

# Effect of Coal and Coke Ash on Blast Furnace Slag Properties: A Comparison Between Pulverized Coal, Charcoal, Fossil-Based Coke, and Biocoke

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Blast furnace (BF) is the most used equipment for production of iron in the world. It is charged mainly with metallurgical coke and ferrous materials. When descending inside the BF, iron-bearing materials start reducing and melting with other burden materials. This melting leads to the formation of so-called primary slags from which the final slag is formed as materials descend inside the furnace. Each charge material has a unique effect on the total composition of the BF slag. Herein, the parts of the slag, which originate from ash of metallurgical coke and pulverized coal, and changes in the final slag compositions and properties are focused on. The global trend is to decrease the use of fossil-based carbon by replacing it with bio-based coal. Ash from coke and pulverized coal eventually dissolve in the final slag, affecting its properties. The purpose herein is to evaluate how BF slag composition changes when fossil-based coke is replaced with biocoke and pulverized coal is replaced with charcoal. Based on mass balance calculations, these replacements have both increasing and decreasing effects on solidus and liquidus temperatures, viscosity, and CaO/SiO<sub>2</sub> and MgO/Al<sub>2</sub>O<sub>3</sub> ratios depending on the used replacement materials.

from coke and injections from tuyere forming a final slag, which is tapped out of the BF together with hot metal.<sup>[1,2]</sup>

A recent global trend in the desire to reduce CO<sub>2</sub> emissions has led to researching different ways to replace fossil-based carbon with bio-based carbon sources. Usually biomass is pretreated, for example, pyrolyzed,<sup>[3–6]</sup> before being used in the BF. The replacement of fossil-based carbon with bio-based carbon will have different effects on the final slag of the BF.

The purpose of this work is to compare the effects different biomasses have on the final BF slag composition and important slag properties such as liquidus and solidus temperatures as well as viscosity. This comparison is based on simulation of solidus and liquidus temperatures as well as viscosities with FactSage computations, for which the final slag compositions are obtained by mass balance calculations with ash compositions taken from literature.

## 1. Introduction


A blast furnace (BF) is the most common equipment for hot metal production in the world. The BF is charged with iron-bearing materials, coke, and occasionally with additional slag forming agents, separately which lead to a layered structure. When charge materials descend, iron-bearing materials begin to reduce and melt. This leads to formation of primary slags. When primary slags descend, they are converted gradually to bosh slag and this is mixed with ash

## 2. Methods and Studied Materials

### 2.1. Fossil-Based Coke, Bio-Based Coke, Pulverized Coal, and Charcoal

Biocoke can be made using different bio-based materials depending on the target use. Availability of biomass and its supply possibilities are dependent on regional guidelines and regulations.<sup>[7]</sup> Several different compositions of biomasses and biochar have been reported in literature.<sup>[8–14]</sup> This work compares the composition of the formed BF slag when fossil-based coke is replaced with bio-based coke and pulverized coal is replaced with charcoal. To conduct this comparison, compositions for each of the coke (metallurgical coke and biocoke where 3 wt% of coal blend is replaced with Swedish wood charcoal<sup>[15]</sup>), pulverized coal,<sup>[16]</sup> and charcoal (produced from pine chips,<sup>[9]</sup> eucalyptus,<sup>[12]</sup> acacia,<sup>[13]</sup> red gum,<sup>[13]</sup> and wheat straw<sup>[13]</sup>) were chosen from literature and ash compositions were scaled to 100% focusing on the four main components, as shown in **Table 1**. Note that the biomass addition in bio-based coke is usually fixed to 3 wt% because it affects negatively the coking process and the coke quality otherwise too much. This percentage can be increased to 5 wt% if the biomass is pretreated.<sup>[17,18]</sup>

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**Table 1.** Ash amount and composition for fossil-based coke, bio-based coke, pulverized coal, and charcoals.

Analysis	Fossil-based coke <sup>[15]</sup>	Bio-based coke <sup>[15]</sup>	Coal <sup>[16]</sup>	Charcoal pine chips <sup>[9]</sup>	Charcoal eucalyptus <sup>[12]</sup>	Charcoal acacia <sup>[13]</sup>	Charcoal red gum <sup>[13]</sup>	Charcoal wheat straw <sup>[13]</sup>
Ash, wt%	12.22	11.53	7.93	1.5	3.01	4.3	1.3	20.45
Ash composition [wt%]								
Al <sub>2</sub> O <sub>3</sub>	32.75	32.65	30.00	5.77	4.11	8.47	12.77	4.01
SiO <sub>2</sub>	65.60	64.96	61.00	16.90	41.10	35.29	52.94	72.24
CaO	1.15	1.74	6.00	61.97	54.79	54.35	29.79	11.52
MgO	0.49	0.65	3.00	15.35	–	1.88	4.51	12.22

## 2.2. Computations

In this section, the final BF slag compositions formed from different kinds of charge materials are compared. Typical slag compositions<sup>[15,16,19]</sup> as well as compositions after replacements are shown in **Table 2**. CaO and MgO are the basic constituents of the slag, whereas SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are the acid constituents.<sup>[2]</sup> Slag formed from coke ash forms 13% of the final slag in a BF, whereas coal ash forms 6%.<sup>[16]</sup> This information is used later in mass balance calculations in the following way: 13% of the final slag composition comes from the slag coke. This amount is removed from the known final slag composition and replaced with the slag originating from bio-based coke. Note that the formed slag amounts vary as the ash amounts and compositions are not same in fossil-based coke and bio-based coke. The solidus and liquidus temperatures (i.e., boundaries of the solid–liquid two-phase region) as well as viscosities presented in this work were calculated using a commercial thermochemical software FactSage version 7.2<sup>[20]</sup> and its FactPS and FToxid databases. These calculations were carried out similarly to authors' previous works presented in MOLTEN 2021 conference.<sup>[21]</sup>

The difference between typical final slag composition and final slag compositions originating from the use of bio-based coke, replacement of coal with charcoal, and the combination

of bio-based coke and charcoal is shown in from **Table 2**. It can be seen that these replacements have an effect on final slag composition, overall decreasing the amount of Al<sub>2</sub>O<sub>3</sub> and increasing the MgO, whereas the amounts of SiO<sub>2</sub> and CaO vary.

## 3. Results and Discussion

### 3.1. Solidus and Liquidus Temperatures and CaO/SiO<sub>2</sub> and MgO/Al<sub>2</sub>O<sub>3</sub> Ratios

The effects these replacements have on final slag properties such as solidus and liquidus temperatures, basicity, MgO/Al<sub>2</sub>O<sub>3</sub>, and CaO/SiO<sub>2</sub> ratios are shown in **Table 3**. The most important slag properties are the liquidus temperature, viscosity, and desulfurizing capacity.<sup>[2]</sup> Final slag should be in liquid form (temperature in the range of 1350–1450 °C) to enable slag tapping from the furnace. An increase seen in solidus and liquidus temperatures can present a problem when planning to replace coke and pulverized coal. The solidus and liquidus temperatures increase in all cases except for one (when wheat straw was used as replacement charcoal) when fossil-based coke is replaced with bio-based coke and pulverized coal is replaced with charcoal. This emphasis on the importance of consideration of materials and the

**Table 2.** Final slag composition for fossil-based coke and differences when fossil-based coke is replaced with bio-based coke, pulverized coal is replaced with charcoal, and both fossil-based coke and pulverized coal are replaced with bio-based coke and charcoal.

	Final slag composition [wt%]			
	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO
Fossil-based coke and coal <sup>[15]</sup>	10.22	40.76	39.47	9.54
Fossil-based coke replaced with bio-based coke <sup>[15]</sup>	10.04	40.50	39.83	9.63
Coal replaced with charcoal (pine chips <sup>[9]</sup> )	8.92	39.20	41.85	10.02
Coal replaced with charcoal (eucalyptus <sup>[12]</sup> )	8.84	39.51	41.92	9.72
Coal replaced with charcoal (acacia <sup>[13]</sup> )	8.94	39.33	42.04	9.69
Coal replaced with charcoal (red gum <sup>[13]</sup> )	9.00	39.61	41.49	9.9
Coal replaced with charcoal (wheat straw <sup>[13]</sup> )	8.26	44.10	37.36	10.28
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (pine chips <sup>[9]</sup> )	8.72	38.91	42.25	10.12
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (eucalyptus <sup>[12]</sup> )	8.63	39.36	42.22	9.79
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (acacia <sup>[13]</sup> )	8.75	39.05	42.42	9.78
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (red gum <sup>[13]</sup> )	8.80	39.33	41.88	10.00
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (wheat straw <sup>[13]</sup> )	8.08	43.89	37.67	10.36

**Table 3.** Effects of the replacements on solidus and liquidus temperatures as well as basicity, MgO/Al<sub>2</sub>O<sub>3</sub>, and CaO/SiO<sub>2</sub> ratios in final slag.

	Solidus temperature (°C)	Liquidus temperature (°C)	MgO/Al <sub>2</sub> O <sub>3</sub> ratio	CaO/SiO <sub>2</sub> ratio	B <sub>4</sub> <sup>a)</sup>
Fossil-based coke and coal <sup>[15]</sup>	1232	1379	0.93	0.97	0.961
Fossil-based coke replaced with bio-based coke <sup>[15]</sup>	1234	1382	0.96	0.98	0.979
Coal replaced with charcoal (pine chips <sup>[9]</sup> )	1315	1399	1.12	1.07	1.078
Coal replaced with charcoal (eucalyptus <sup>[12]</sup> )	1214	1392	1.10	1.06	1.068
Coal replaced with charcoal (acacia <sup>[13]</sup> )	1214	1394	1.08	1.07	1.071
Coal replaced with charcoal (red gum <sup>[13]</sup> )	1239	1389	1.10	1.05	1.057
Coal replaced with charcoal (wheat straw <sup>[13]</sup> )	1209	1367	1.24	0.85	0.910
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (pine chips <sup>[9]</sup> )	1316	1410	1.16	1.09	1.099
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (eucalyptus <sup>[12]</sup> )	1315	1400	1.13	1.07	1.084
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (acacia <sup>[13]</sup> )	1315	1405	1.12	1.09	1.092
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (red gum <sup>[13]</sup> )	1315	1398	1.14	1.06	1.078
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (wheat straw <sup>[13]</sup> )	1209	1371	1.28	0.86	0.924

<sup>a)</sup>Basicity B<sub>4</sub> = (CaO + MgO)/(SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>).

composition of the slag charge material forms when replacing fossil-based materials with bio-based materials.

MgO/Al<sub>2</sub>O<sub>3</sub> ratio has also an effect on liquidus temperature; the minimum in liquidus temperature (≈1320 °C) can be found with MgO/Al<sub>2</sub>O<sub>3</sub> ratio at around 0.78 and liquidus temperature increases after this point.<sup>[16,22]</sup> An increase in CaO/SiO<sub>2</sub> ratio was also found to increase sulfur distribution ratio (%S)/%[S].<sup>[2,23]</sup>

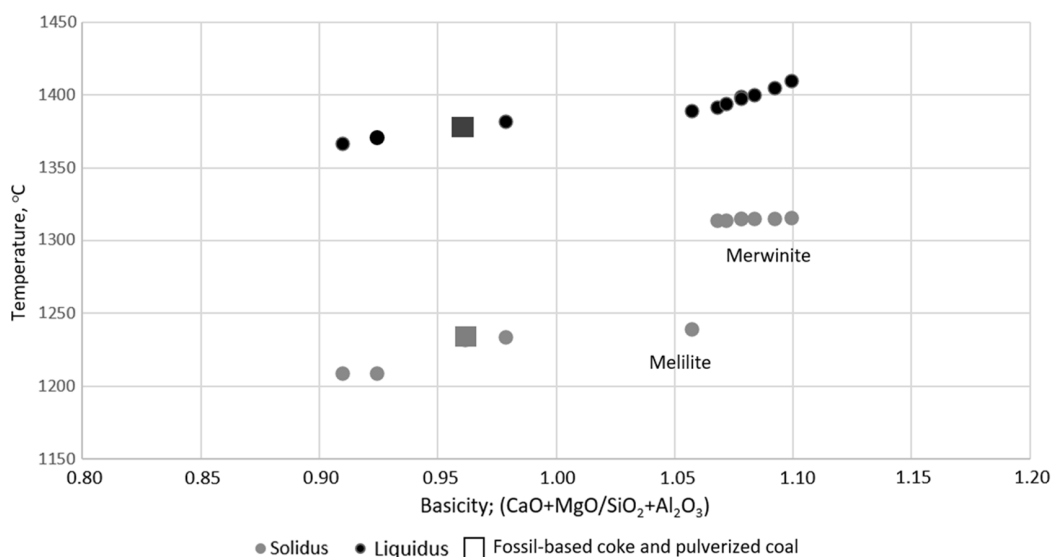
In the BF process, required final slag basicity is a compromise between desulfurizing capacity, binding power of alkalis, and liquidus temperature. When replacing fossil-based coke with bio-based coke and/or pulverized coal with charcoal, any changes in final slag composition should be evaluated according to the process requirements.

To further discuss this matter, **Figure 1** is shown, where solidus and liquidus temperatures are shown as a function of

basicity. There seems to be a jump in the solidus and liquidus temperatures at a certain basicity rate. This can occur due to the first solid phase formed at basicity of 1.057, and under the first formed solid phase is melilite with basicity of 1.068 and over the first solid phase formed is merwinite.

### 3.2. Viscosity

Viscosity reported in literature has a minimum with MgO/Al<sub>2</sub>O<sub>3</sub> ratio at around 0.81.<sup>[16,22]</sup> **Table 4** shows calculated viscosities in liquidus temperatures and in a temperature range between 1400 and 1600 °C. Overall, as expected, viscosities decrease when temperature increases. When comparing viscosities with different replacements made with bio-based materials, differences can be seen.



**Figure 1.** Solidus and liquidus temperatures as a function of basicity.

**Table 4.** Effects of the replacements on viscosity.

Viscosity (P)	Liquidus	1400 °C	1425 °C	1450 °C	1475 °C	1500 °C	1525 °C	1550 °C	1575 °C	1600 °C
Fossil-based coke and coal <sup>[15]</sup>	6.02	5.24	4.46	3.81	3.28	2.83	2.45	2.13	1.86	1.64
Fossil-based coke replaced with bio-based coke <sup>[15]</sup>	5.70	5.06	4.31	3.69	3.17	2.74	2.38	2.07	1.81	1.59
Coal replaced with charcoal (pine chips <sup>[9]</sup> )	4.29	4.27	3.65	3.13	2.70	2.34	2.04	1.78	1.56	1.37
Coal replaced with charcoal (eucalyptus <sup>[12]</sup> )	4.57	4.34	3.71	3.19	2.75	2.38	2.07	1.81	1.58	1.39
Coal replaced with charcoal (acacia <sup>[13]</sup> )	4.49	4.32	3.69	3.17	2.73	2.37	2.06	1.80	1.58	1.39
Coal replaced with charcoal (red gum <sup>[13]</sup> )	4.74	4.41	3.77	3.24	2.79	2.42	2.10	1.83	1.61	1.41
Coal replaced with charcoal (wheat straw <sup>[13]</sup> )	7.36	5.89	5.01	4.28	3.68	3.17	2.75	2.39	2.09	1.83
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (pine chips <sup>[9]</sup> )	3.88	–	3.53	3.03	2.62	2.27	1.98	1.73	1.52	1.33
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (eucalyptus <sup>[12]</sup> )	4.24	4.24	3.62	3.11	2.69	2.33	2.02	1.77	1.55	1.37
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (acacia <sup>[13]</sup> )	4.05	–	3.58	3.07	2.65	2.30	2.00	1.75	1.53	1.35
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (red gum <sup>[13]</sup> )	4.33	4.27	3.65	3.13	2.70	2.34	2.04	1.78	1.56	1.37
Fossil-based coke replaced with bio-based coke and coal replaced with charcoal (wheat straw <sup>[13]</sup> )	6.93	5.71	4.86	4.15	3.57	3.08	2.67	2.32	2.03	1.78
Conventional BF slag <sup>[24]</sup>	–	5.55	4.70	4.00	3.42	2.94	2.54	2.20	1.92	1.68

Measured viscosities for CaO–SiO<sub>2</sub>–MgO–Al<sub>2</sub>O<sub>3</sub> slags are presented in literature.<sup>[24,25]</sup> The final slags in this work coincide with slags called low-alumina slags (alumina < 15%)<sup>[24]</sup> and when looking at measured viscosities at the temperature range 1400–1670 °C, the viscosities are reported between 1.7 and 19 P. Furthermore, for a conventional BF slag (SiO<sub>2</sub> 36.4%, CaO 43.6%, MgO 5.0%, and Al<sub>2</sub>O<sub>3</sub> 15.0%), the viscosity at 1400 °C is 7.7 P and 1450 °C 5.1 P.<sup>[25]</sup> Calculated viscosities for this conventional BF slag are also shown in Table 4, where calculated viscosities can be seen to be lower than those measured. This means that calculated viscosities presented in this work are most likely also lower than what measured viscosities would be.

During the tapping in a BF, slag temperature varies. For example, in literature, the temperature at the end of tapping can descend to as low as 1300 °C.<sup>[26]</sup> This temperature is so low that some of the calculated solidus temperatures in this work are higher. When an industrial BF is operated with fossil-based metallurgical coke and pulverized carbon and the desire to replace fossil-based carbon with bio-based carbon is raised, this change in solidus and liquidus temperatures as well as in viscosities should be taken into account when making the replacement decision.

## 4. Conclusion

The motivation behind this work was the fact that the use of fossil-based carbon should be decreased. One way to decrease this is to use bio-based alternatives, i.e., in a BF biocoke would be used instead of fossil-based coke and charcoal would be used instead of coal. In this work, biocoke and charcoals found in literature were used to calculate the effect these replacements have on the final BF slag compositions and properties. The effects these changes in composition have on the liquidus and solidus

temperatures as well as viscosity were calculated. Basicity, solidus, and liquidus temperatures are increased in all but two calculated cases. In contrast, viscosity is decreased in all but two of the calculated cases. It is good to note that these are not the same two cases. Thus, it is important to realize that when replacing fossil-based carbon with bio-based carbon there will be differences in final slag composition, and the slag will behave differently. In the context of the chosen industrial process (BF in this work), these effects and differences have to be evaluated before deciding on the used biomaterial.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

Research data are not shared.

## Keywords

ash, biocoke, blast furnaces, charcoal, coke, slag

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