Impact of Substituting Coke with Biomass on the Mineralogical Composition of the Iron Ore Agglomerate

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Received: 11 May 2020; Accepted: 3 July 2020; Published: 8 July 2020

Abstract: Coke breeze is a special type of fossil fuel that significantly contributes to environmental pollution. Therefore, ways and opportunities to reduce its negative impact on climate change are being sought. Alternative fuels constitute one of the opportunities where biomass can play an important role. Biomass represents a new fuel for the sintering process and an attractive way to decrease CO\textsubscript{2} emissions. Today, biomass is not considered for complete substitution of coke. Opportunities for its partial substitution are instead being sought. Each type of fuel is characterized by different properties and thus also by an appropriate scope of its substitution in an agglomeration mixture. This study covers the available options and the potential impact of this substitution on the structural and mineralogical composition of the agglomerate. These experiments were carried out by substituting coke breeze with biomass (hydrolyzed lignin). To perform the experimental sintering, a sintering apparatus—laboratory sintering pan (LSP)—was used, which was fully equipped with measuring devices and analyzers. The samples of agglomerates prepared by substituting 0%, 20%, 50% and 86% of coke breeze with biomass (hydrolyzed lignin) in dried form were analyzed by chemical and microscopic analysis-The representation of individual minerals in agglomerates was determined by powder X-ray diffraction analysis. Based on the results of the study regarding the impact of partial coke substitution with biomass on the mineralogical composition of the agglomerate, it can be stated that it is possible to substitute about 50% of coke with lignin in the sintering process. When lignin was used to substitute up to 50% of coke, agglomerates with minimal variations in the chemical and mineralogical composition were produced.

Keywords: biomass; emission; fuel; microstructure; mineralogical composition; iron ore agglomerate

1. Introduction

Biomass is currently seeing its renaissance. The number of people on Earth is continuously rising, economic growth of countries is increasing, and concurrently, their dependence on energy is also growing due to the above. The demand for energy is becoming a global strategic issue. The consumption of all types of fossil fuels is rising, which constantly deepens the problem of climate change. Hence, we turn to renewable energy sources increasing often. Biomass is considered a renewable energy source, as it takes a relatively short time to regenerate consumed reserves. Compared to the past, we now have technologies that can transform renewable energy sources into materials with high energy value and utilize them as an energy source. This will considerably relieve the detrimental effects on our environment. Efficient processing of renewable sources makes biomass an alternative source of energy.

Under certain conditions, alternative sources of energy can be used in energy-intensive processes, such as sintering process employed in the production of blast furnace agglomerate. However, this
technology does not allow the complete substitution of a traditional energy source—coke with biomass, because biomass has different chemical—physical properties that would substantially alter both technological and quality parameters of the agglomerate. Nevertheless, its partial substitution which takes into consideration compliance with optimal energy requirements for fuel and final quality of the agglomerate, especially its strength and reducibility, is feasible. Hence, such conditions need to be maintained that will enable the production of sufficient amount of melt which will form a steady bonding phase of sintered ore raw materials, achieving acceptable porosity of the sinter required for its good reducibility.

The strength of the sintering product is directly derived from the formed bonding phase and its characteristics, particularly its amount and mineralogical composition. Since all components of the sinter mixtures contribute to the formation of the bonding phase, namely metal-bearing, slag-forming and fuel parts of a mixture, the quality of both bonding phase and agglomerate as a whole changes necessarily when there is any change in ratios or replacement of a component.

When a portion of traditional fuel–coke is replaced by biomass, one may expect that the bonding phase formed will be affected by the presence of biomass ash as well. Thus, the quality of fuel has a direct impact not only on thermal conditions during combustion in the course of sintering, but also on other properties of agglomerate through a potential effect on the bonding phase, i.e., on the mineralogical composition. Therefore, when substituting coke with biomass, it is necessary to take into account this aspect as well. The original components of gangue minerals—SiO$_2$, Al$_2$O$_3$, CaO and MgO—are the chemical components constituting the sinter mixture that primarily contribute to the formation of the bonding phase. Calcium ferrites (CF, C$_2$F, etc.) are the main and, at the same time, the most desired bonding phases of rich iron ore agglomerates in terms of mineralogical composition. They considerably affect the quality parameters that are monitored the most closely—strength and reducibility of agglomerate—improving both of these properties.

Due to the conditions of agglomerate production, complex types of calcium ferrites–quaternary aluminum silicoferrites of calcium with stoichiometric formulas Ca$_2$(Ca,Mg,Fe$^{2+}$,Fe$^{3+}$,Al)$_6$(Fe$_3$Si$_3$Al$_6$O$_{20}$ and Ca$_3$(Ca,Fe)$_3^+$(Fe,Al)$_{3}^{3+}$O$_{31}$, SFCA—are present predominantly. Aluminum silicoferrites of calcium are primarily defined by the pseudoquaternary oxide system Fe$_2$O$_3$–CaO–SiO$_2$–Al$_2$O$_3$ and their chemical composition essentially affects the mineralogical composition of the bonding phase.

The significant effect of input raw materials make up on the chemical composition of aluminum silicoferrites of calcium has also been confirmed in the study [1], where the author lists examples of SFCA composition average values in agglomerates from various regions of the world based on the richness of iron ore. The high content of Fe$_2$O$_3$ and the lower content of SiO$_2$ and Al$_2$O$_3$ in SFCA is typical for agglomerates prepared from rich iron ore. Almost a twofold content of SiO$_2$ in calcium ferrites compared to ferrites of rich agglomerates is a common feature of agglomerates produced from ore with a high content of silicon (poorer iron ore), which proves a significant effect of input raw material makeup of the chemical composition of aluminum silicoferrites of calcium. In addition to the basic components with the highest representation, i.e., Fe$_2$O$_3$, CaO, SiO$_2$ and Al$_2$O$_3$, MgO is also present in SFCA at the concentrations up to 3 wt%. The presence of other constituents is fully dependent on their local concentration in an agglomeration mass [1].

The final properties of the agglomerate are determined not only by its chemical composition, but also by the mineralogical (i.e., phase) composition to a substantial extent. Mineralogical composition can have diverse structural form depending on the conditions of agglomerate production. Essentially, it concerns the crystalline and glassy phases. A relatively large portion of mass has the form of solid solutions of varying composition, which makes it difficult to assess the share of contribution of individual phases quantitatively and qualitatively to the strength of agglomerate. It follows from the above that not only the chemical composition of input components of the mixture, but also their physical properties and technological conditions of the sintering process must be taken into consideration in the production of the agglomerate. In general, all technological parameters indeed
affect the mineralogical composition and structure of the agglomerate, which then affect the strength properties of the agglomerate.

In the submitted study, the model agglomeration sintering focuses on the fuel part of the sinter mixtures to assess the impact of partially substituting coke breeze with biomass on the structural and mineralogical composition of agglomerate with regard to the substitution level of applied fuel.

2. Materials and Methods

Experimental sintering of sinter mixtures was carried out on a laboratory sintering pan at the Faculty of materials, metallurgy and recycling, Technical University of Košice, Letňá, Slovakia to produce a standard agglomerate (coke breeze used as fuel) and an agglomerate with partial substitution of coke breeze with biomass (hydrolyzed lignin). In laboratory experiments, the sinter mixture consisting of materials applied in operating conditions was used for sintering. A chemical analysis of input raw materials of the sinter mixture’s metal-bearing and slag-forming parts is shown in Table 1.

All laboratory sintering was performed under the same conditions and with the same charge raw materials. Only the substitution level of the tested substitute fuel varied. The agglomeration ore:concentrate ratio was 1:1. Two types of agglomerates were examined: standard agglomerate prepared solely with coke breeze and agglomerate with 20%, 50% and 86% substitution of coke breeze with biomass (hydrolyzed lignin). The substitution was performed based on the equivalent calorific value. This means one calorific unit of coke was replaced by an equivalent amount of hydrolyzed lignin. Since the calorific value of substitute fuel is lower than the one of coke (Table 2), the total share of fuel in raw sinter mixture increased with the rising substitution level to retain approximately the same calorific value of the sinter mixture.

The replacement of fuel increased the amount of volatile combustible in the sinter mixture as well because lignin has a higher share of volatile combustible than coke (Table 2). This is the main difference between a reference sample and samples with substitution of fuel in terms of fuel components. The share of carbon remained roughly constant in all cases. Even though the substitution fuel contains little ash, the bigger amounts at higher substitution levels compensated for the low shares of ash in the substitute fuel. Hence, the amount of ash of the total fuel stayed approximately the same.

Coke was supplied from a sinter plant. It is an undersized fraction obtained from the production of metallurgical coke. This fraction is classified as coke breeze and is the most appropriate and the most widely used fuel in the production of agglomerate today. Biomass is technical hydrolyzed
lignin. Technically, hydrolyzed lignin is a byproduct of the distillation of wood in the production of ethanol. Over time, the industrial production of ethanol has turned out to be highly energy-intensive and was stopped, leaving only huge dumps of wood waste, which are a vast sources of energy. The characteristics of hydrolyzed lignin and its comparison with coke breeze were studied in the study of Fröhlichová et al. [2].

The chemical analysis of input raw materials and agglomerates was carried out using an XRF spectrometer ARL 9900S (Thermo Fisher Scientific, Waltham, MA, USA). The samples were analyzed in a powdery state. Chemical composition of input raw materials for the production of agglomerate and chemical composition of agglomerate constitute the input information bases for a structural description of given agglomerates.

To determine the mineralogical composition, an X-ray diffraction method was employed which has now become one of the fundamental structural analytical methods in the field of material research and technological process management. The Rietveld method has become established in a broad spectrum of applications based on practical experience and comparative measurements. Its application using powerful software (TOPAS version 4, Brucker, Billerica, MA, USA) provides reliable results for the content of minerals from the measured crystallographic data.

Diffractograms were acquired using a SEIFERT XRD 3003/PTS diffractometer (General Electric Company, Boston, MA, USA). Measurement parameters are shown in Table 3.

| Generator | 35 kV, 40 mA |
|-----------|-------------|
| X-ray radiation | Co-line focus |
| Filter | Fe |
| Scan step | 0.02 theta |
| Range of measuring | 10–130° 2 theta |
| Input slits | 3 mm, 2 mm |
| * PSD detector | Meteor 1D |

*—Position sensitive detector.

Diffraction records were analyzed by ZDS-Search Match program with PDF2 database and by TOPAS program. Diffraction records were evaluated by DIFFRAC.EVA (Search-Match, KARLSRUHE & VIERSEN, Bruker, Billerica, MA, USA) with PDF2 and TOPAS software (version 4, Bruker, Billerica, MA, USA) using the Rietveld method.

3. Results and Discussion

Since, in general, all technological parameters affect the mineralogical composition and structure of the agglomerate, which then affect its mechanical properties (which then affect the mechanical properties of the agglomerate), the question arises how the substitution of coke breeze with biomass will affect the mineralogical composition of agglomerate with regard to the substitution level of applied fuel. For this purpose, comparison of coke breeze and an alternative fuel was made from the perspective of chemical composition and energy value. It is documented in Table 2 [3].

It follows from the results that hydrolyzed lignin has a higher content of water, higher content of volatile combustible and a lower content of ash and fixed carbon. Carbon is primarily bound to hydrogen and oxygen in the form of macromolecular cellulose (C₆H₁₀O₅) with a certain degree of polymerization, which corresponds to the content of volatile combustible. Content of fixed carbon in hydrolyzed lignin is four times lower than in coke powder. Content of total carbon is not at a comparable level. The details of chemical composition given above and their effect on the energy potential have been confirmed by the measured calorific values. Substitute fuels constitute, based on their analysis, a different type of fuel than coke powder, which is reflected in changed sintering conditions as well. Differences in calorific value, content and type of combustible substances, content and composition of ash or physical nature can cause changes in the mineralogical composition.
of agglomerates leading to changes in total quality parameters. Content of ash and its chemical composition in the compared fuels are documented in Table 4.

### Table 4. Chemical composition (wt%) of ash samples as determined by X-ray fluorescence (XRF) spectrometry.

| Sample      | Content of Ash (%) | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | P$_2$O$_5$ | CaO | MgO | K$_2$O | Na$_2$O |
|-------------|---------------------|---------|-------------|-------------|------------|-----|-----|--------|--------|
| 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   |

According to the chemical analysis of ash in compared fuels, it is apparent they have an identical chemical basis, yet there are differences in the content of individual constituents. The basic component of ash in both fuels is SiO$_2$, while P$_2$ (mass ratio of CaO/SiO$_2$) of lignin corresponds to the value of 0.21 and P$_2$ of coke is 0.09. Lignin is characterized by a higher content of SiO$_2$ and CaO and a lower content of Al$_2$O$_3$ and Fe$_2$O$_3$. Based on chemical composition analysis, elements present in ash in these fuels can be essentially divided into two groups: group of elements facilitating the formation of melt (Fe, K and Na) and group of dominant elements (Si, Al, Ca). The ratio of oxides of dominant elements SiO$_2$/Al$_2$O$_3$ in the ash of lignin is 7.91 and its value in the ash of coke is 1.66. The sum of alkaline bases in the ash of lignin is 3.37 and its value in the ash of coke powder is 3.86%, which indicates a minor difference. It is presumed that changes in the composition of ash in both fuels will affect the creation and formation of the bonding phase.

The calculated chemical composition of agglomeration mixture for the initial basicity is documented in Table 5. Based on calculated chemical composition, agglomerates were prepared with 0, 20, 50% and 86% substitution of coke breeze with biomass.

### Table 5. Chemical composition (wt%) of sinter mixtures.

| Sinter Mixture | Fe  | CaO | MgO | Al$_2$O$_3$ | SiO$_2$ | K$_2$O | MnO | S   | Basicity |
|----------------|-----|-----|-----|-------------|---------|--------|-----|-----|----------|
| Z0 (0%)        | 49.76| 10.48| 1.41| 0.74        | 6.39    | 2.35   | 0.025| 0.069| 1.67     |
| Z1 (20%)       | 48.21| 11.19| 1.42| 0.74        | 6.12    | 2.35   | 0.030| 0.060| 1.84     |
| Z2 (50%)       | 48.53| 10.70| 1.30| 0.85        | 6.01    | 0.23   | 0.045| 0.057| 1.75     |
| Z3 (86%)       | 49.60| 9.24 | 1.89| 0.65        | 5.64    | 0.25   | 0.047| 0.052| 1.68     |

The chemical composition of standard agglomerate (A0—0% lignin) and agglomerate with alternative fuel (A1—0%, A2—50%, A3—86% lignin)—biomass—is documented in Table 6.

### Table 6. Chemical composition (wt%) of agglomerate.

| Agglomerate | Fe  | CaO | MgO | Al$_2$O$_3$ | SiO$_2$ | K$_2$O | MnO | S   | C       | Basicity |
|-------------|-----|-----|-----|-------------|---------|--------|-----|-----|---------|----------|
| A0 a        | 54.24| 9.50| 11.72| 1.89        | 0.89    | 7.23   | 0.039| 0.030| 0.023   | 0.188    | 1.68     |
| A1 b        | 53.53| 7.63| 12.62| 1.70        | 0.98    | 6.70   | 0.043| 0.076| 0.029   | 0.117    | 1.86     |
| A2 c        | 54.48| 9.64| 12.33| 1.90        | 0.87    | 7.12   | 0.046| 0.041| 0.064   | 0.088    | 1.78     |
| A3 d        | 54.07| 7.91| 13.05| 1.96        | 1.29    | 7.414  | 0.045| 0.047| 0.019   | 0.117    | 1.73     |

A higher content of residual carbon was determined in the standard agglomerate compared to the agglomerates with biomass, which is related to the conditions of fuel combustion in the sintered layer. It is apparent based on thermal decomposition that alternative fuels burn out faster than coke powder, which is linked to their structure. Alternative fuels are characterized by higher porosity, and thus also by higher reactivity, than coke breeze.
3.1. Structural Analysis of Agglomerates

The macrostructure of representative samples of agglomerate prepared with various substitution levels of applied fuel (0, 20, 50, 86) is shown in Figure 1 and their microstructure in Figure 2.

**Figure 1.** Macrostructure of agglomerate produced using coke + lignin. (a) Coke; (b) coke + 20% lignin; (c) coke + 50% lignin; (d) coke + 86% lignin.

**Figure 2.** Microstructure of agglomerate produced using coke + lignin. (a) Coke; (b) coke + 20% lignin; (c) coke + 50% lignin; (d) coke + 86% lignin. M—magnetite; H—hematite; SFCA—silicoferrites of calcium and aluminum, SiCa—larnite.
3.1.1. Standard Agglomerate (a)

Following the visual assessment of acquired agglomerates, it can be stated that the standard agglomerate without the addition of lignin (Figure 1a) seems compact. Grains in the metal-bearing part are connected by the melt phase and the compact shape of sinter indicates a sufficient amount of formed melt phase. With regard to the porosity, the agglomerate is characterized predominantly by large pores or cavities.

It is apparent based on optical microscopy (Figure 2) that the structure of agglomerate without the addition of lignin is more coarse-grained and heterogeneous, comprising areas of unreacted ore grains and an area characterized by hematite and magnetite precipitating from the melt. In the upper section of the photo documentation on the right, there is a melt area with hematite, SFCA and silicates as dominant minerals. Hematite can be found as primary (original mineral) and secondary or recrystallized—formed by oxidation of magnetite crystals in the liquid phase or by oxidation of magnetite in the solid phase.

3.1.2. Substituted Agglomerates (b, c, d)

The visual assessment of agglomerate with 20% substitution of lignin (Figure 1b) is different compared to the standard agglomerate. The agglomerate has a more fine-grained, heterogeneously porous structure. Larger pores and even cavities are visible, but small pores can be seen as well. Isolated areas of sintered ore grains can be found in the structure of the agglomerate. The cause of ore grain sintering is their melting accompanied by the formation of a smaller amount of liquid phase (melt) compared to the standard agglomerate. A small number of areas with grains of the original charge were observed. The predominant part of the agglomerate is characterized by the transition of sintered grains to the plastic state, i.e., to the area of softening. The mutual binding of grains is improved by the application of higher temperature; that is by the formation of a larger quantity of melt and extension of the contact surface of grains as a result of pressure deformation caused by sucked gas. The amount of liquid phase and its properties after the solidification and also after the recrystallization, as the case may be, will have a substantial effect on the change in the mineralogical composition of the agglomerate.

It can be stated, based on the results of optical microscopy (Figure 2b), that the structure of agglomerate is homogeneous, made up of fine-grained aggregates connected by the melt phase with relatively evenly distributed pores. The structure of agglomerate consists of several mineral phases, while the major ones are hematite and fine-grained magnetite, silicoferrites of calcium and aluminum (SFCA), dicalcium silicate and the glassy phase as in the case of the standard agglomerate. These phases are complexly distributed together with pores.

Compared to the previous agglomerate, the agglomerate with 50% substitution of coke (Figure 1c) also has a fine-grained structure, but it is more porous, characterized by both larger and smaller pores, which is related to the level of substitution with biomass and the kinetics of combustion. Pores are formed in places where the fuel has burned out and their diameters vary during melting of adjacent grains when edges become rounded and small cavities are enlarged due to the increase of surface tension. The dimension of the resulting pores depends on the size of fuel grains.

The amount of the formed binding melt phase, assessed on the basis of macroanalysis, is smaller compared to the previous agglomerate. Grains of the original ore, grains coated with a film of the melt phase or grains partially modified in the sintering process are visible in the photo documentation.

The microstructure of the agglomerate (Figure 2c) is more heterogeneous compared to the previous agglomerate. Areas with larger pores were observed in the image. Grains of hematite and magnetite are located in the matrix of glassy silicates and silicoferrites of calcium and aluminum (SFCA). Magnetite is the prevailing oxide mineral. The sintered ore grains are connected without a significant change in their shape, which is an accompanying sign of the formation of a smaller quantity of melt phase owing to the decrease in temperature in the sintered layer. The needle-like formations of dicalcium silicate are well visible in the image.
The agglomerate with 86% substitution of coke has a different morphologic nature of macrostructure (Figure 1d) compared to the previous agglomerates. The original ore grains coated with a fine film of the melt phase prevail in the structure of agglomerate. This nature of the agglomerate suggests the formation of a very low quantity of melt phase as a result of the insufficient temperature between the grains of the charge. The amount of heat released by combustion of fuel and the amount of accumulated heat in the sintered layer could not provide the sufficient thermal conditions for the formation of an optimal quantity of the melt phase. Reactions between solid phases immediately affecting the formation of the melt phase play an important role in the formation of the agglomeration melt. At a low temperature, only a part of the charge melts and a large portion of products of reactions in the solid state pass unchanged to the structure of the final agglomerate.

The structure of agglomerate comprises the primary and secondary grains of hematite, magnetite and probably also the silicate represented mainly by larnite. The predominant part of the secondary magnetite was formed by the reduction of the primary hematite, which is the basic ferriferous component of the initial metal-bearing charge. The grains of magnetite are characterized by irregular shapes corresponding to polyhedrons with sharp edges.

The mineralogical composition of agglomerates with different substitution levels of the applied fuel was identified using the X-ray analysis. The quantification of mineralogical composition using the Rietveld method was carried out by the powder diffraction technique. The mineralogical compositions of various produced agglomerates are given in Table 7. These results show how the use of a substitute fuel affected the amount of different minerals in the agglomerate.

Table 7. Mineralogical composition of agglomerate.

| Identified Mineralogical Composition | A0     | A1     | A2     | A3     |
|-------------------------------------|--------|--------|--------|--------|
| Chemical Formula                    | Mineralogical Name | Content (wt%) |
| Fe₃O₄                               | Magnetite          | 35.3 35.0 23.0 41.2 |
| Fe₂O₃                               | Hematite           | 25.2 18.8 17.9 29.5 |
| Ca₃.18Fe₇Al₁₄.66O₂₈                 | SFCA-I             | 15.5 18.1 25.5 - |
| Ca₂.45Fe₉O₁₁Al₁₇.₄Fe₁₆Si₀₆O₂₀       | SFCA              | 10.0 11.7 14.3 - |
| Ca₂SiO₄                             | Larnite            | 4.0 4.9 5.1 18.9 |
| Ca₃(AlFe)₃O₅                        | Brownmillerite     | 1.5 2.1 3.3 - |
| Ca₅Fe₅O₁₇                           | Hedenbergite       | 6.1 7.1 9.3 - |
| SiO₂                                | Quartz             | 3.4 2.3 1.6 3.9 |
| Ca₂Fe₁₀O₂₅                           | -                  | - - - 4.1 |
| FeO                                 | Wüstite            | - - - 2.5 |

The share of substitute fuel and the formation of mineralogical compounds of the agglomerate in the course of the sintering process are shown in Figure 3. These minerals are represented by complex calcium ferrites in association with iron oxides and a limited amount of silicates. Quartz and wüstite are present in small quantity.

It is clear from the X-ray analysis that there was no change in the mineralogical composition, i.e., no formation of new minerals, at 20% and 50% substitution of coke breeze with biomass. There was a substantial change in the share of individual minerals, as it is shown in Figure 3. At 20% and 50% substitution, there was a decrease in the majority oxide (magnetite, hematite) and increase in the bonding phases represented by silicoferrites (SFCA-I and SFCA) and silicates (larnite, hedenbergite). The share of non-assimilated SiO₂ (quartz) drops slightly compared to the standard agglomerate. At 86% substitution, the share of SiO₂ rose by 2.3%. It may indicate a lower rate of agglomeration ore assimilation, which is the main carrier of SiO₂ in the sintering charge.
The presence of wüstite was not confirmed in other agglomerates. The increased content of hematite and magnetite in the agglomerate at 86% substitution was related to the value of 41.2%, which corresponds to the increase by 5.9 against the standard.

As the partial substitution of coke with biomass occurred at low temperature. This could be the cause of the higher amount of FeO in the agglomerate with the highest (86%) substitution, i.e., increase in magnetite and thus in hematite as well.

On the basis of the above, it can be stated that as the partial substitution of coke with biomass of 20% and 50% increased, the amount of both oxide decreased. On the contrary, a considerably opposite trend was observed at 86% substitution, i.e., increase in magnetite and thus in hematite as well. The increased content of hematite and magnetite in the agglomerate at 86% substitution was related to the presence of the original grains of sintering ore and concentrate, in which no mineralogical change occurred at low temperature.

Silicoferrites of calcium and aluminum are the key bonding phase in agglomerates on which the overall quality of agglomerate depends. In the standard agglomerate, there are both forms of complex silicoferrites SFCA-I and SFCA, while the higher values are achieved by the high iron modification of SFCA-I. As the substitution increases up to 50%, both forms of SFCA are growing, while the high iron form SFCA-I dominates just like in the case of the standard agglomerate. Neither of the forms of silicoferrites of calcium and aluminum was identified in the agglomerate by increasing the substitution to the value of 86%. By contrast, the share of the silicate Ca₉SiO₄ rose sharply. While its value was growing slightly and rose by 1.1% against the standard agglomerate at the substitution of up to 50%, a step change and an increase by 14.9% is observed at 86% substitution.

A new phase—wüstite (FeO)—was identified in the agglomerate with 86% substitution. The presence of wüstite was not confirmed in other agglomerates. The effect of FeO on the formation of ferrites is negative because it stabilizes magnetite and Fe₂O₃, which is bound in it [4]. Due to the higher reactivity of lignin, the vertical sintering rate increased, which resulted in shortening of the total sintering time and thus shortening of the time during which potential oxidation of FeO could occur. This could be the cause of the higher amount of FeO in the agglomerate with the highest (86%) substitution of coke with lignin, when the lowest temperatures were reached in the sintered layer.
Silicoferrites of calcium and aluminum, which function as the bonding phase in the structure of agglomerate, are characterized by good strength and reducibility. Their absence at 86% substitution and the presence of larnite result in reduced strength and possibly also decreased reducibility of the agglomerate. Crumbly, disintegrating agglomerate is the outcome of the above.

In most cases, the identified silicate bonding phase constitutes an undesired phase. However, it is an accompanying phase in the production of all basic agglomerates. The silicate, which is in most cases represented as larnite (2CaO.SiO$_2$) or hedenbergite, does not ensure sufficient strength and formation of quality agglomerate.

Webster et al. [5] examined the formation of complex silicoferrites and observed the formation of SFCA and SFCA-I from chemically pure reagents Fe$_2$O$_3$, SiO$_2$, CaCO$_3$ and Al(OH)$_3$ in a slightly reducing atmosphere of pO$_2 = 10^{-3}$ atm. The course of calcium ferrite formation from the reactions in the solid state to the formation of the melt is the outcome of this study, which is illustrated in Figure 4.

![Figure 4. Course of calcium ferrite formation in agglomerate reproduced from [5], with permission from Webster, 2013.](image)

It is apparent from the said dependence that thermal conditions play an important role in the sintered layer. The issue of creation and formation of complex silicoferrites has been addressed by a number of research papers [6–14].

Fuel plays a crucial role in the assurance of thermal conditions in the sintered layer, while each fuel has its specific properties and is a carrier of a varying number of components for the sintering mixture. The above applies particularly when the substitution of coke breeze is performed according to the energy value. The preservation of the energy value of a fuel mixture is directly related to the amount of fixed carbon in fuels. As it follows from Table 2, the substitute fuel has four times lower content of fixed carbon and incomparably higher content of volatile combustible. The volatile combustible reduces the calorific value of fuel and shifts its ignition temperature to lower values. The mixture of fuels with two ignition temperatures expands the combustion zone and decreases the maximum reached temperature.

The maximum temperatures and sintering time with the substitution of coke with biomass documented in Table 8 confirm this fact.

| Agglomerate | Biomass % | T1 Max °C | T2 Max °C | T3 Max °C | T4 Max °C | Time h |
|-------------|-----------|------------|------------|------------|------------|--------|
| A0          | 0         | 1293       | 1380       | 1369       | 525        | 0:20:50|
| A1          | 20        | 1100       | 1218       | 1320       | 661        | 0:19:59|
| A2          | 50        | 997        | 1103       | 1190       | 508        | 0:15:27|
| A3          | 86        | 1074       | 1062       | 877        | 569        | 0:12:03|

Table 8. Reached temperatures and sintering times.
The obtained results of temperature curves along the height of the sintered layer match the previous research on the creation and formation of the ferritic phases in the structure of agglomerate.

The formation of agglomerate with satisfactory strength properties is conditioned by the accomplishment of such thermal conditions in the sintered layer that would provide the complete melting of charge in one part of microvolumes, the partial melting of charge in another part of microvolumes and the preservation of the solid state in other microvolumes. The rate of melt formation, the amount of melt, the chemical and mineralogical composition and the method of agglomerate cooling determine the final properties of the agglomerate, including its strength. With a small amount of sintering melt in the sintered layer, a low-strength diffusion bond is formed, and the agglomerate has a low strength. This was reflected in the agglomerate with 86% substitution of coke with lignin. The resulting strength is also influenced by the mineralogical composition of the agglomerate, in which hematite and magnetite have the highest strength in the final structure of the agglomerate, followed by calcium ferrites and SFCA complex compounds. On the contrary, dicalcium silicate (\( \text{Ca}_2\text{SiO}_4 \)) has the lowest strength. The SFCA complex compounds generally form a bonding phase in the agglomerate.

The effect of coke powder substitution with lignin on the strength properties of the agglomerate shows certain differences. In a series of sinterings with lignin, the agglomerate showed a lower abrasion compared to the standard at up to 50% substitution of coke, which was also reflected in an increase in the strength of the agglomerate. These agglomerates had an ISO\(_{+6.3}\) strength in the range of 63–65% and an ISO\(_{-0.5}\) abrasion index in the range of 6–7%. A further increase in the substitution coefficient has already had a negative impact on the strength properties. At 86% substitution, the ISO\(_{+6.3}\) strength of 55% and the ISO\(_{-0.5}\) abrasion index of 10% were achieved. Industrially produced agglomerates have the ISO\(_{+6.3}\) strengths in the range of 65–78% and the ISO\(_{-0.5}\) abrasion index of 4–9% [15], which also corresponds to laboratory-produced agglomerates with the substitution of coke with lignin up to 50%. The proportion of silicoferrites of calcium and aluminum (SFCA) increased in the resulting structure of agglomerates produced with up to 50% substitution of coke with lignin, which could have a positive effect on the final strength of these agglomerates, as these compounds formed an appropriate bonding phase between iron oxides, calcium ferrites and calcium silicates.

The properties of produced agglomerate are determined by the requirements of blast furnace technology and consequently its production technology. Chemical, physical, mechanical and metallurgical properties constitute the essential requirements for the blast furnace agglomerate. The reducibility is very important for estimate agglomerate suitability to blast furnace process. The reducibility of agglomerates produced using lignin was realized in high-temperature reducibility test. The test sample is reduced isothermally at 950 °C using a reducing gas (CO and N\(_2\)) and in certain time intervals, its weight is determined until the degree of reduction reaches 65%. The reducibility index is expressed as a rate of reduction, i.e., the time needed to achieve the 60% degree of reduction. The reducibility index (dR/dt) of standard agglomerate was 1.08%/min. The agglomerates with substitution of coke powder by lignin reached the higher values of reducibility (dR/dt = 1.12–1.25%/min). From the point of view of the metallurgical properties of the agglomerate, we can evaluate the replacement of coke with lignin positively.

Increasing volume of coke substitution with biomass results in the decrease of maximum temperatures in the sintered layer and shortening of the sintering time. This is indicated by the faster progress of the combustion zone in the sintered layer due to the higher reactivity of biomass.

It follows from the above that the heat generated by the mixed fuel at 86% substitution does not suffice for the formation of the silicoferrite phase, which has probably caused the deficit of SFCA-I and SFCA phases in the structure of agglomerate.

The agglomerate always contains desired and suitable phases and, conversely, undesired and unsuitable phases. Redistribution of quantity between the appropriate phases (e.g., decreasing the proportion of iron oxides and increasing the proportion of SFCA and calcium ferrites) does not significantly decrease the quality of the agglomerate—which was also achieved at 20–50% substitution.
of coke with lignin. In addition, these agglomerates had standard chemical, physical and mechanical properties and lower emissions of nitrogen and sulfur oxides were achieved in the production.

4. Conclusions

This study studied the impact of substituting coke with biomass on the mineralogical composition of the agglomerate. The samples of agglomerates were prepared using 20, 50% and 86% substitution of coke breeze with biomass (hydrolyzed lignin). It is clear from the results of the X-ray analysis that the mineralogical composition of agglomerates with 20% and 50% substitution did not change, i.e., no new minerals were identified compared to the standard agglomerate. The share of individual minerals changed significantly. There was a decrease in the share of majority minerals (magnetite, hematite) and an increase in the minerals represented by silicoferrites (SFCA-1 and SFCA) and silicates (larnite, hedenbergite) against the standard agglomerate. As the substitution increases up to 50%, both forms of SFCA are growing, while the high iron form SFCA-1 dominates just like in the case of the standard agglomerate. Both forms of complex silicoferrites are characterized by good strength and reducibility. They function as the bonding phase in the structure of agglomerate; hence, their presence in the agglomerate is desirable.

There was a considerable change in the mineralogical composition when 86% of coke breeze was substituted with biomass.

The deficit of complex silicoferrites SFCA-1 and SFCA and the considerable increase in the silicate $Ca_2SiO_4$ were the fundamental changes identified based on the mineralogical composition at 86% substitution.

The absence of the formation of silicoferrites of calcium and aluminum can be attributed to the thermal conditions in the sintered layer. At 86% substitution, the heat generated by the mixed fuel probably no longer sufficed for their formation.

In the process of agglomerate cooling, the identified majority silicate bonding phase $Ca_2SiO_4$ in the agglomerate with 86% substitution is accompanied with volume changes causing internal stress and reduction of strength in the structure of the agglomerate due to the polymorphic transformation. The agglomerate is characterized by the reduction of strength–it crumbles and disintegrates.

It can be stated based on the results of the study aimed at the impact of substituting coke breeze with biomass (hydrolyzed lignin) on the mineralogical composition of the agglomerate that: it is possible to substitute about 50% of coke with lignin in the agglomeration; agglomerates with minimal variations in the chemical and mineralogical composition were produced at up to 50% coke substitution using lignin; lignin is one of the most suitable substitutes for coke breeze in the sintering process.

Author Contributions: M.F., J.L., R.F. and M.D. performed the experimental analysis; M.F. carried out the investigation, conceptualization, preparation of the original draft, review and editing; J.L. evaluated the results and performed the formal analysis; R.F. carried out the investigation and validation; M.D. performed the visualization and the project administration. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Slovak Research and Development Agency (SRDA), Slovak Republic, number APVV–16-0513.

Conflicts of Interest: The authors declare no conflict of interest.

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