

MINERAL PHASES IN IRON ORE SINTERS PRODUCED WITH OAK SAWDUST SUBSTITUTE FUEL

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Abstract

In this paper, the effect of oak sawdust – a cheap substitute fuel on the quality of sinter in terms of its phase composition is evaluated. The samples of sinters prepared with 5, 9, and 13% equivalent fixed carbon substitution of coke breeze by oak sawdust were analyzed by light microscopy, SEM-EDS and powder XRD analysis. The microstructure of sinters in places with fuel residues consisted of well-integrated secondary mineral phases, confirming good conditions for sintering. The phase analysis has shown a predominance of low-Fe SFCA modification over the high-Fe SFCA-I and the increasing trend in the ratio of magnetite with an increasing degree of fuel substitution up to 8%. As a conclusion, the sinters made with a partial replacement of fuel are in terms of the total phase composition comparable to sinter fueled with coke only and therefore qualitatively satisfactory for blast furnace process.

Keywords: Biomass; Oak sawdust; Mineral phases; SFCA; Iron ore sinter

1. Introduction

Iron ore sinters used as metalliferous feed for blast furnace pig iron production, consist of a set of mineral phases, which determine their properties. Sinters are formed by partial melting of fine-grained components of raw sinter mixture – sintering iron ore, ore concentrate, limestone, dolomite and return sinter. The heat required for this process is provided by ground fuel evenly blended in micropellets delivered to sintering grate. Thus, most of today sinters bring into the blast furnace besides iron also basic substances for basicity adjustment. This is reflected in the phase composition: the main iron oxides are bound with bonding phase consisting of calcium ferrites and calcium silicates. Minerals that did not crystallize remain the part of a very small proportion of glass.

In the recent years, the research of calcium ferrites increased rapidly. It has been found, that the most of calcium ferrites appearing in iron ore sinters are complex in composition. For these, a term silico-ferrite of calcium and aluminum was adopted with the acronym SFCA. In this study, these ferrites are denoted as aluminosilicoferrites of calcium, because the previously mentioned name does not correspond to the real structure [1]. However, the use of acronym SFCA and SFCA-I, respectively, remained for easy comparison with other researches.

The role of metallurgical companies, in addition to the production of quality steel is also reduction of greenhouse gases emissions into the atmosphere. An application of alternative fuels with neutral carbon balance in metallurgical processes is one of the ways to accomplish this objective.

Most of attention in the field of alternative fuels is dedicated to the blast furnace, which is the largest consumer of coke in ironworks [2,3]. Another technological hub, where the application of substitute fuels can be considered is the sinter plant. The requirements for iron ores sintering fuel are incomparably lower than those for the blast furnace, which is a great advantage allowing us to operate with a wider range of alternatives.

The research of plant biomass fuels used in sintering charge conducted worldwide has gradually identified the most appropriate species usable for this purpose. Among the most important criteria for assessing the feasibility of a particular fuel, besides the environmental aspect, belongs mainly the strength of produced sinter. Several authors concluded that the most appropriate for iron ore sintering is thermally treated biomass – carbonized wood material, i.e. charcoal [4]. Charcoal, a carbon neutral fuel, which is much lower in sulfur and nitrogen than coke, produces less SO_x and NO_x after burning and improves the sintering speed by its high reactivity [5]. On the other hand, strength of sinters made with

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partial substitution of coke breeze by charcoal evaluated by tumbler index decreases as the alternative fuel ratio increases; therefore, the fuel substitution ratio is limited, mostly to 40% on the mass or fixed carbon basis [6-8]. The use of biomass in raw state has been proven disadvantageous due to the high moisture content and low calorific value [9, 10]. The result of sintering trials with raw biomass as an only blended fuel was poorly sintered sinter or unsintered mixture [11]. As a conclusion, biomass substitute fuel should not be blended alone, but always in a mixture with coke. Besides the technical characteristics of alternative fuels, the most important factor is the price of such fuels. Preparation of carbonized biomass is energetically demanding and therefore costly [12]. Despite the discouraging experiences of several authors with the use of non-pyrolised biomass for the production of sinter, there were also successful experiments of iron ore sintering with this type of fuel, listed below, all based on the equivalent calorific heat input. Nut shells representing fruit biomass, which is an available source of biomass in some countries, has been previously tested for the purpose of sintering [13]. Besides sinters made using walnut shells, whose phase composition was analyzed in the previous work [14], there have been also carried out sintering trials with a waste product from wood processing – sawdust. During replacement of coke by oak wood sawdust were obtained sinters with minimum or acceptable strength worsening, if the substitution of coke was below 20% [15]. Similar testing of biomass blended into the sinter mixture showed almost unchanged tumbler and abrasion indexes, when the replacement with corn, crushed bark and wood sawdust was up to 20% [16].

The aim of this paper is to investigate the phase composition of the sinters produced with a partial substitution of coke by oak sawdust from previous study [15], which proved to be of satisfactory quality. In contrast to mentioned studies, the substitution was based on the total fixed carbon input, as proposed Cheng et al. [4].

2. Materials and method

2.1 Raw materials

Input raw materials used for the sintering were standard raw materials from metallurgical works in Slovakia. The chemical composition of ores, fluxes and fuels is shown in the Table 1.

The nature of the fine-grained ore concentrate is strongly magnetite-based according to FeO and Fe₂O₃ ratio as shown in Table 1. After microscopic examinations published earlier [17] the main gangue minerals, besides major quartz, are the members of clinopyroxene group – aegirine–augite series with the general formula (Ca,Na)(Fe³⁺,Mg,Fe²⁺)Si₂O₆.

Table 1. Chemical composition of raw materials (dry basis) / wt%

	Magnetite concentrate	Hematite ore	Dolomite	Lime stone	Coke	Oak sawdust
Fe _{tot}	67.91	56.19	-	-	2.76	0.05
FeO	28.45	0.72	-	-	-	-
Fe ₂ O ₃	65.57	79.55	-	-	3.94	0.07
SiO ₂	4.92	17.2	2.37	1.35	5.03	0.62
CaO	0.21	0.1	30.28	49.63	0.99	0.36
MgO	0.34	0.27	19.96	4.44	0.41	0.04
Al ₂ O ₃	0.18	0.59	1.16	0.89	3.06	0.1
K ₂ O	-	-	-	-	0.23	0.14
LOI*	NA	NA	46.23	43.69	85.5	98.5

* – loss on ignition; NA – not analyzed

Hematite sintering ore used in this study is a mechanical mixture of Fe₂O₃–SiO₂ [17]. This is confirmed by the paper from Mašlejová et al. [18] evaluating ores from the same source, where the quartz contents measured with XRD varied between 13.5–30.4wt%.

As a substitute fuel was chosen sawdust from oak *Quercus petraea/robur*. This is a tree which is found not only in Slovakia but also in many European countries and its wood is widely industrially processed, which makes oak sawdust available source of waste biomass.

Sawdust analysis is presented in Table 2. On the basis of the determined humidity, studied fuel can be considered a dried state; it is therefore not a raw biomass, with moisture content around 50wt% and higher [19]. The main component of oak sawdust is volatile matter, which lowers the ignition temperature of the fuel. In the volatile combustible hydrogen is concentrated, which is gradually released during combustion. The carbon content in sawdust combustible is significantly lower than that of coke. This fact is due to high content of oxygen. Even though oxygen content was not analyzed, its proportion can be well estimated by the representation of other components in fuel. The bulk biomass thus contains over 40wt% of oxygen, which corresponds to similar types of plant biomass [19]. In contrast, the proportion of oxygen in the organic substance of coking coal is minimal and therefore it cannot be expected in combustible matter of coke. An important aspect in terms of ecology are lower proportions of sulfur and nitrogen, which by burning substitute fuel, reduce the total amount of sulfur and nitrogen oxides in flue gas. There is 10 times less remaining ash from sawdust than from coke and calorific value of sawdust is about 10 MJ lower than that of coke breeze.



Table 2. Proximate and ultimate analysis of used fuels

	Unit	Coke breeze	Oak sawdust
Proximate analysis			
Moisture	W ^a / wt%	0.8	4.1
Fixed carbon	FC ^d / wt%	82.51	16.35
Volatile matter	V ^d / wt%	3	82.1
Ash	A ^d / wt%	14.5	1.5
Calorific value	Q _i ^d / MJ·kg ⁻¹	28.39	18
Ultimate analysis			
Carbon	C ^{daf} / wt%	96.9	50.6
Hydrogen	H ^{daf} / wt%	0.79	5.96
Nitrogen	N ^{daf} / wt%	0.84	0.19
Sulfur	S ^d / wt%	0.59	0.05

2.2 Preparation of sinter mixtures and sintering trials

Studied sinters were produced in a laboratory sintering equipment – pot from the sinter mixture based on hematite ore, magnetite concentrate, limestone, dolomite and coke breeze or oak sawdust as a fuel. The basicity (ratio of $(CaO+MgO)/(SiO_2+Al_2O_3)$, all components in wt%) of the mixture for the preparation of all sinters was at the level of 1.6 to 1.8. Because this paper is strongly specialized on the mineralogical description of sinters, only concise information about the sintering trials will be presented below. Parameters of sintering pot and conditions of production are described in the work of Legemza et al. [20].

There were 2 types of examined sinters: a reference sinter fueled with coke only, and 3 sinters fueled with partial substitution of coke with oak sawdust. The substitution was based on the equivalent fixed carbon ratio, which means, that one fixed carbon unit of coke was substituted by one fixed carbon unit of oak sawdust. For example, when the fuel substitution was at the level of 5%, 95% of the overall sinter mixture fixed carbon was from coke and 5% from oak sawdust. Because the fixed carbon content in oak sawdust is lower than that in coke breeze (16.35wt% and 82.51wt%, respectively), to maintain the approximately constant fixed carbon in sinter mixtures, the total ratio of fuel in the raw sinter mixtures increased as the substitution grade increased, as documented by samples characteristics in Table 3. Furthermore, as shown in Fig. 1, with the fuel substitution increased also the amount of the volatile combustibles in sinter mixture. From the viewpoint of the fuel components, this is the main difference between the reference charge and the samples with

fuel substitution. The ratio of fixed carbon remained approximately constant in all cases (≈ 3 wt%). Despite the oak sawdust is low in ash, the bigger proportions at higher substitution levels compensated the low ash ratios in substitute fuel, therefore, the amount of total fuel ash remained almost the same.

Note that the size of alternative fuel particles remained the same as the coke. From each sinter cake, a representative sample was taken.

Table 3. Characteristics of studied samples

Designation	Base sinter	Sinters with oak sawdust partial fuel substitution		
	A	O5	O9	O13
Fuel in the sinter mixture / wt%	3.4	4.41	4.79	5.81
Coke substitution / % of the fixed carbon content	-	5	9	13

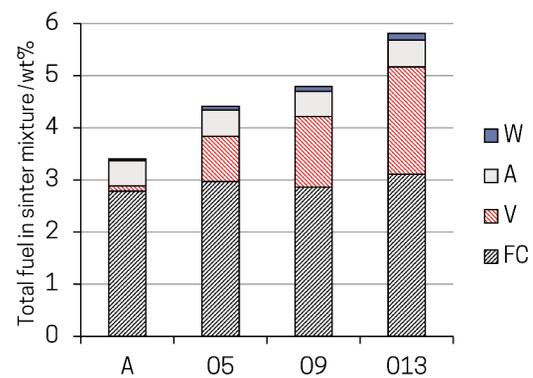


Figure 1. Total amount of the fuel and its components in sinter mixtures (W – moisture, A – ash, V – volatile matter, FC – fixed carbon; all components in analytical state)

At granulation, the mixtures with fuel replacement needed more moisture to achieve acceptable permeability during sintering, so the moisture of sinter mixtures A, O5, O9 and O13 was 7, 8.1, 8.5 and 9wt%, respectively.

At sintering trials, temperature profiles were obtained, as graphically presented in Fig. 2. As can be seen, increased substitution of the coke fuel shifted the beginning of fuel burning towards the shorter sintering times and the total sintering times are reduced the more, the substitution grade increased. This is in good agreement with results published elsewhere [4,5,8]. There are 2 reasons for this phenomenon: 1) the high proportion of volatile matter in oak promotes the earlier ignition of the fuel mixture, and, 2) the reactivity of the oak sawdust is higher than that of the coke. The highest temperature

was reached by the sintering of sample O5, with increased substitution rate the peak temperatures dropped slightly. The lowest peak temperature was reached by the reference sample, which has also an irregular temperature profile. The relationship between temperature characteristics of sintering trials and the mineral phases will be discussed later.

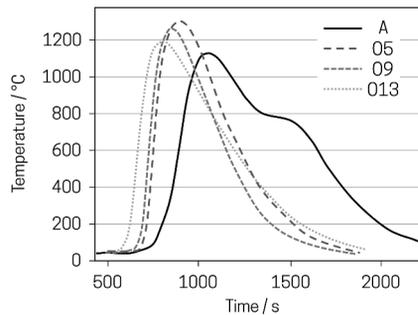


Figure 2. Temperature profiles of sintering trials

2.3 Method

Sinter samples were prepared for microscopic observation by vacuum potting in epoxy resin, grinded and polished. In order to remove the amorphous phase, the etching in hydrochloric and nitric acid solutions has been applied.

For the analysis by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), the conductive layer of Au-Pd mixture was applied to the surface of the samples. These elements were disregarded during the element quantification of the analyzed phases.

To quantify the mineral phases and identify specific modifications of chemical compounds identified using light microscopy (LM) and SEM, powder X-Ray diffraction (XRD) analysis was used. The samples were analyzed by apparatus Seifert XRD 3003 PTS. The parameters of the measurements are shown in Table 4. The diffraction patterns were analyzed using DIFFRAC.EVA (Search-Match) software with the database PDF2 and by program TOPAS that uses the Rietveld method. In contrast to the sinters from previous research [14] this time were used data for aluminosilicoferrites of calcium by the authors Mumme et al., [21] and Hamilton et al., [22], the accuracy of which has been confirmed by research of SFCA-s formation in sinters [23-25].

Table 4. Parameters of XRD measurement

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

3. Microscopic observation

3.1 The microstructure in the vicinity of the fuel grains

Due to different combustion conditions in the sintering bed in horizontal as well as vertical directions and considerably inhomogeneous distribution of material, a part of the final sinters consists of remaining unburned fuel. The examination of such residues is the only option to assess the impact of the fuel grains and minerals contained therein on the local sinter microstructure.

The particles of incompletely burned coke breeze are shown in Fig. 3. The melt in this area did not have the suitable conditions for full crystallization during cooling, as evidenced by the significant amount of amorphous phase enveloping not only the pore walls but also subhedral hematite crystals in the vicinity. The entire area can be defined as two-phased.

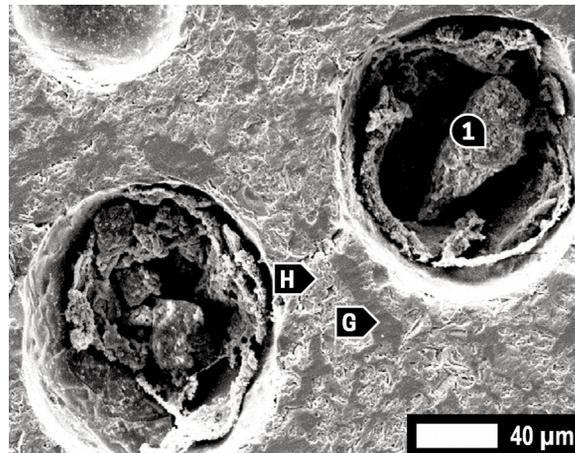


Figure 3. Residues of coke breeze grains in the sinter (SEM); H – hematite, G – glass, 1 – coke particle analyzed in Table 5

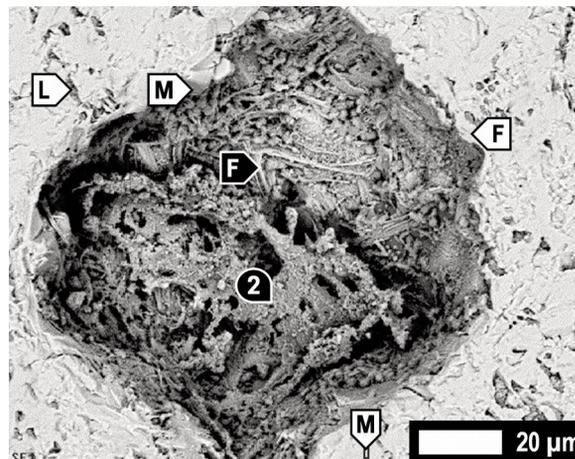


Figure 4. The microstructure of pore with oak sawdust residue (SEM); F – SFCA, M – magnetite, L – larnite 2 – sawdust particle analyzed in Table 5

Similarly, unburned grain of wood sawdust is shown in Fig. 4. In this case the phase composition is richer, as it was possible to identify three mineral phases. Due to the absence of a glass phase, mineral crystals did not have enough space for perfect crystallization and crystal shapes are heavily influenced by the presence of neighboring crystals. The melt in the vicinity of the burning oak sawdust grain was saturated with Fe^{3+} ions, which gave rise to the iron based compounds – SFCA and magnetite. Because of almost the same light reflectance in the light microscope as well as due to the lack of contrast in the picture from SEM it is not possible to visually determine the ratio of the two phases. Separately performed spot EDS analyses showed an increased calcium content in the magnetite grains (up to 8wt%), so this type can be more accurately classified as calciomagnetite. The presence of magnesium cations was not demonstrated. Of course, this applied for the presented microstructure, the ionic substitution in magnetite across the sinter can differ. Several subhedral calciomagnetite crystals can be seen in the upper half of the picture. Morphologically can be identified also SFCA crystals, which grow into the pore space and are also the part of the surrounding matrix. Among SFCA crystals in the pore can be recognized not only magnetite but also the remains of fuel. The third phase, which is less represented, is larnite Ca_2SiO_4 – in the matrix around the pore are its contrasting dark crystals.

The advanced stage of oxidation of the fuel grains causes difficulty in their identification. Although generally, identified coke residues seem to be more compact than those of oak sawdust. In contrast to previous charcoal and nut shells residues observations in the sinter [14], there were not identified any crystalline mineral components that would resemble unassimilated ash, in the pores of the burnt fuel. The fine particles of ash could be carried away by flow of sucked air or react with surrounding melt [26].

3.2 Identification of the type of fuel in the structure of the sinter

The most reliable way of identifying fuel residues is SEM-EDS analysis. It should be noted however, that it could not be used in the same way as in the analysis of inorganic minerals.

While ignoring carbon, other elements were put into the mutual ratios and recalculated to oxides. The obtained chemical composition was thus compared with the composition of ash from external analysis (Table 5). According to that, ash coke is composed of three major components with ratio over 20wt% – SiO_2 , Fe_2O_3 and Al_2O_3 . Analysis of ash from the burnt oak sawdust shows the majority of silicon oxide as well, but there is also a greater amount of CaO and potassium oxide. Quantitative evaluation of the fuel

Table 5. EDS analyses of fuels in Fig. 3, and Fig. 4 and comparison with the ICP-AES / wt%

Component	Coke breeze		Oak sawdust	
	ICP-AES	EDS (Fig. 3)*	ICP-AES	EDS (Fig. 4)*
Fe_2O_3	27.2	10.3	4.48	57
SiO_2	34.7	10	41.06	7.6
CaO	6.8	7.5	23.83	24
MgO	2.8	1.6	2.62	-
Al_2O_3	21.1	70.7	6.69	11.5
MnO	0.12	-	0.82	-
P_2O_5	0.64	-	0.36	-
Na_2O	1.1	-	2.07	-
K_2O	1.6	-	9.33	-

* - recalculation to ash (all iron was regarded as Fe^{3+})

residues by EDS showed the percentages of oxide components widely differing from chemical analysis. Since similar results repeated while analyzing several different grains it can be concluded that, for the determination of chemical composition of ash in the carbonaceous matter, the method could not be applied without distortion.

The main identification feature for determination of the origin of the grains were therefore EDS spectra alone. Each detected element was in both cases characterized by a different intensity in the spectrum. Typical for coke were extremely high intensities for aluminum (Fig. 5). The intensities of other elements are thus less pronounced. This fact has been reflected in the erroneous percentage calculations in Table 5. The spectrum of oak sawdust had also increased intensities of Al, but in contrast to coke, these were always outstripped by intensities of calcium and sometimes silicon. Because calcium made the biggest difference between the two fuels, crucial in the assessment were: the percentage of calcium and ratios of relative intensities Al/Ca. From the above mentioned follows that even though the EDS analyzes were not usable, the graphic differences on the spectra allowed safe identification of fuel residues in the sinter.

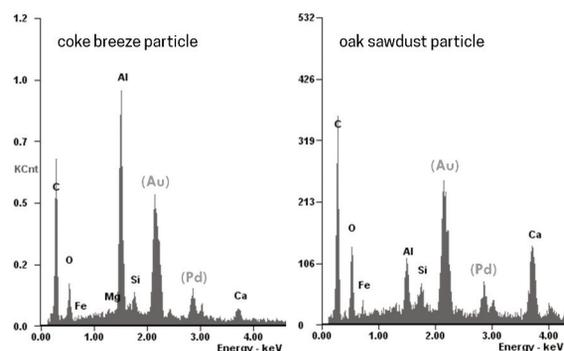


Figure 5. EDS spectra of coke breeze and oak sawdust residues



4. Comparison of the overall phase composition

4.1 Analysis of powder diffractogram

The section of the measured diffraction pattern of all tested sinters is shown in Fig. 6. The selected range for demonstration was from 25 to 55° 2θ, where the diffraction peaks of most stages are best visible.

Since these sinters were produced using the material directly from metallurgical plant, phase composition is relatively rich and produced phases often have the diffraction peaks at the same 2θ positions. For this reason, in the image there are independently only the peaks corresponding to hematite and quartz – 28 and 48, and 31° 2θ, respectively.

Taking into account the diffraction patterns of all sinters; most visible are diffraction peaks of the two most abundant phases – magnetite and hematite. Those produce the highest peaks at the positions of ~ 39 and ~ 41.5° 2θ.

The best identifiable peaks SFCA-I and SFCA are at the positions ~ 32 and 33° 2θ, respectively.

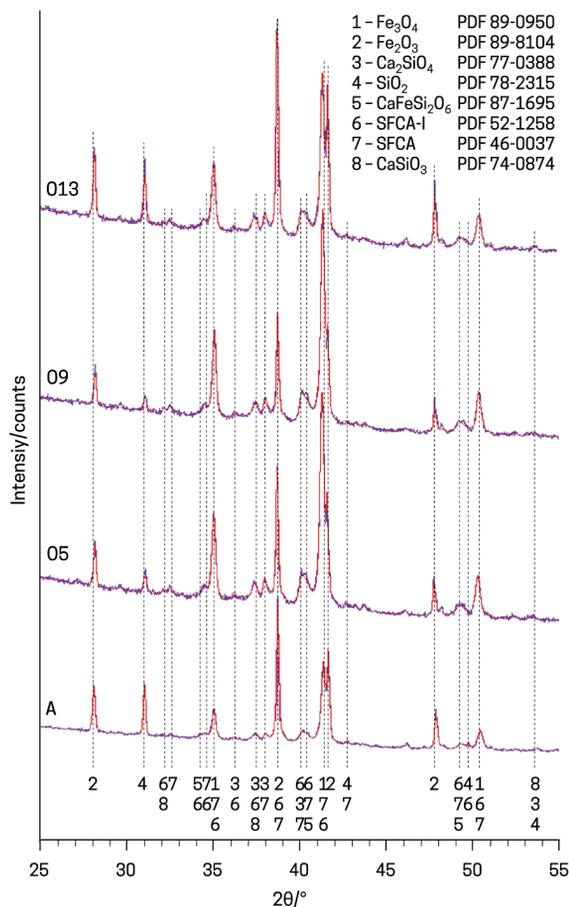


Figure 6. The section and comparison of measured diffraction pattern of all sinters. The blue and the red line indicate the measured and the calculated diffraction pattern, respectively

The least abundant phase identified on the diffraction pattern – pseudowollastonite CaSiO_3 , created a small peak at a position of about 53.5° 2θ, where there is also a hint of quartz, which can be seen in the pattern from the sample A. The more detailed study of this position confirmed pseudowollastonite, which can be seen in the larger diffraction peaks at this position from the samples with the addition of oak sawdust.

The phases, which were confirmed by microscopic observation of sinters but were not identified by diffraction, were dolomite $\text{CaMg}(\text{CO}_3)_2$, monocalcium ferrite CaFe_2O_4 , periclase MgO , and amorphous phase – glass.

Despite the good discernibility of dolomite in the sinter macrostructure (white grains contrasting with the dark matrix of the sinter) this phase represented such a small fraction that in the diffraction pattern did not appear any indications of diffraction peaks at the 2θ positions typical for this compound. The same applies for CaFe_2O_4 and MgO .

Note that srebrodolskite $\text{Ca}_2\text{Fe}_2\text{O}_5$ is not indicated in diffractogram, but its presence, although in small quantities, was confirmed.

Glass is sometimes, in simpler descriptions of the phase composition, included into one group with other silicates, because it is mostly made up of non-crystallized silicates. Glass phase was not identified during the evaluation of diffraction patterns.

Comparing the diffraction pattern of all samples it must be noted that the main difference is in the height of diffraction peaks of individual mineral phases. There are no diffraction peaks indicating the presence of different phases in the sinters. That means that only the proportion of the phases in the samples changed. Pseudowollastonite is an exception but, as mentioned earlier, it did not create any diffraction peak in the sample A.

4.2. The development of phase composition at fuel substitution

The quantification of mineral phases using the Rietveld method is shown in Table 6. By these results it can be seen how the use of substitute fuel affected the presence and a number of phases in the sinter.

Sintering ore was hematite based, with quartz as the main gangue component. Quartz was preserved in the finished sinters in the form of unreacted parts and since being the only one from the identified phases that can be clearly considered the primary phase, it can also be used to express the degree of sintering ore assimilation [14]. Quartz is the most abundant in the reference sinter, in other cases its ratio has decreased and this also means better conditions for the transition into the melt phase, and a participation in the formation of new phases. According to this criterion,

Table 6. The phase composition of sinters by XRD analysis / wt%

Phase	Formula	Space group	A	O5	O9	O13
magnetite	Fe ₃ O ₄	(227) <i>Fd-3m</i>	28.73	34.54	37.25	29.84
hematite	Fe ₂ O ₃	(167) <i>R-3c</i>	36.73	18.55	15.44	30.47
srebrodolskite	Ca ₂ Fe ₂ O ₅	(062) <i>Pnma</i>	-	0.47	0.26	0.24
SFCA-I		(002) <i>P-1</i>	9.65	11.98	11.9	9.15
SFCA		(002) <i>P-1</i>	6.44	17.98	18.43	13.83
larnite	Ca ₂ SiO ₄	(014) <i>P2₁/c</i>	6.25	9.45	9.28	8.49
hedenbergite	CaFeSi ₂ O ₆	(015) <i>C2/c</i>	3.36	3.37	3.59	2.82
pseudowollastonite	CaSiO ₃	(002) <i>P-1</i>	-	0.77	0.82	0.77
quartz	SiO ₂	(152) <i>P3₁21</i>	8.84	2.89	3.04	4.39

the best temperature conditions were achieved during sintering of the sample O5, which is in very good agreement with the temperature profiles in Fig. 2.

Into the ratio of magnetite are also counted magnesium spinels and calciomagnetite or a mixture of both. At XRD analysis, the incidence of these compounds showed as very slight shifts from the ideal diffraction peak for the pure magnetite and therefore they are not included in this table separately. Furthermore, the content of Mg²⁺ or Ca²⁺ in spinels was not constant.

The presence of wüstite in the sinters was not observed even after careful microscopic examinations using etching. This means that FeO is mainly the part of magnetite and to a lesser extent, hedenbergite CaFeSi₂O₆. As an admixture component it is also present in larnite Ca₂SiO₄, and pseudowollastonite CaSiO₃ (in both compounds approximately 5 wt%). Moreover, FeO makes a significant portion of the glass (often about 20 wt%). An increased transition of FeO into silicates because of applied substitute fuel was not observed. Certain small proportions of Fe²⁺ in aluminosilicoferrites of calcium are declared also by Webster et al. [25], but for the purpose of this research the only considered form of iron in the ferrites was Fe³⁺.

The parameter FeO from chemical analysis of the sinter is one of the most used indicators of the quality of the sinter, while a higher proportion of FeO is associated with higher strength. From above-mentioned follows, that most of FeO in examined sinters is fixed in magnetite. If, based on the given facts, we shall consider that the FeO content in the sinter is directly linked to the content of magnetite [27], we can assign the Fe₃O₄ analysis the same significance as FeO.

The main emphasis in terms of mineral phases in the contemporary sinters is given to aluminosilicoferrites of calcium. The ideal binder phase with excellent strength and reducing properties is called high-Fe type SFCA-I [23-25], so its increased ratio in the structure is associated with high quality products. This phase is followed by a low-Fe type SFCA with which it

alternates in the structure.

The development of major mineral phases ratios with increasing degree of fuel substitution is shown in the graph at Fig. 7. In all cases, the initial increase of magnetite and calcium ferrite was observed, the only decline occurred at the largest substitution. The amount of magnetite grows from 0 to 7% of fuel substitution; the 13% substitution sample contained less magnetite, but still more than the reference sample. The proportion of SFCA also has a growing trend up to 8%, the sample O13 contained about twice as much SFCA as sinter produced only with coke. By polynomial trend curves the ratios of Fe₃O₄, SFCA, and SFCA-I phases reach maxima at about 8% substitution.

Using of the knowledge about the effects of these phases on the quality of sinters, it can be inferred from observed trends that the strength of sinters did not deteriorate with the increase of fuel substitution, which can be seen on the increase of Fe₃O₄ and both SFCA phases that act as a binder in the sinter. The prevalence of SFCA over SFCA-I usually means that the temperatures reached in the sintering bed are more favorable for the formation of low-Fe type. From this point of view, the peak temperatures presented in Fig. 2 support such trends in phase ratios, as in Fig. 7. Only the points for 9 % substitution are slightly higher than for 5 %, but it is necessary to take into account

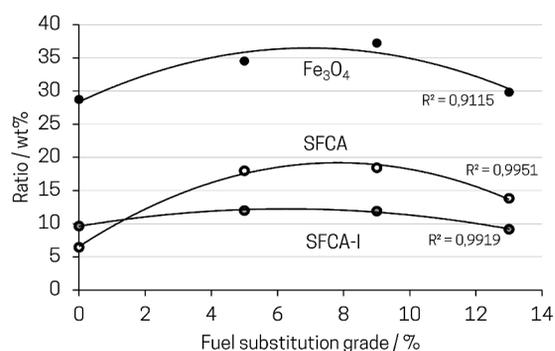


Figure 7. The development of magnetite, SFCA-I, and SFCA ratio in the samples with an increase of fuel substitution



the deviation caused by the complexity of the whole sintering process. Another reason for SFCA prevalence will be discussed below. The temperatures correspond also with the development of magnetite, which as a carrier of FeO has better conditions for formation at higher temperatures. This development could suggest slightly lower reducibility of sinters with alternative fuels; on the other hand, it could be compensated by higher amount of voids and pores remaining after burned biomass, ergo higher reaction surface of sinter [6]. All this applies to the sample O13, where there is a decrease in all three phases – Fe₃O₄, SFCA, and SFCA-I.

5. The properties of mineral phases in the experimental sinters

The composition of aluminosilicoferrites of calcium of low-Fe type identified in the sinters produced with alternative fuels is shown in Table 7. These ferrites are typical for their high content of SiO₂ and significantly lower contents of Al₂O₃, in comparison with the published results. Ferrites prepared from pure materials under simulated sintering conditions in pO₂ = 5 × 10⁻³ atm in work of Webster et al. [23] sintered at temperatures from 1280 to 1185 °C, have an average content of SiO₂ of 4.6wt%, which is substantially less than SFCA in Table 7, as the lowest measured SiO₂ concentration was 9.2wt%. There are extreme differences in Al₂O₃ ratios– 8.6wt% in the mentioned paper, here 2.1wt% at the most.

Table 7. Statistical evaluation of identified SFCA / wt% (16 point analyses)

Component	avg	median	modus	min	max
Fe ₂ O ₃	70.2	70.8	67.1	64.4	74.8
CaO	14.9	14.8	14.7	13	17
SiO ₂	11.9	11.7	11.7	9.2	15.7
Al ₂ O ₃	1.7	1.7	1.8	0.6	2.1
MgO	1.3	0.9	0.8	0	3.5
total	100	99.9	96.1		

The comparison of high-Fe SFCA-I in this study (Table 8) with SFCA-I prepared in pO₂ = 5 × 10⁻³ atm at 1180 °C in work of Webster et al. [24] shows the difference in SiO₂ – 0.19wt% compared to a minimum of 4.9wt% in studied sinters. The SFCA and SFCA-I compositional features will be discussed thereafter. Despite these differences, the diffraction data used in the above-mentioned papers were also successfully used for this research, without observing deviations in the diffraction patterns indicating differences in the structure of the compounds.

Table 8. Statistical evaluation of identified SFCA-I / wt% (4 point analyses)

Component	avg	median	min	max
Fe ₂ O ₃	80	80.5	77.1	81.9
CaO	12.1	12.2	11	12.9
SiO ₂	5.7	5.5	4.9	6.7
Al ₂ O ₃	1	1	0.5	1.5
MgO	1.3	1.5	0	2.3
total	100	100.6		

For a sample O13 were typical microstructure areas with prevalence of low-Fe SFCA ferrites and magnetite. A demonstration of such an area documents the Fig. 8. The picture with lower magnification produced by light microscopy in Fig. 8 a) shows the state after the etching with hydrochloric acid and nitric acid, therefore some phases absent on the image, i.e. the ones completely dissolved. In the hedenbergitic field on the right, there are hints of dicalcium silicate, but most of its crystals were present in the glassy phase, which was almost completely etched off (only local tracks remained). In the picture, there are therefore seen empty dark areas between the crystal phases that have been highlighted. The original porosity can be recognized by the typical spheroidal shape. An example of such pore is visible in the lower left part of the Fig. 8 a). The whole area is mainly composed of magnetite, which is bound together by variously oriented columnar crystals of SFCA. These have the lightest color in the picture. Magnetite, which is usually lighter than calcium ferrites in light microscope, was partially dyed by etching and here appears as a darker phase.

The detail of this area is shown in Fig. 8 b). This image has been produced by SEM, therefore different phases with their shades of gray are not contrasting. At the central fused crystal, the phases can be distinguished by the fineness of the surface created by grinding and polishing of the sample – a massive portion on the left consists of magnetite with a rougher surface on which grows the elongated crystal of low-Fe SFCA. Since such crystals precipitated from the melt in direct contact with magnetite, the glass phase did not primarily fulfill the binding function, it was present more like caulking filler. Also because of this, the etching removed only glass and larnite. On several SFCA crystals, despite the cut, is very well observable subhedral habit that is generally disturbed by anhedral magnetite. Such phase composition corresponds more to reducing conditions, in which hematite does not appear in the final structure [25].

The etching of glass phases also revealed crystal habits of other important compounds in the sinter. A short time period for crystal growth, due to the arrival of cooling zone in partially molten sinter, conserved



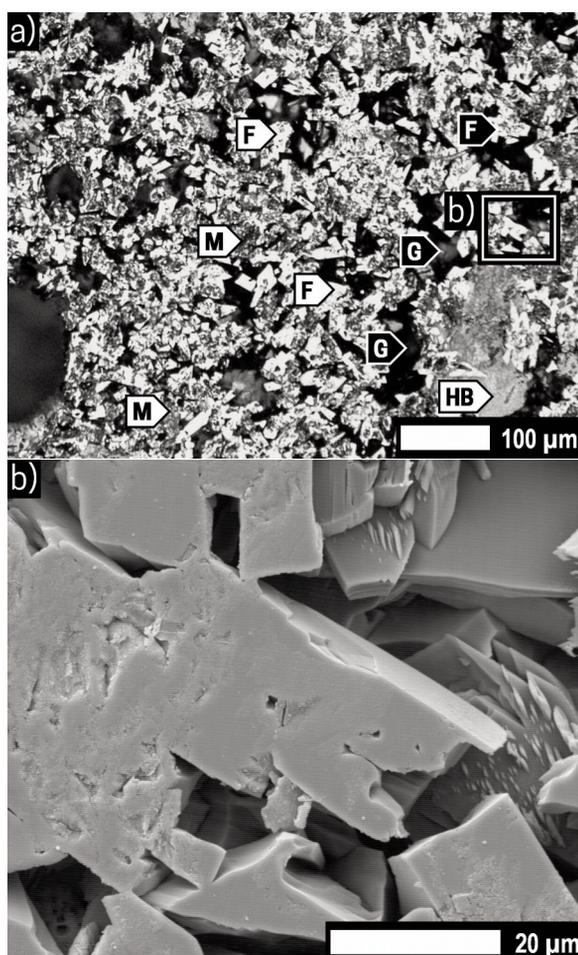


Figure 8. A typical magnetite-ferritic microstructure area in the sinter Ó13 (LM, SEM); M – magnetite, F – SFCA, HB – hedenbergite, G – areas after etching off glass

precipitating crystals in various stages of growth. Because glass solidifies as the last phase, minerals were not restricted in growth and are present in the euhedral shape. The least developed habit is the dendritic one. This state of secondary hematite is captured in the Fig. 9. At the ends of crystals, the transition into the middle stage – skeletal is observable. This shape forms, if the crystal growth is more energetically favorable at the corners, and not in the center [28]. A good example is also a secondary hematite in the Fig. 10.

The imperfectly developed crystals of minerals form only a small fraction in the structure of the sinters made using oak sawdust. Nevertheless, there was observed a slight increase in the incidence of this phenomenon compared with the reference sample. The sintering trials performed with substitute fuel are shorter than those with coke breeze, which means less time available for active formation of mineral phases and, obviously, less time for their crystallization.

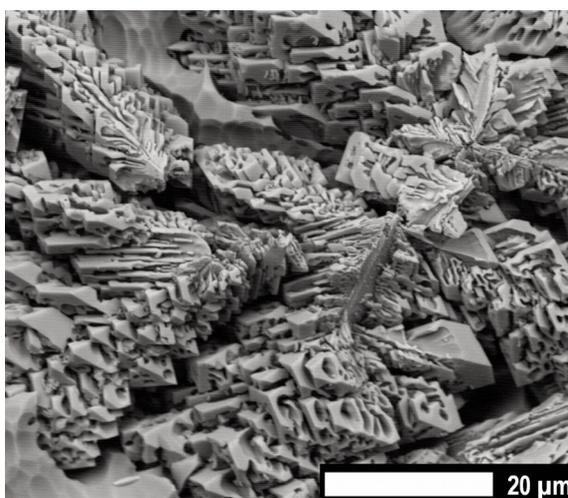


Figure 9. A transition between dendritic and skeletal habits of secondary hematite (SEM)

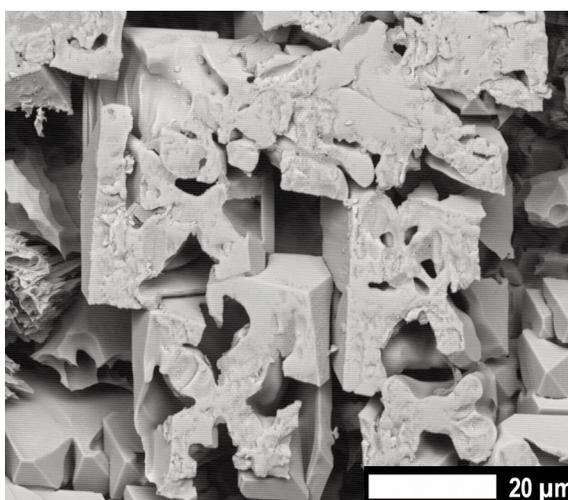


Figure 10. Skeletal secondary hematite crystals after glass phase etching (SEM)

These conditions are suitable for the formation of dendrites and skeletal shapes.

6. Discussion

6.1. Conditions for the mineralization process

Temperature curves obtained by sintering trials showed, that sufficiently high temperatures occur, when fuel replacement has been applied. By substitution based on the equal fixed carbon content, almost the same energy is brought into the sinter mixture, but distributed more uniformly in the bed, contrary to the coke, where the energy is cumulated in 2/3 of mass, compared to sawdust. This can be one of the reasons of the good sintering conditions. On the other hand, this applies only to a certain substitution ratio, definitely not for absolute substitution.

It should be noted, that the temperature profile

corresponding to the reference sample without fuel replacement tends to be imperfect. Besides the lowest peak temperature, an irregularity at cooling is also observable. Usually, the sinters fueled with coke breeze only are sintered at higher temperatures compared to sinters with alternative fuels. Because the complexity of the sintering process and many affecting factors it is not easy to say, what was the exact reason for lower temperatures reached. On the other hand, the produced sinter A consisted of 25.7wt% of secondary phases (when secondary hematite and magnetite are not accounted), so during the sintering the reactions between fine particles and generation of melt went well. In general, all sinters in this study were successfully sintered.

When pyrolyzed biomass was combusted together with coke breeze, different ignition beginnings of both fuels resulted in widening of the flame front, as indicated in [29]. According to Fig. 2, no obvious widening of the flame front was observed, when sawdust was used. Thus, the heat for the mineralization process was concentrated into a relatively short period.

The main difference between conventional sintering fuel and biomass fuel used here, is the volatile matter content. The composition of these combustibles is different from that for coal, as demonstrated by chemical analysis in Table 2. Because of the high oxygen content in biomass fuel, carbon oxides – $\text{CO}_2 \sim 40\text{vol}\%$ and $\text{CO} \sim 25\text{vol}\%$ are primarily formed, followed by hydrogen $\text{H}_2 \sim 20\text{vol}\%$ and methane $\text{CH}_4 \sim 10\text{vol}\%$ [30]. The amount of released hydrogen is directly proportional to the achieved temperature.

Kawaguchi and Hara [11] and Abreu et al. [12] reported, that volatile matter from the biomass fuels released during the sintering was not utilized in the process and left the sinter bed with the exhaust gas. The published results [10, 31] also show an increase of CO in fuel substitution, which in addition to its low involvement in the reduction of oxides points to less efficient combustion of solid fuel.

According to these findings, reducing action of gaseous reductants released from oak sawdust was not very advanced and the majority of these volatiles left the sintering bed probably without beneficial effect. Nevertheless, the gaseous phase was favorable for the preservation of the amount of magnetite, which was observed in the structure of sinter with fuel substitution. Whether the volatiles carried out any reduction work or not, by gradual temperature rise and subsequent melting magnetite is the last phase present in the solid state [25]. Without the action of volatiles with reducing nature, it could be oxidized to hematite in the strong air flow. In addition, observed structures undergoing advanced melting with secondary phases are the mark of good bonding of particles in the experimental sinter.

Umadevi et al. [32] observed more hematite and less calcium ferrites with increasing grate suction pressure. Additionally, a little less magnetite was also connected with more oxidizing air flow, which was caused by modified negative pressure. Such conditions represent the opposite of the current study. Since the oxygen content in sintering bed is diluted with fuels' volatile matter, the tendency of increasing of calcium ferrites and magnetite is in agreement with discussed work.

It would be appropriate to use the potential of exhaust gas with volatiles from sawdust in the process of recirculation of waste gases to adjust lower temperatures attained at the top of the sintering bed, which is a frequent problem in substitution of coke breeze [33].

To determine the specific effect of burning fuel with a high content of volatile constituents on the development of the microstructure of iron ore sinter, further research is necessary that could help reveal to what extent and with what result are released volatiles involved in the formation of mineral phases in the sinters.

6.2. Effect of gangue on mineral phases

Gangue minerals with wider chemical composition, i.e. silicates or aluminosilicates from raw materials were not identified in the final sinter. Only one gangue was in the same state as in the ore – quartz. The reason for this is that the mentioned complex gangue was fine grained and thus accessible for smooth assimilation reactions and melting. Quartz in the coarser ore particles could not take part in the chemical reactions with the rest of sintered mass. Nevertheless, the advanced presence of silicates, i.e. larnite, hedenbergite and pseudowollastonite, is caused by high volume of silica in the sinter mixture. Similar results were obtained in the work of Mansurova et al. [34], where quartzite iron ores (15.4wt% SiO_2) and magnetite skarns (14.6wt% SiO_2) were used. Of course, biomass fuel does not play any role in this.

By the comparison of SiO_2 content in SFCA phases with current literature, more Si^{4+} cations are involved in the SFCA and SFCA-I, respectively. In recently realized researches focused on the complex calcium ferrites formation the influence of CaO/SiO_2 ratio was also examined. However, Webster et al. [35] did not publish the chemical composition of synthesized ferrites in their work, thus the influence of raw mixture basicity on the SFCA chemistry remained unknown. In the work of Luo et al. [36], SFCA with approx. 11wt% SiO_2 was analyzed with SEM-EDS. In this case, raw mixture contained added silicate minerals, behavior of which has been studied. Malysheva et al. [37] worked with ores and concentrates slightly higher in SiO_2 , so the resulting



sinters contained up to 7.2wt% SiO₂; the SiO₂ contents in analyzed SFCA-I crystals were intermediate between those in study of Webster et al. [24] and this study. In short, varying SiO₂ contents in SFCA phases testifies higher accumulation ability of Si⁴⁺ cations by SFCA and SFCA-I lattices in direct dependence on sinter mixture silica content; that all without suppression of their formation.

6.3. The SFCA/SFCA-I ratio

The peculiarity of sinters produced with a partial fuel substitution by oak sawdust is SFCA/SFCA-I ratio, which is always in favor of SFCA. According to research of the formation of these phases [23-25], SFCA and SFCA-I are initially formed independently, but with increasing temperature SFCA-I may begin to participate in the ongoing creation of SFCA. Therefore, a low-Fe SFCA is also often called the high-temperature one. This may suggest that the SFCA/SFCA-I ratio depends on temperature. Temperature is the most important factor in the assimilation of quartz from sintering ore and, as documented also in Table 6, quartz assimilation in experimental sinters was in more advanced stage than in the reference sample. A comparable phase composition, with low quartz residue in the sinter, with nutshells used as substitute fuel [14] indicates that assimilated SiO₂ is not the main reason for the inverse SFCA/SFCA-I ratio.

According to very close SiO₂ concentration in ash from coke and sawdust, the total ash composition in the sinter mixture changed insignificantly.

The ability to micropellets formation of raw charge was not the same in all samples. As mentioned in the description of the samples, a slightly higher humidity was required for micropellets formation containing oak sawdust to achieve the optimum size and permeability of the sinter mixture. Variable moisture of sinter mixture was used as a control parameter for the speed of sintering by Zhou et al. [38], who observed in the microstructure of sinter an increased amount of columnar SFCA, i.e. low-Fe type SFCA at higher humidity. Similar results were obtained also by Chen et al. [39]. This fact might also explain the change in the phase composition of the sinters after the application of oak sawdust.

Even though magnetite-SFCA structure is not considered better than hematite-SFCA-I [10, 23-25], from the satisfactory quality point of view it is still acceptable. In addition, the research by Pownceby et al. [40] considered sinter matrix with low-Fe SFCA dominance as having acceptable strength compared to SFCA-I dominated microstructure, where the strength characteristics of sinters with such structure were not so good.

7. Conclusions

In this article, phase composition of experimental sinters produced with the substitution of coke breeze by oak sawdust based on fuel fixed carbon content was examined. Identification technique based on EDS analysis of fuel residues in sinters was presented.

Available high temperatures, gaseous phase containing volatile substances from oak sawdust, as well as higher moisture content in the sinter mixture were favorable to preservation of the magnetite phase and the low-Fe SFCA type prevalence over the high-Fe SFCA-I. The ratios of magnetite and calcium ferrites increased up to fuel substitution level of 8%, then a decline in the ratios occurred. Also, a wider Si⁴⁺ transition into the SFCA and SFCA-I lattices was noticed, as a result of raw materials richer in SiO₂. A somewhat superior dendritic-skeletal crystallization was observed in the structure, with increasing substitution of fuel.

The conducted research showed that the application of alternative fuels with high content of volatile combustibles could also provide conditions in the sintering bed for the formation of mineral phases in such proportions that significant degradation of the sinter properties does not occur. While respecting the main objective of reducing the environmental load of sinter plant, it is still possible to recommend the use of non-pyrolised biomass for sintering of iron ores.

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MINERALNE FAZE U SINTERU GVOZDENE RUDE PROIZVEDENE UZ SUPSTITUCIJSKO GORIVO OD HRASTOVE PILJEVINE

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Apstrakt

U ovom radu se ocenjuje efekat koji hrastova piljevina, jeftino supstitucijsko gorivo, ima na kvalitet sintera što se tiče njegovog faznog sastava. Uzorci sintera pripremljeni sa 5, 9, i 13% vezanog ugljenika iz hrastove piljevine koji zamenjuje ekvivalentni sadržaj vezanog ugljenika iz koksa, analizirani su svetlosnom mikroskopijom, SEM-EDS i XRD analizom praha. Mikrostruktura sintera na mestima sa ostacima goriva sastojala se od dobro integrisanih sekundarnih mineralnih faza koje su potvrdile dobre uslove za sinterovanje. Fazna analiza je pokazala da preovlađuje SFCA modifikacija u odnosu na SFCA-I, kao i trend povećanja udela magnetita i do 8% sa povećanim stepenom supstitucije goriva. Može se zaključiti da je sinter napravljen parcijalnom zamenom goriva sličan sinteru napravljenom samo sa koksom kao gorivom, te da je stoga kvalitativno zadovoljavajuć za procese u visokim pećima.

Ključne reči: Biomasa; Hrastova piljevina; Mineralne faze; SFCA; Sinter gvozdene rude.

