Analysis of the Influence of Biomass Addition in Coal Mixture for Metallurgical Coke Production

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Abstract
Metallurgical coke is a common material used for hot metal production in blast furnaces. In addition to the fuel function, it has a physical assignment, supporting the load inside the reactor, and chemical, supplying carbon to hot metal. However, due to growing discourse on environmental issues, the production of hot metal via coke blast furnace has been in evidence. This process is responsible for about 70%

Index terms—biomass; coke; cokemaking; ironmaking; steelmaking.

1 Introduction
teelmaking processes have a high-energy consumption and coal is the main source, and steel production has been responsible for 7-9% of CO\textsubscript{2} emissions in recent years, largely due to the use of fossil fuels. To produce 1.85 t of steels emitted around 3.3 t of CO\textsubscript{2}, which puts the steel sector in the spotlight of the environmental discussion (Holappa, 2020).

In the steel industry, the process that emits more CO\textsubscript{2} is the blast furnace (about 70%) due to the high consumption of fossil fuels, including coke (Orth, 2007). For this reason, efforts to reduce CO\textsubscript{2} emissions must focus on the blast furnace, with solutions to minimize the effects of burning coke and coal. In addition, coke, as well as coal, represents about 40% of the final cost of steel, which makes producers look for sustainable alternatives to compose the coke mixture.

For Noldin (2005), the inevitable dependence on the use of metallurgical coke puts conventional blast furnaces in a difficult situation, due to environmental restrictions and to the global scarcity and exorbitant prices of this raw material. This new scenario of huge demand for steel in China, which is the largest coke exporter.

One of the alternatives that has been studied, mainly to mitigate environmental impacts, is the replacement of part of coal used in coke making by biomass. Thus, there would be a reduction in CO\textsubscript{2} emissions, since biomass can be considered neutral in emissions as it captures this from the atmosphere during photosynthesis process. In addition, the photosynthesis can generate a drop in the cost of steel production, since the price difference between coal and biomass can be considerable.

Biomass is all vegetable or animal organic matter that is used in the production of energy. Like other renewable sources, biomass can be considered neutral in CO\textsubscript{2} emissions. Compared to fossil fuels, biomass has a higher volatile content, less carbon and a lower calorific value, lower sulfur content, lower ash content, higher hydrogen content, and may be interesting for its use in the steel industry. For Quan (2016), compared to plastic and other waste, biomass is a source of perspective for the replacement of fossil fuels in the future, as it is abundant, renewable, clean, and carbon neutral.

The great gain in substituting part of coal for biomass in metallurgical coke production is in the environmental. What makes biomass neutral in CO\textsubscript{2} emissions is the so-called carbon cycle. Burning biomass causes the release of CO\textsubscript{2} into the atmosphere. However, plants, through photosynthesis, transform CO\textsubscript{2} and water into carbohydrates, which make up their living mass, releasing oxygen. Thus, the use of biomass, not in a predatory way, does not change the average composition of the atmosphere over time. In this approach, the GGE balance is negative, which means that the overall sequestration of CO\textsubscript{2} from the atmosphere for the cultivation of biomass is greater than the CO\textsubscript{2} emissions during the production process. In addition, the low sulfur content in biomass results in very low emissions of SO\textsubscript{x}. This can result in the use of biomass to supply the energy and reducers necessary for the production of hot metal, guaranteeing an ecologically correct operation.
5 B) BIOMASSES

Studies involving the use of biomass in steelmaking processes have been gaining strength due to the factors mentioned. Particularly in the cokemaking, most studies involve charcoal fines or wood residues such as sawdust and bark. All studies in this line show that when adding biomass to coal mixture for coke production, there is a drop in coke quality. However, there are results that, in a certain limit, are viable and can bring economic and environmental gains without considerable loss of coke quality.

In view of these facts, this work aims to discuss the use of biomass, replacing fossil fuels, in coal mixtures used in cokemaking for metallurgical coke production. The use of biomass in the coke oven will be shown, presenting some works that have been developed around the world and making a critical analysis, pointing out the pros and cons of this use. Some environmental aspects of the use of biomass will also be discussed. Finally, some suggestions will be given for future work on the use of biomass in steelmaking processes.

2 II.

3 Development

In the development of this work, some important concepts about coke, its production, about biomass, and its application in the production of metallurgical coke will be shown. At the end, an environmental analysis, an actualization of political discourses, and simulation of possible scenarios that can be reached by steel companies will be made.

4 a) Coke Production

The coke production process was developed in England in the late 16th century, and at first, the coke produced was not used in hot metal production, that was basically produced in charcoal blast furnaces. After the industrial revolution, coke became an essential fuel for hot metal and steel production, increasing the productivity of blast furnaces (Ricketts, 2000).

Metallurgical coke is produced through coal distillation at temperatures of approximately 1000 °C. This process is called cokeification, and occurs in batteries containing retorts (long, high and strict) in the case of By-product coke ovens or in chambers when the Heat Recovery coke oven is used (Mourão, 2011).

The coke produced must have high resistance properties to avoid degradation inside blast furnace, as well as containing high carbon content, low reactivity, low ash, and sulfur content.

Steelmakers have the coke oven integrated into the steelmaking plant, but there are also independent producers whose main customers are steelmakers. In coke plants, 1000kg of coal produce around (AISE, 1999):

- 750kg of coke (690kg of blast furnace coke, and 60kg of coke breeze); ? 36kg of tar (which includes: 2.5kg of naphthalene, 15kg of light oils, and 18.5kg of tar); ? 7.28kg of total benzol (comprising: 5.35kg of benzene, 1.25kg of toluene, and 0.68kg of xylene); ? 12kg of ammonium sulfate.

World steel production in 2019 was about 1.6 billion tonnes, most of this production is via coke blast furnace, that is, a large production is required to serve steel mills. As can be seen in figure 1, world coke production in 2018 reached 629 million tons. In the blast furnace, coke has some main functions, including:

- Acts as a generator of reducing gases: its gasification generates reducing gases that are responsible for changing iron oxides to metallic iron. ? Acts as a combustible material: as coke burning reactions are exothermic, they generate heat for reactions to reduce oxides and fuse metallic iron. ? Enriching hot metal carbon content, acting as hot metal fuel. ? And finally, it supports the layers of metallic charge, thus allowing permeable beds to be generated for the passage of upward gases.

To perform the functions listed in the blast furnace, coke must present (Rizzo, 2009): These variables presented will affect the operational control of the blast furnace, the permeability of the load, iron ore reduction reactions, and characteristics of hot metal produced. Many tests are done with coke before being used in a blast furnace. The most important ones are CRI (Coke Reactivity index), CSR (Coke Strength after Reaction), DI (Drum Index), average size, compression resistance, among others. In addition, it is important to characterization the materials that will compose the mixtures, so that it is possible to predict the coke quality. Maximum carbon content

5 b) Biomasses

Biomass can be defined as the total mass of organic substances that occur in a habitat. The forms of biomass on our planet are many, and varied. According to their origin, biomasses are divided into four basic categories defined by Rocha (2011) as:

- Crops for energy production -grown mainly to generate energy; ? Post-harvest waste -waste generated during harvest such as straw, wood waste and natural waste. They are interesting because they have low cost. ? Organic by-products -are residues from the industrial processing of biomass, livestock manure, vegetable fibers, etc.; ? Organic waste -includes sewage effluents, domestic, commercial, and industrial waste.

To use biomass in the smelting process, the most interesting categories are harvest for energy, in the case of charcoal, and the post-harvest residues, which are the types of biomass considered in this work. The amount of waste after harvest can reach 50% of production by weight, and in some cases, such as coffee and soy. Table 2 shows the production of crops in 2019, according to the Food and Agricultural Organization of the United
The use of biomass is the oldest method for providing energy. However, the use of biomass as a renewable energy source must undergo a development of technology. In addition to the positive environmental effects of using biomass as a fuel, it can be said that greenhouse gases are emitted during their burning, but the amount is the same produced by the natural decomposition process. In addition, in the case of plant biomass, during its growth, carbon dioxide is consumed during photosynthesis, which can generate a positive balance when analyzing the emission (Campos, 2018).

In photosynthesis process CO2 capture from the atmosphere is reduced to organic compounds, and the

6 Table 1:

more the phytosystem is growing, the more carbon it removes from the atmosphere, calling "carbon sequestration". In growing ecosystems, such as soybean, cotton, and castor plantations, among others, the removal of carbon dioxide from the air via photosynthesis is high, reaching up to 35t CO2 / hectare (EMBRAPA, 2007).

In addition to chemical properties, biomasses differ in their physical properties like lower density, and greater porosity. To analyze economic aspects, is necessary evaluate two restrictions. First, it is necessary to know whether the biomass to be exploited energetically has no other uses (industrial or food). Second, if all the costs of the biomass harvested are compatible with the energy benefits and comparable with other fuels. Finally, technological restrictions are due to the existence or not of reliable processes and operations to convert biomass into fuels.

c) Influence of Biomass Addition in Coal mixtures for Coke-making

The use of biomass in the industrial sector has been gaining ground for presenting unique properties such as renewability, carbon neutrality, low sulfur content, low ash content, high reactivity, among others, which, when properly treated, are able to replace fossil fuel in the production of coke, for example (Mouza, 2016). For the steel industry, it is not advantageous to use biomass in its raw state, and therefore, it is necessary to convert them through processes such as torrefaction, pyrolysis, combustion, etc.

Biomass, according to Babich (2019), can be used in steel mills in three different ways, such as injection into blast furnaces or electric arc furnaces, incorporation into cargo materials or into the mixture of coal for coke or generation of reducing gas. performed an analysis of biomass in coal mixture using a pilot furnace with concentrations of 2%, 4%, and 6% with different types of biomass such as rice husk, soy, coconut, macadamia husk, coffee husk, and charcoal. The biomasses with concentrations of 6%, presented a good behavior due to their presence does not alter the swelling index and to reduce the sulfur content and its fluidity.

The calcined rice husk with a 6% concentration was used in an industrial test. Its addition to the coal mixture increased the average size of the coke, without changing its mechanical resistance. In figure ??, it is possible to observe a comparison of the data obtained on the industrial scale compared to the standard coke produced. It is possible to notice that there were no changes in the DI, its reactivity was maintained and the ash content had an increase due to the presence of silicon oxides in the rice husk. The drop in DI can be attributed to the increase in the inert content of the mixture, decreasing its coking power. According to Kubota (2008), the greater participation of aggregates above 1.5mm increases the concentration and propagation of cracks, depreciating the mechanical resistance of the coke.

Carvalho (2021) found an inverse and direct relationship between biomass participation in CSR and CRI, respectively. In figure 4, it is possible to notice that the addition of 2% of sawdust generated a drop of 3.9 % in the CSR and an increase of 0.63 % in CRI. In the addition of 5%, there was a significant drop of 12.29 % in CSR and an increase of 2.54 % in CRI. When compared to sawdust 2%, wood 2% showed a lower drop in CSR values (1.5%) and a smaller increase in CRI values (0.12 %). Wood 5% showed a higher CSR value (66.14 %) compared to the sawdust level 5% (59.74 %), with an increase in CRI to 23.65 % against 22.65% of sawdust.

Another important point is the sulfur content, which is not desired in hot metal production. Liziero (2017) concludes in his work that whenever biomass is added to the coal mixture, there will be a decrease in the sulfur content of the mixture, as shown in figure 5. Regarding the ash content of coke with the addition of biomass, a linear decrease with the increase in biomass can be seen in the dispersion diagram shown in figure 6. This behavior is expected since the ash contents of biomasses tend to be much lower than coals used in coke mixtures.

In this way, the insertion of biomass improves the coke ash balance, with a direct reflection on the drop in fuel consumption in the blast furnace. For each 1% reduction in ash in coke, 7kg /t hot metal is saved in coke rate practiced in the blast furnace (Silva, 2016). In addition, the low ash content of biomass is interesting for the coking process, since there is a decrease in tar formation. Some additives can improve the coking capacity of a coal mixture and, therefore, can partially reduce the negative effects of biomass additions. This can be seen in figure 7. The left side micrograph (a) refers to biocoque obtained without the addition of an additive, showing that surfaces of residual biomass particles are poorly assimilated in the coke matrix, evidenced by the well-defined limits of inclusions. The encapsulation of charcoal particles in the coke matrix was considerably improved when 2% of an organic additive was added to the mixture (b). CRI and CSR also tend to improve since the addition of an additive reduce the reactivity of coke (Mathieson, 2015).
These presented studies show that biocoque, coke produced with the addition of biomass, can be an adequate substitute for conventional fossil fuels with the potential to reduce CO₂ emissions and reduce costs in the steel industry.

8 d) Environmental Evaluation

Environmental changes have become one of the most important issues in global politics. The Kyoto Protocol, introduced in 1997, was the first international agreement to reduce greenhouse gases. The Paris agreement, signed in 2015 and valid since November 2016, determined an increase in the planet’s temperature by 2°C by 2100. This agreement was ratified by 179 countries that were in different stages of implementation and development of their environmental policies. Countries that have ratified the agreement recognize that the need to take action against climate change will imply accelerated policies and regulations that inevitably affect the industrial competitiveness of all nations and their respective economies. In parallel, several countries have set their own targets for reducing emissions. Table 5 shows some goals presented by countries in COP 21 for reducing greenhouse gas emissions. Even with all these goals set by the countries, it will still be difficult to reach the global goal. The effort will have to be greater, and each contribution can be useful. Therefore, replacing fossil fuels with biomass in the steel industry will be interesting to help in this process. Thus, it will be presented how much it is possible to contribute with the partial replacement of coal in the cokemaking.

According to Sathler (2017), a Brazilian steel company in 2016 had an average coke rate and injection rate of, respectively, 295kg/t of hot metal and 188 kg/t of hot metal. For Silva (2016), it is necessary around 1.2 tons of coal to produce 1 ton of coke, therefore, for this situation, the consumption of 1 coal to produce 1 ton of hot metal is 188kg in PCI and 354kg of coal in coke. Consider equation 1 presented by ??arvalho (2003): 1C +0.5 O₂ + 1.88N₂ = 0.9CO₂ + 0.1CO + 1.88N₂ 2 (1)

Doing a simple stoichiometric calculation, it is possible to say that burning 1 ton of carbon produces 3.3 tons of CO₂. It is possible to find in the literature several characterizations of coal with an average carbon content of 85%. Concluding, 542kg of coal have 460kg of carbon, and its burning emits 1520kg of CO₂, that is, the emission in a blast furnace process reaches 1520kg/t of hot metal. Considering only the share of emissions from coke, this value would be 1168.2kg/t of hot metal.

The main question is how much CO₂ can be avoided with the use of biomass in coal mixtures for cokemaking. Researches developed by Silva (2008), Campos (2018), Suopajärvi (2017), among others, analyzing the use of biomass in coke production, point out that it is possible to use an average of 6% of the biomass in coal mixture, producing coke with qualities and requirements to be used in a blast furnace. Therefore, if we consider the data presented above (354kg of coking coal per ton of hot metal), replacing 6% of coal used in coke production by biomass, there would be a decrease of 22kg of coal per ton of hot metal produced. Finally, the contribution of coke burning to CO₂ emissions in a blast furnace would be 1095.6kg of CO₂ /t of hot metal, a decrease of 72.6kg of CO₂ /t of hot metal.

When considering world production, this value can be significant. According to the World Steel Association (2021), hot metal production in 2019 reached 1.2 billion tons, that is, considering that all hot metal was produced via a coke blast furnace and that 6% of the coking coal was replaced by biomass, around 87 million tonnes of CO₂ emissions would be avoided in one year.

9 III.

10 Conclusions

The addition of biomass in coal mixture can be used in a certain limit. Researches shows that an average quantity is around 6%, without an expressive change in coke quality. The quantity used can vary according to the granulometry and type of biomass, which case presented show the differences.

The Δ increase with the increase of biomass in the mixture. This was associated with the quantity of inert content, which influences in the mechanical resistance. In addition, the coarse granulometry decreases more than the fines one.

The addition of biomass to the coal mixture is still considerably low, despite significantly influencing the cost and CO₂ emission, since it acts with a lower CRS and a higher CRI in relation to the coke conventionally used by steel companies.

In terms of the environment, the use of 6% of biomass in the blast furnace is capable of reducing CO₂ emissions by up to 6.21% per ton of hot metal, according to the calculations carried out, and despite being a low value; it causes an immense effect when considering the annual 87 million tonnes of reduced CO₂ emissions.

It is necessary to optimize the processes for obtaining, transporting and stocking biomass so that they can compete with fossil fuels as a raw material for the cokemaking. Cooperation between industrial sectors and agribusiness is essential. The development of alternatives is extremely important in order to guarantee an increase in the useful life of the coke plant.

Obviously, these numbers are just to provoke reflection and point some numbers of the use of biomass in the coke production. Other factors must be analyzed for use, but it is a fact that environmental restrictions are
Figure 1: Figure 1:

Figure 2: Figure 2:

Figure 3:
Figure 3: Figure 4:

Figure 4: Figure 5:
Figure 5: Figure 6:

Figure 6: Figure 7:
Coke properties for blast furnace uses (Rizzo, 2009)

| Properties          | Coke Quality |
|---------------------|--------------|
| Moisture            | < 6.0%       |
| Fixed Carbon        | 65-75%       |
| Ash                 | < 10.5%      |
| Volatiles           | < 1.2%       |
| Sulfur              | < 0.7%       |
| Phosphor            | < 0.045%     |
| Alkalis             | < 0.35%      |
| Density             | 180-350 kg/m³|
| Drum Index (150/15) | > 85%        |
| CSR                 | > 65.5%      |
| CRI                 | 21 a 25.5%   |
| Compression Strength| 130-160 kgf/cm³|
| Particle Size       | 45-60 mm     |

Figure 7:

| Biomasses     | Production (10³ t) | Residues* (10³ t) |
|---------------|--------------------|-------------------|
| Sugar cane    | 1.949.310,1        | 633.525,8         |
| Soya          | 333.671,7          | 166.835,5         |
| Maize         | 1.148.487,3        | 492.701,1         |
| Coffee        | 10.035,6           | 5.017,8           |
| Rice          | 755.473,8          | 151.094,8         |

[Note: *Calculated according to CARVALHO, 1992.]

Figure 8: Table 2:

| Countries | Goals                                                                 |
|-----------|------------------------------------------------------------------------|
| Australia | 5-25% lower than 2000, until 2020                                       |
| Brazil    | 37% lower than 2005 until 2025 and 43% until 2030                      |
| Canada    | 17% lower than 2005, until 2020                                        |
| China     | 20-25% reduction in emissions per unit of GDP from 2005, until 2020    |
| European  | Reduce 20% until 2020, 40% until 2030 and 80-95% until 2050 (compared with 1990) |
| Russia    | 15-20% lower than 1990, until 2020                                     |
| USA       | 17% lower than 2005, until 2020                                        |

Figure 9: Table 3:
increasingly demanding, and the steel industry must adapt to meet the environmental schedule and show that it is a strong sector, which aims a sustainable production.
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