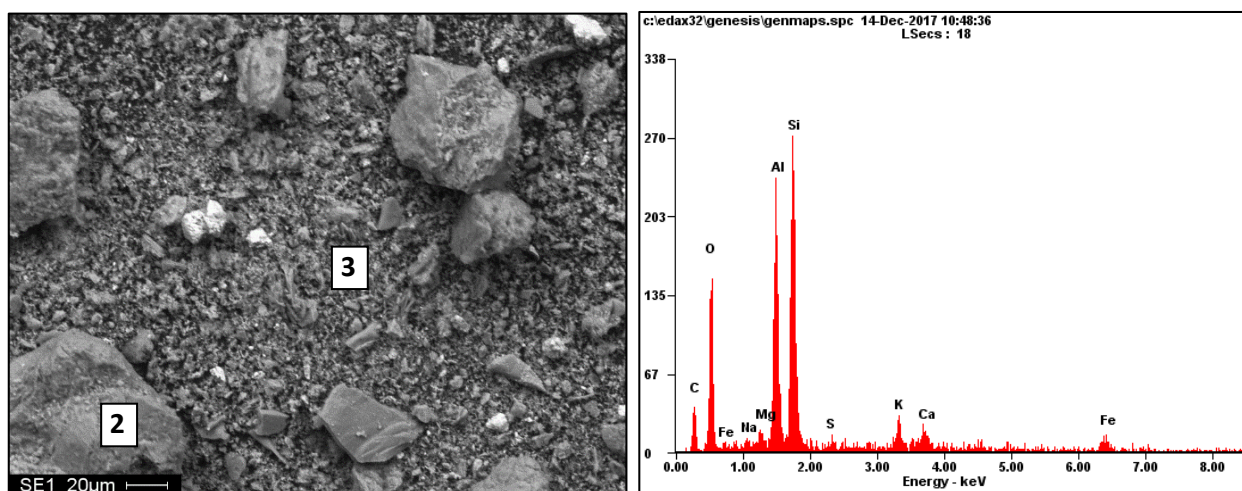


Fig. 3. SEM and EDX analyses of the ash from the coke breeze. 1 – surface analysis

characterized by a different intensity in the spectrum. Typical for the coke breeze and lignin were high intensities for aluminium and silicon (Fig. 2, 3). The most of the quartz crystals remain intact and are present as angular particles. The results from the wide-area EDS analysis are consistent (even though they are semiquantitative) with the results of the XRF method.

3.4. X-ray phase analysis of the ash samples

To determine the relative occurrence of the different phases in the ash of the compared materials was used the X-ray phase

analysis, which is a complementary method to a chemical analysis. From a mineralogical point of view, it is assumed that ash consists of three types of components: crystalline minerals, unburnt carbon particles and non-crystalline aluminosilicates or other glass oxides.

The XRD system evaluated the percentage of the crystalline mineral phases and the proportion of non-crystalline (amorphous or glassy) material in the ash samples derived from ashing of the coke breeze and lignin. The XRD pattern of the ash from the coke breeze is shown in Fig. 4. and ash from lignin in Fig. 5. The biomass ashes have highly crystalline character with a limited occurrence of an inorganic amorphous material and an organic

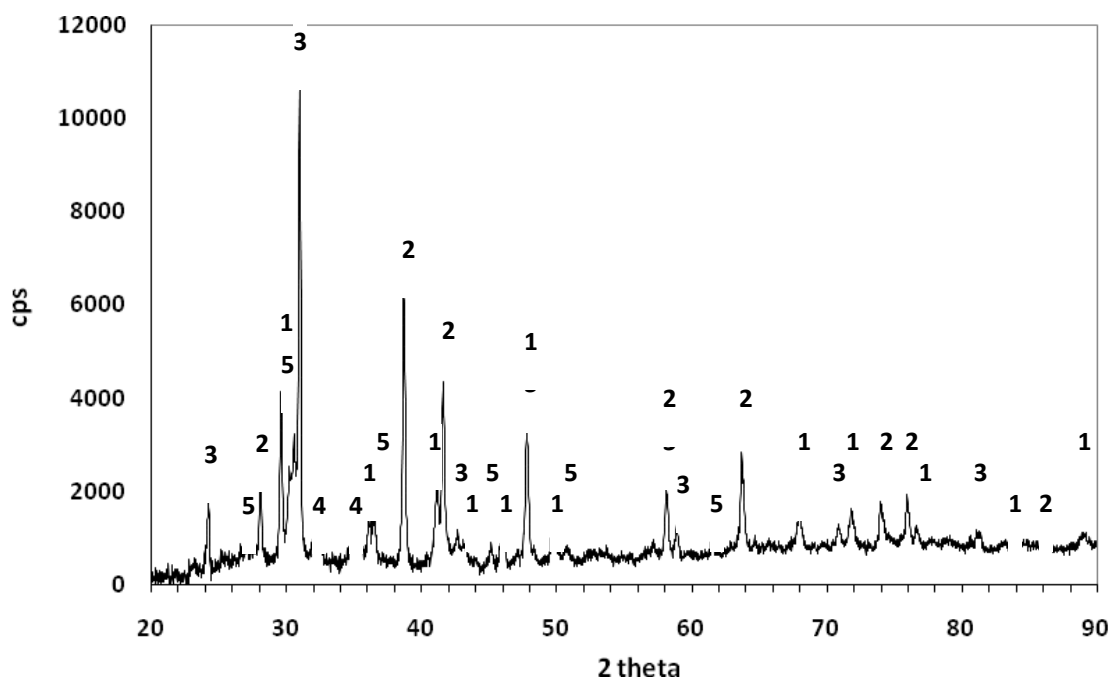


Fig. 4. XRD patterns of the ash from the coke breeze (1 – Mullite, 2 – Hematite, 3 – Quartz, 4 – Augite, 5 – Anhydrite)

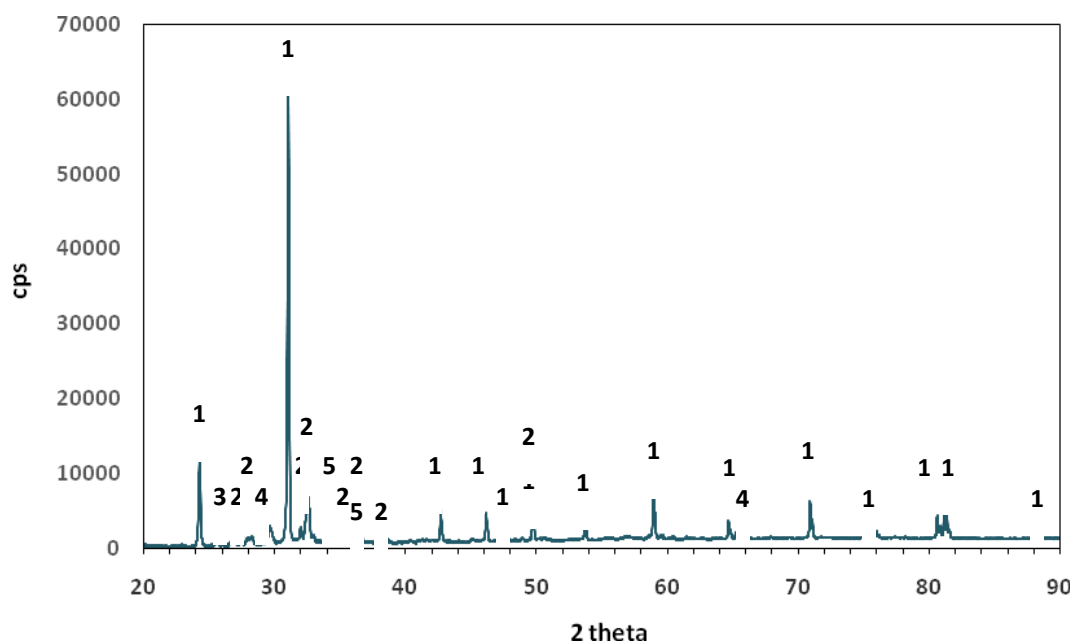


Fig. 5. XRD patterns of the ash from lignin (1 – Mullite, 2 – Hematite, 3 – Quartz, 4 – Augite, 5 – Anhydrite)

matter. Various species of carbonate, sulphate, silicate classes were identified in the ashes and most of them are newly formed minerals during biomass combustion.

The dominant minerals of the ash from the coke breeze were mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), hematite (Fe_2O_3), and quartz (SiO_2).

The dominant minerals of the ash from lignin were quartz (SiO_2), oligoclase ($\text{CaAl}_2\text{Si}_2\text{O}_8$), Hornblende ($(\text{Ca},\text{Na})_2(\text{Mg},\text{Fe},\text{Al})_5(\text{Si},\text{Al})_8\text{O}_{22}(\text{OH},\text{F})_2$). The phase composition are indicated in the Table 7.

TABLE 7

The phase composition of the ash samples as determined by X-ray analysis

Identified phase composition		Lignin	Coke breeze
Chemical Formula	Mineralogical name	Content [wt %]	Content [wt %]
SiO_2	Quartz	53.2	16.1
CaSO_4	Anhydrite	5.6	8.2
Fe_2O_3	Hematite	0.4	20.8
$\text{CaAl}_2\text{Si}_2\text{O}_8$	Oligoclase	21.9	—
$(\text{Ca},\text{Na})_2(\text{Mg},\text{Fe},\text{Al})_5(\text{Si},\text{Al})_8\text{O}_{22}(\text{OH},\text{F})_2$	Hornblende	12.4	—
CaCO_3	Calcite	5.4	—
$(\text{Mg},\text{Fe})_2\text{Si}_2\text{O}_6$	Sekaniinite	1.1	—
$\text{Al}_6\text{Si}_2\text{O}_{13}$	Mullite	—	37.9
TiO_2	Rutile	—	1.3
$\text{Ca}(\text{Mg},\text{Fe})\text{Si}_2\text{O}_6$	Augite	—	15.7
Degree of crystallinity		79.9	21.2
Amorphous		20.1	78.8

The identified mineral phases in the both ashes can be divided into as primary and secondary minerals. Primary minerals are actually the original constituents found in the source fuel, secondary minerals were generated during combustion of the fuel.

Quartz (SiO_2) found in both ash samples is considered a primary mineral. Due to its high melting temperature, it is essentially non-reactive in the combustion process and represents relatively large monomineralic particles. It is a hard mineral often represented by angular to round grains. Quartz forms the base phase in the ash of lignin (53.2%), which is also consistent with the chemical analysis of ash. Oligoclase is the second most represented phase in lignin and its occurrence can be explained by the high concentration of SiO_2 and Al_2O_3 , which interact with each other to form aluminosilicates which in reaction with Ca form $\text{CaAl}_2\text{Si}_2\text{O}_8$ (oligoclase). Lime can come from Ca bound in organic matter. Hornblende is another significant phase identified in ash of lignin (12.4%). This mineral belongs to the group of silicate minerals. The formation of this mineral is consistent with the chemical composition of ash [15-16].

Anhydrite is identified in the both ash samples. Anhydrite and its precursor minerals can be formed by the reaction between Ca and S released from the organic material.

The limestone identified in the ash of the lignin is present due to the low combustion temperature (550°C), which is not sufficient for its decomposition (min. 680°C). Limestone or dolomite are common minerals in coal.

The dominant phase in the coke breeze ash is the mullite silicate phase (37.9%). It is the secondary phase that is formed by the reaction of SiO_2 and Al_2O_3 in the combustion process. The formation of this phase corresponds to the determined chemical composition of ash. There is also a significant representation of hematite (20.8%). This is an iron oxide mineral that is rare in coals, but may be produced by oxidation of other minerals such as pyrite or siderite during the combustion process. Hematite may be formed from iron that is bound in some way with the organic matter, especially for the lignite and wood ash materials [14-16].

Rutile is the natural mineral form of TiO_2 in plutonic and metamorphic rocks. In ash of the coke breeze it is a mineral of secondary origin. Both ash samples contain an amorphous phase that is characterized by components without a defined crystal structure. Most amorphous minerals are unstable and tend to dissolve more easily.

4. Conclusions

The present research was focused on the characterization and comparison of the ashes from the coke breeze and lignin. The results of the average characteristics and the energy content of both fuels are consistent with the literary findings characterizing the differences between biomass and fossil fuel. Lignin contains 4 times less ash than the coke breeze and its calorific value is lower by 5 MJ/kg, which is a highly positive indicator for the agglomeration process.

The fusion characteristics of lignin and the coke breeze ashes are different. The thermal characteristics of lignin expressed by DT, ST and HT compared to DT, ST, HT of the coke breeze are lower, but the lignin FT is higher and reaches 1490°C compared to FT of the coke breeze 1432°C . It can be stated that lignin ash melts (HT-FT) over a wide temperature range of 305°C . Such a significant change in the coke breeze between HT and FT has not been recorded and it can be stated that this is a continuous melting process between DT, ST, HT and FT without any leap changes.

From the chemical analysis of the ash of the compared fuels it is obvious that their chemical base is the same, but the differences are in the content of the individual components. The relative component changes are also a result in changes in temperature characteristics. On the basis of the ternary diagram $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ it can be stated that lignin falls within the area of the high-silica system and the coke in the mullitic region. Higher melting temperature can therefore be attributed to the high-silica system. The viscosity of the silica melt at such low temperatures is considerable and probably higher than the viscosity of the mullitic composition melt.

The XRD shows that the coke breeze is mainly composed of SiO_2 and lignin $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ (mullite).

Based on these findings and the simplified characteristics of the compared fuels and ashes, it is possible to conclude that lignin appears to be a suitable partial replacement for the coke breeze in the agglomeration process. The confirmation of this conclusion needs to be supported by an experimental study of sintering of agglomeration mixtures with the addition of lignin on a laboratory sintering pan. The application of this substitution in the agglomeration process have to correlate with the requirements on agglomerate quality and economy and the on the environmental impact.

The results of the lignin analysis suggest that the orientation on its use in the agglomeration process is a correct direction.

In conclusion, it is possible to state that the major positive feature of increasing the share of alternative fuels, such as biomass, in the process of agglomeration is not only seen in reducing the negative impact of fossil fuels, but also in saving of reduced reserves of those fuels. It is necessary for this investigation to continue at least until the new technologies are developed for obtaining and applying other forms of energy without negative impacts on the environment.

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REFERENCES

- [1] J. Hehlmann, W. Szeja, M. Jodkowski, *Rocz. Ochr. Sr.* **13** (1), 891-902 (2011).
- [2] J. Łabaj, M. Jodkowski, *Metalurgija* **55** (1), 44-46, (2016).
- [3] N. Yanqing, T. Hongzhang, W. Xuebin, L. Zhengning, L. Haiyu, L. Yang, X. Tongmo, *Bioresource Technol.* **101**, 9373-9381, (2010).
- [4] N. Koukouzasa, C.R. Wardb, D. Papanikolaoua, L. Zhongsheng, Ch. Ketikidis, *J. Hazard. Mater.* **169**, 100-107, (2009).
- [5] S.V. Vassilev, D. Baxter, L.K. Andersen, Ch.G. Vassileva, *Fuel* **89**, (5), 913-933, (2010).
- [6] X. Fang, L. Jia, *Bioresource Technol.* **104**, 769-774, (2012).
- [7] E. Karampinis, P. Grammelis, B. Zethraeus, J. Andrijevskaia, Ü. Kask, L. Kask, S. Hoyne, P. Phelan, L. Casini, G. Picchi, A. Sandak, J. Sandak, 20th European Biomass Conference and Exhibition, Milan, (2012).
- [8] J. Werkelin, B. Skrifvars, M. Hupa, *Biomass Bioenerg.* **29** 6, 451-466, (2005).
- [9] M. Holubčík, J. Jandačka, M. Malcho, *The Holistic Approach to Environment* **5** (3), 119-125, (2015).
- [10] <http://en.bionet.su/product/>
- [11] STN EN 14775, 2009: Solid biofuels. Determination of ash content.
- [12] STN ISO 540, 2008: Hard coal and coke: Determination of ash fusibility.
- [13] T.F. Wall, R.A. Creelman, R.P. Gupta, S.K. Gupta, C. Coin, A. Lowe, *Prog Energy Combust.* **24**, 345-53, (1998).
- [14] A.A. Tortosa Masia, B.J.P. Buhre, R.P. Gupta, T.F. Wall, *Fuel Process Technol.* **88**, 1071-1081, (2007).
- [15] M. B. Golovko, *Coke Chem. Ussr*, **58** (8), 279-283, (2015).
- [16] S.V. Vassilev, K. Kitano, S. Takeda, T. Takashi, *Fuel Process Technol.* **45**, 27-51, (1995).