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BIOMASS AS A SOURCE OF ENERGY IN IRON ORE AGGLOMERATE PRODUCTION PROCESS

BIOMASA JAKO ŹRÓDŁO ENERGII W PROCESIE PRODUKCJI AGLOMERATÓW RUDY ŻELAZA

This article contains characteristics of selected types of biomass, which can be considered as an alternative fuel in the production of iron ore agglomerate.

Selected types of biomass were evaluated by chemical analysis, X-ray phase analysis and microscopic analysis using the camera on microscope Olympus BX 51. Biomass was characterized according to its structure, chemical composition and chemical composition of ash. The obtained data were confronted with the data for coke breeze and based on the results, conclusions were made about the possible use of selected types of biomass as an alternative fuel in the process of iron ore agglomerate production.

Keywords: agglomerate, biomass, coke breeze, ash, alkalia, phase composition, microstructure

Artykuł zawiera charakterystykę wybranych rodzajów biomasy, które mogą być uznane jako paliwo alternatywne w produkcji aglomeratów rudy żelaza. Wyselekcjonowane rodzaje biomasy poddano ocenie za pomocą analizy chemicznej, rentgenowskiej analizy fazowej oraz analizy mikroskopowej z użyciem kamery mikroskopu Olympus BX 51. Scharakteryzowano również strukturę, skład chemiczny i skład chemiczny popiołu biomasy. Uzyskane dane porównano z danymi dotyczącymi koksiku i na podstawie otrzymanych wyników opracowano wnioski odnośnie do możliwości korzystania z wybranych rodzajów biomasy jako paliwa alternatywnego w procesie produkcji aglomeratu rudy żelaza.

1. Introduction

Strategy for climate change, energy market and energy security are very unstable conditions characterizing the present time and it is obvious that they will remain highly relevant in the future. These visions oblige us to seek new technologies and improve, modernize as well as intensify contemporary technologies. This topic closely relates to the production of pig iron and subsequent steel production. Blast furnace production of pig iron cannot be perceived only in terms of furnace unit, i.e. blast furnace, but mainly in terms of charge preparation, that is, the process of production of iron ore agglomerate or coke-making process. Both technologies have significant consequences for environmental quality as well as for energy and related economic indicators of process technologies.

The agglomerate production technology is closely related to coke production in terms of environment and energy. Currently, the basic fuel component of agglomeration charge is coke breeze occurring as the undersize product in the production of metallurgical coke in the coke oven battery [1-2]. Coke is characterized as the most expensive and the most deficient input material in the pig iron production process. This is the reason for the constant search for alternative, replacement fuels, which would reduce the consumption of coke and improve the quality of the environment by reducing emissions, especially CO_2. Biomass of plant origin is currently considered as the most promising material with many advantages over fossil fuels. From the environmental point of view, it is primarily a neutral carbon balance when the amount of CO_2 released by energy use corresponds to that absorbed by the plant during its life from the environment and built into its cell structures through the photosynthetic process. Any consideration of the potentials for replacing fossil fuels either in the production of pig iron, coke or agglomerate requires a thorough analysis. Based only on the obtained results, it is possible to analyze and verify, in the laboratory setting, these possibilities. From the current experimental work and the obtained results, it is clearly an area that indicates the direction which will probably be inevitable in the future.

It is just up to us to move this area of knowledge to the more real concepts.

It is necessary to examine this possibility and consider using materials from biomass in the agglomeration process and, as far as possible, from local sources of biomass in the Slovak Republic.

Alternative fuels must be seen as economically available and environmentally sound materials.

Currently, there is relatively little information in the literature regarding this field of research, but initial experiments

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show that biomass as a renewable energy source can be also considered for the metallurgical industry purposes.

So far, studies have indicated a potential for emissions reduction and productivity increase using biomass in agglomeration of iron ore [3-14]. However, a more thorough analysis is necessary with respect to the impact of biomass on the properties of the final product, blast furnace agglomerate, which must meet strict quality requirements in terms of the blast furnace process.

If we seriously consider the potential for using biomass in the metallurgical industry, it is primarily important to carefully analyze this material and assess the possibilities of its use in terms of its chemical and physical properties and confront these with the properties of the currently used coke breeze.

Based on these considerations, the article describes characteristics of selected types of biomass which can be considered as an alternative fuel in the production of iron ore agglomerate. Biomass is characterized according to its structure, chemical composition and chemical composition of ash. The obtained data are confronted with the data for coke breeze, and based on the results, conclusions are made about the possible use of selected types of biomass as an alternative fuel in the process of iron ore agglomerate production.

2. Work methodology and materials

Biomass can be defined as organic matter, created by living organisms during their lives using conversion of inorganic materials by biochemical processes. For green plants, the most important biochemical process is photosynthesis enabled by green dye - chlorophyll. An essential part is the light from the sun. The photosynthetic reaction is described by the following chemical equation:

$$12H_2O + 6CO_2 + light \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O \qquad (1)$$

The theory of neutrality regarding the carbon dioxide emitted into the air during the combustion of biomass is based on the fact that the amount of released CO_2 have been absorbed by a plant during its lifetime so as a result, there is no production of new CO_2. In contrast to fossil fuels, biomass is a renewable energy source and carbon dioxide can be thus even recycled.

The chemical composition of biomass differs from one plant species to another, but on average, plants contain about 25% of lignin and 75% of polysaccharides. Two major components of polysaccharides are cellulose and hemicellulose. Cellulose is the building unit of fibers that give plants necessary strength. Hemicellulose is a component of the pulp but it is not stable. Lignin component acts as the glue that holds together the cellulose fibers.

The skeleton of cell walls of woody biomass consists of cellulose whose chains have a crystalline structure. Cellulose consists of β-D-glucopyranose units which are connected into linear chains. A summary formula of cellulose is $(C_6H_{10}O_5)_n$ where n is a degree of polymerization, i.e. a number of molecules in the macromolecule chain. Linear macromolecules of cellulose in the cell walls form supramolecular aggregates (fibrils) with highly ordered crystalline and less ordered amorphous regions. Cellulose macromolecules are arranged into elementary fibrils called microfibrils [15].

The length of elementary fibrils in various wood species depends on the degree of polymerization of cellulose macromolecule. Microfibrils form fibrils (Fig. 1).
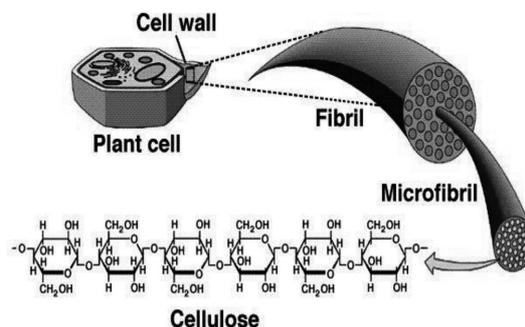

Fig. 1. Arrangement of fibrils, microfilbris, and cellulose in cell walls [16]

In the inner parts of the wood cell wall, hemicellulose forms individual layers of the cell wall. The supramolecular structure of most hemicellulose types is amorphous. Intercellular matter consists mainly of lignin which encases the cellulose and hemicellulose and gives wood the strength. Lignin is an amorphous biopolymer. A spatial molecule contains an aromatic structural unit.

The cause of amorphous nature of lignin macromolecules is spatial cross-linking and a low concentration of hydroxyl groups capable of forming hydrogen bonds between macromolecules.

Chemically, wood contains about 50% carbon, 43% oxygen and the remainder being hydrogen, nitrogen and minerals.

Based on the theoretical knowledge of cell structure of woody biomass and considering several aspects including its availability, we prepared for this study samples of woody biomass i.e. charcoal, sawdust, pine and oak wood. The selected types of biomass were dried at 105°C and, subsequently, a sieve analysis was performed, Table 1.

TABLE 1

The sieve analysis of coke breeze and biomass

Fraction, %	Coke breeze	Charcoal	Oak sawdust	Pine sawdust
>2	41.20	28.63	6.70	3.43
1.6-2	14.17	7.23	3.65	0.99
1-1.6	11.27	7.04	4.58	2.50
1-0.5	11.48	10.48	13.70	26.34
0.5-0.315	4.29	5.70	19.92	30.24
<0.315	17.58	40.93	51.44	36.50
Total	100	100	100	100

The samples thus prepared were subjected to a microscopic study using a camera on the Olympus BX 51 M microscope with a magnification of 10x. Interchangeable objective lenses were dry 5x, dry 10x, dry 100x and immersion 40x.

To estimate the phase composition of ash, the method of X-ray diffraction was used. A SEIFERT XRD 3003/PTS diffractometer was used to scan the samples. The measurement parameters are presented in Table. 2.

Measurement conditions

Generator	35 kV, 40 mA
X-ray radiation	Co-line focus
Filter	Fe
Scan step	0.02 theta
Range of measuring	10 - 130°2theta
Input slits	3 mm, 2 mm
PSD Detector	Meteor1D

A diffraction record was analysed using the ZDS-Search Match software with the PDF2 database and TOPAS program.

3. Results and discussion

A microscopic structure of charcoal is shown in Figure 2. Substantial components of the matter are libriform fibers with a small diameter arranged closely side by side.
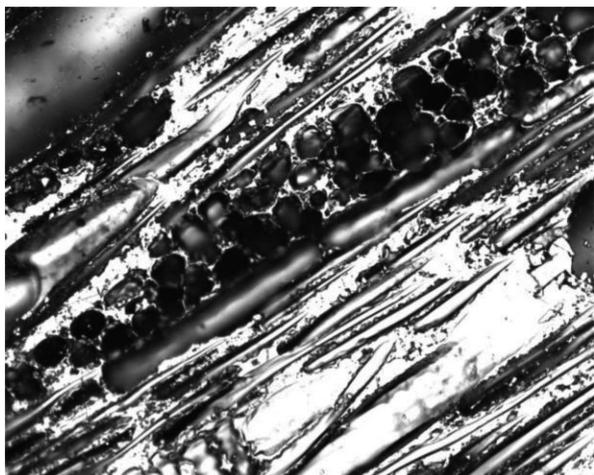

Fig. 2. Microstructure of charcoal, mag. 20x

Soft pine wood has a finely porous, regular structure composed of two basic building elements – tracheids (Figure 3) and parenchymal cells (Figure 4).
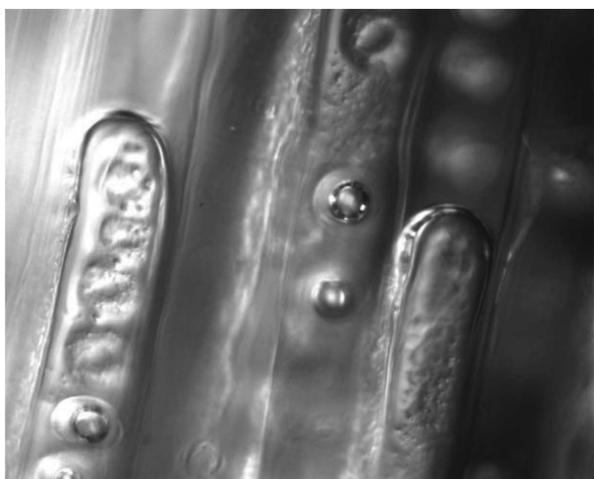

Fig. 3. Tracheids of pine sawdust, mag. 400x

Tracheids are veins present in the woody parts of plants in the form of tubes composed of elongated cells. They are prevalent building units and form 87-95% of the total wood volume. They are closed, elongated cells with different endings and their shape, size and cell wall thickness are affected by their function in the growing tree.
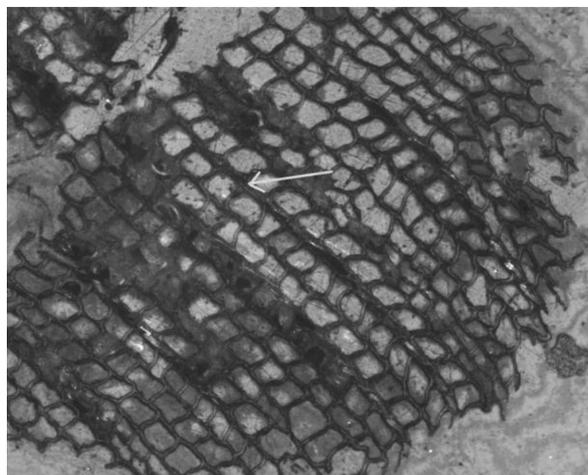

Fig. 4. Pine sawdust cross-section – the parenchymal cells of pine sawdust, mag. 100x

The pine sawdust parenchymal cells, as shown in the image, have a shape of shorter prisms or cylinders. They make up 5-10% of the total volume of wood. The arrow in the picture shows a thin spot.

Thin spots in cell walls serve for the transport of organic substances and water with mineral substances between cells.

Sclerenchymatic cells of oak sawdust are documented in Figure 5.
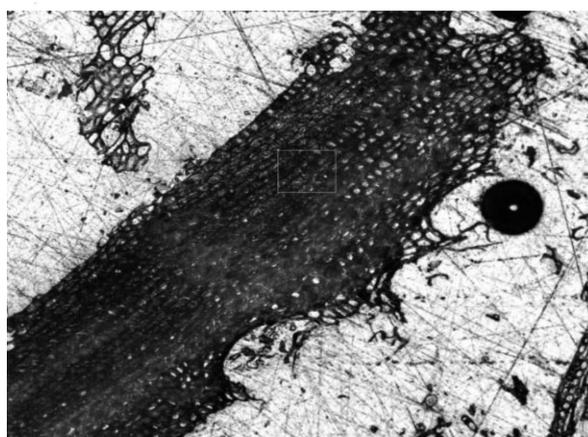

Fig. 5. Sclerenchymatic cells of oak sawdust, mag.100x

A substantial portion of oak sawdust consists of sclerenchymatic cells that form groups of thick-walled libriform fibers. The details of sclerenchymatic cells are shown in Figure 6.

The amount of libriform fibers in wood and, mainly, the cell wall thickness affect the density and strength of the wood. Absorbed water is stored in the submicroscopic crevices, which is very important in terms of wood hydroscopicity.

Biomass assessment, only based on the microstructural construction of cellular matter, does not provide a sufficient

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picture of the possibilities of its use as an alternative fuel in the agglomeration process. Therefore, in further study, an analysis of the chemical and phase composition of the given materials was performed. Since the process of fossil and non-fossil fuels is accompanied by the emergence of ash, it is very important to characterize ash in terms of its chemical composition.
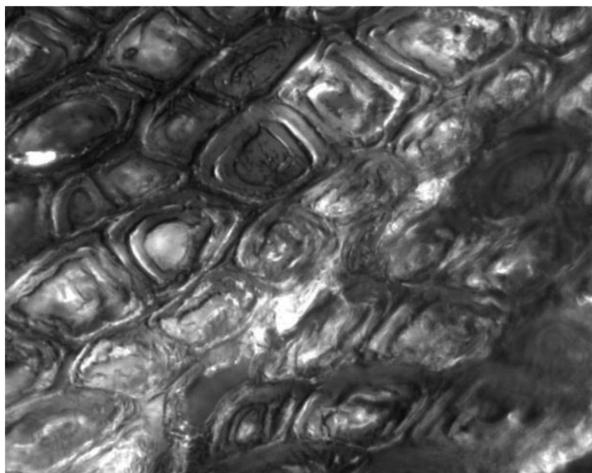

Fig. 6. Details of sclerenchymatic cells, mag. 1000x

The ash content in the fuel is expressed by the following formula:

$$A = \frac{m_p}{m_d} * 100\% \qquad (2)$$

where m_p is the mass of ash; g m_d is the mass of absolutely dry sample of fuel, g.

Ash is formed from minerals that are found in the fuel and it mainly consists of inorganic element oxides: SiO_2, MgO, CaO, Al_2O_3, Fe_2O_3, K_2O, Na_2O.

The results of the chemical analysis of biomass compared to the standard fuel, coke breeze, are presented in Table 3.

TABLE 3

Chemical composition of breeze coke and biomass (wt.%)

	Coke breeze	Char-coal	Pine sawdust	Oak sawdust
Water, %	0.8	2.2	4.5	4.1
Ash, %	14.5	3.5	0.9	1.5
Volatiles, %	3.5	8.2	85.6	83.4
Sulfur, %	0.59	0.054	0.051	0.052
Hydrogen %	0.79	1.51	6.15	5.96
Carbon,%	96.9	93.2	50.3	50.60
Nitrogen, %	0.84	0.45	0.08	0.19
Heat of combustion, MJ/kg	33.46	33.63	21.02	19.49
Calorific value of orig. sample, MJ/kg	28.16	30.46	15.94	16.56
Calorific value of dry sample MJ/kg	28.39	32.15	18.81	18.00
Phosphorus,%	0.044	–	–	–
Chlorine, %	0.030	–	–	–

Chemically, coke is composed of combustible carbon, hydrogen, oxygen, nitrogen, combustible sulfur and non-combustible constituents deposited after complete combustion, mainly in ash. A higher content of ash reduces the energy potential of the fuel and therefore, it is best to use low ash types. However, for the agglomeration of iron-bearing materials, the composition of this mineral phase is important and, in this respect, some benefits of biomass are worth mentioning.

The major component of coke is carbon with a fraction of above 80%; the remaining elements are present in significantly smaller quantities. However, these accompanying substances often determine the usability of fuel. Coke is one of the main carriers of sulfur in metallurgical processes and emphasis is also placed on monitoring of the ash composition which plays important role in the blast furnace agglomerate production process. The main components are SiO_2, Al_2O_3 and Fe_2O_3; the prevailing acidic character is caused mainly by silica content in the ash of about 50%.

Charcoal underwent advanced treatment as evidenced by high levels of bound carbon content and calorific value as well as low volatiles. The sulfur concentration is acceptable (0.054%). The charcoal calorific value is 32.15 MJ/kg, i.e. higher than for coke breeze. Because the ash composition does not change during pyrolysis, it can be assumed that the raw wood is composed of the same mineral phases.

The elemental composition of biomass (sawdust, pine and oak) is not very variable. Compared to the fossil fuel, biomass contains about twice as high the amount of oxygen and less carbon. A difference in the hydrogen content is not very significant. In a comprehensive evaluation, the sulfur content in biomass is very plausible when compared to coke breeze. It is significantly lower in charcoal and even lower in pine and oak sawdust. The sulfur content in biomass, compared to fossil fuels, is generally very low and, therefore, less sulfur dioxide is generated during the combustion process.

There is a significant difference in the content of volatile combustibles. Biomass contains a large amount of volatile combustibles – around 75% in general. The content of volatile combustibles in biomass reviewed here varied within 85.6 and 83.4%. A disadvantage of fuel is ash which is significantly lower in biomass than in fossil fuels, Table 4.

TABLE 4

Ash composition of the coke breeze and biomass, wt.%

	coke	charcoal	pine	oak
Fe_2O_3	27.2	1.47	6.53	4.48
SiO_2	34.7	6.3	46.63	41.06
CaO	6.8	37.01	15.28	23.83
MgO	2.8	12.50	3.00	2.62
Al_2O_3	21.1	0.85	11.73	6.69
MnO	0.15	4.54	0.66	0.82
P_2O_5	0.64	0.81	0.44	0.36
Na_2O	1.1	0.33	0.69	2.07
K_2O	1.6	11.42	5.60	9.33
Alkalinity	**0.2**	**6.7**	**0.3**	**0.6**

Ash is one of the three main components of the fuel. The ash is a solid unburned fuel residue which results from the combustion process. It is formed in the reaction of minerals with oxygen and mainly consists of oxides of elements of the minerals that are contained in the biomass (K_2O, Na_2O, CaO, MgO, Fe_2O_3, Al_2O_3, SiO_2, P_2O_5). In general, the ash content is much lower in biomass fuels than in other types of fuel, which guarantees a smaller particulate matter content in the flue gas. The ash content in biofuels is determined by the chemical structure of each type of biomass as well as contamination of soil from which biomass take nutrients. In Table 4, the chemical composition of ash for the analyzed biomass types is presented.

The results of chemical analysis of the ash show that the charcoal ash has an alkaline character with a low content of SiO_2 and high contents of CaO and MgO. Sawdust from pine and oak wood is, on the other hand, characterized by high contents of acidic components SiO_2 and Al_2O_3 and in comparison with charcoal, it has an acidic character. Coke breeze contains several times more ash than biomass and it has an acidic character. In terms of its use in the agglomeration process, it is clear that for the basic agglomerate production, a higher content of the added basic component, generally in the form of $CaCO_3$, is necessary, which results in the increased demand for coke.

Other undesirable constituents of the ash are alkali metal oxides Na_2O and K_2O. Their contents are given in Table 4.

Alkali metal oxides are transferred with the fuel into the final product, i.e. the agglomerate. Carriers of alkalis into the blast furnace, besides agglomerate and pellets, are also raw materials that are delivered directly into the blast furnace, i.e. lumpy ore, limestone or dolomite. Exceeding the allowable alkali content in the blast furnace charge per ton of pig iron may cause failure of technological process and reduce the performance of blast furnaces [17].

To identify the form of alkali in coke and biomass, an X-ray phase analysis was carried out.

Based on the X-ray phase analysis, the following mineral components were identified in the evaluated biomass. The identified phases are presented in Table 5.

Based on the results of X-ray phase analysis, it is clear that the alkalis are not in a crystalline form, but they constitute a component of the amorphous phase which was identified in all the evaluated biomass and coke ashes.

In the production of coke from coal, virtually all alkalis remain in coke and through the coke, they are brought into the sintering mix and subsequently into the blast furnace. When using biomass in the process of agglomeration, biomass combustion is accompanied by production of ash which, compared to coke ash, has a significantly higher alkali content, mainly in the form of K_2O and Na_2O.

Alkaline compounds in the agglomerate are generally found in the form of alkali silicates, but they can also occur in other alkaline compounds, such as $(K)Na_2O.SiO_2$, $(K)Na_2O.Al_2O_3.xSiO_2$, $(K)Na_2O.Fe_2O_3$ and, to a small extent, also as $(K)Na_2CO_3$ or $(K)NaCl$. Any alkali content in excess of 0.2% has a negative effect on the metallurgical properties of the agglomerates.

Part of alkalis that enter the blast furnace pass into the final blast furnace slag may reduce its viscosity and, hence, increase its fluidity which is important for the subsequent removal of slag from the blast furnace.

TABLE 5

Phase composition of biomass

Identified phase composition		coke	charcoal	pine	oak
Chemical formula	Mineralo-gical name	Content wt.%	Content wt.%	Content wt.%	Content wt.%
$(Ca_{0.94}Mg_{0.06})CO_3$	Calcite	-	57.3	15.7	-
$MgCO_3$	Magnesite	-	26.8	-	12.1
$Ca_6Mn_6O_{16}$	-	-	15.9	-	-
$Al_{1.25}Si_{0.75}O_{4.87}$	Mullite	50.4	-	-	-
$CaFeSi_2O_6$	Hedenbergite	4.3	-	-	-
$CaSO_4$	Anhydrite	8.0	-	-	-
SiO_2	Quartz	15.9	-	54.9	10.2
$Ca_2Fe_{1.54}Al_{0.46}O_5$	Brownmil-lerite		-	10.2	-
Fe_2O_3	Hematite	16.5	-	10.9	-
Fe_3O_4	Magnetite	4.9	-	-	-
MgO	Periclase	-	-	6.1	-
$CaCO_3$	Calcite	-	-	-	56.0
CaO	Lime	-	-	-	19.8
Amorphous	-	**19.6**	**41.0**	**44.0**	**84.0**

4. Conclusions

The use of solid biomass as an alternative fuel in the process of production of iron ore agglomerate is determined by its chemical and physical properties and, therefore, it is important to take these properties into account.

The results obtained in the analysis of selected types of biomass can be summarized by the following conclusions:

1. Coke breeze and *pyrolytically processed biomass*, charcoal, have most similar properties. In terms of the chemical composition, the advantage of charcoal is its lower content of ash and sulfur. The carbon content is comparable to that of coke breeze. Higher water and volatile substance contents are a drawback. Increased moisture in biomass is its typical characteristic that significantly and mostly negatively affects the combustion process. It reduces the calorific value of fuel as part of the energy is consumed to evaporate the water contained in the fuel. It reduces the efficiency of the combustion process, which results in the formation of a large amount of unburned residuum in the ash with no energy effect.

Energy properties of biomass represent a critical parameter that determines its suitability to serve as an alternative fuel in the agglomeration process. Based on a comparison of energy values of coke breeze and charcoal, it is seen that their calorific values range at comparable levels.

In terms of a comparison of chemical properties, partial replacement of coke with charcoal can be recommended. However, costs for biomass processing will be fully reflected

in the price of fuel, which ultimately will be a key indicator of its applicability in the agglomeration process.

2. There are much more significant differences when comparing coke breeze to the raw biomass, i.e. sawdust from oak and pine wood. Wood biomass has higher water content, higher content of volatile matter and less carbon, which is a negative indicator in terms of energy. A result of these characteristics of biomass is almost a half lower calorific value in comparison with the reference coke breeze.

In a comprehensive assessment, biomass has a very favorable sulfur content which is about 10 times lower than in the reference coke breeze.

Significant differences are observed in the quantity and composition of the ash. The evaluated biomass has 10 to 15 times lower ash content than the reference coke breeze.

Alkalinity of ash pine sawdust is 0.3 and that of oak sawdust is 0.6; it contains less alkaline ingredients. At the same time, the more significant carriers of alkalis are $K_2O + Na_2O$.

Wood biomass (pine sawdust and oak sawdust) is characterized by acidic ash and it contains significant quantities of alkali oxides which are unwanted in the agglomeration process. A positive side, however, is that the ash content in biomass, compared to coke breeze, is very low.

The results of analysis of selected biomass types suggest that the orientation on their use in 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 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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