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CHARCOAL FINES AS AN ADDITIVE IN METALLURGICAL COKE PRODUCTION

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Abstract. *Stable pig iron production by blast furnaces is linked to the chemical, physical and metallurgical properties of raw materials, especially of the metallurgical coke. The challenge of coke production is to produce coke at low cost and high quality. In this context, this work evaluated the charcoal fines use in the coals mixture for cokemaking, reducing the use of expensive mineral coals, maintaining the required quality for the pig iron production by blast furnaces, as well proposed a route to minimize the CO2 emission from the steelmaking process. Pilot scale tests were performed with up to 20% of charcoal fines in the blend. The metallurgical coke analyzes showed the technical and commercial viability for use in up to 2% of charcoal fines in the blend of mineral coals.*

Keywords: *charcoal fines, metallurgical coke, CO_2 emission.*

1. INTRODUCTION

The steel industry is looking for alternatives to reduce raw material costs and to maintain market competitiveness, which are essential to the survival of organizations. According to Da Silva (2011), the coal is responsible by 30% of steel price. An alternative way to reduce its costs is to produce metallurgical coke using mineral coal added alternative materials as saw in previously studies, Ruiz (1990), Menéndez (1997), PIS (2002), Ka Wing Ng (2011) and Da Silva (2016).

The metallurgical coke must have some physical-chemical characteristics for to be used in blast furnaces, these characteristics can be measured by some indexes such as CSR (Coke strength after reaction rate), CRI (Coke reactivity index), DI (Drum index), porosity, fluidity and sulfur contend.

Charcoal is a renewable energy source and Brazil is the largest charcoal producer in the world. Those facts became the charcoal viable economically for be used in blends with mineral coal to produce metallurgical coke. Around 25% of charcoal production is composed of fines, which it has lower price than charcoal. The charcoal fines (smaller than 9 mm) are obtained from charcoal degradation since its carbonization, transportation until its application.

Nowadays, the utilization of friendly environment materials in the industry are desirable, and this way, the charcoal compared to mineral coal presents advantage, the charcoal is obtained from reforested wood. This procedure allows to remove oxygen dioxide (CO_2) from atmosphere (1.8t CO_2/t dry wood), to emit oxygen to atmosphere (1.3t O_2/t dry wood) and increase carbon stock (20 kg CO_2/tree year).

The utilization of charcoal fines to produce metallurgical coke has some advantages like reduce raw materials costs, it makes the Brazilian's steel more competitive in international market. The utilization of charcoal fines decrease the volume of mineral coal importation and to create an alternative and low-cost route to reduce CO_2 emissions in pig iron route.

The figure 1 below shows pig iron route using charcoal and mineral coal, its CO_2 emissions and the removal.

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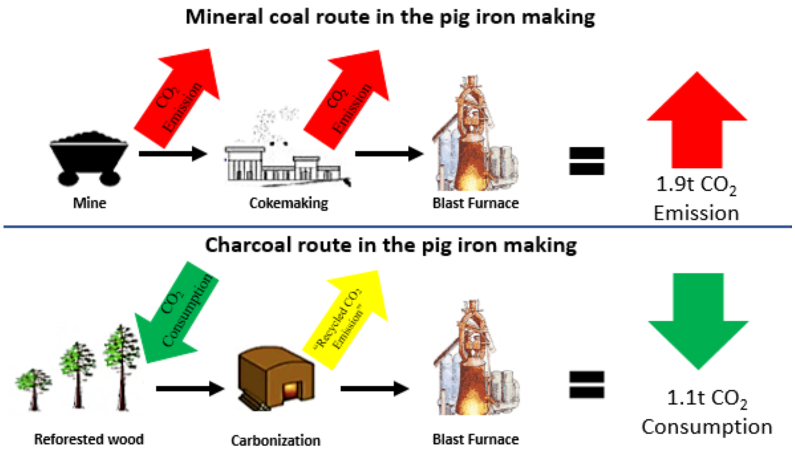

Figure 1. Charcoal and mineral coal route. Moura (2006)

Medrado (2008) developed tests to observe the influence, in the coke quality, of charcoal fines (CF) to substitute some fractions of mineral coal in blend to produce metallurgical coke. Was noted the viability of use fractions until 2% of charcoal fines. The table 1 shows the results of those tests.

Table 1. Results of Medrano's tests. Medrano (2008)

Blends	Average Size	DI	Reactivity	Ash	Sulfur contend	Fixed carbon
	(mm)	(%)	(%)	(%)	(%)	(%)
Regular blend (RB)	80.4	79.3	24.5	11.4	0.63	87.9
98%RB + 2%CF	75.5	79.7	22.8	10.8	0.58	87.0
96% RB + 4%CF	79.2	79.2	26.3	10.6	0.57	87.2
94% RB + 6%CF	78.6	79.0	29.3	10.5	0.56	87.6

According to Macphee (2009), the utilization of charcoal fines in the production of metallurgical coke has as main objective to reduce pig iron production costs and decrease CO_2 emissions in the atmosphere. As objective to produce metallurgical coke with acceptable properties by blast furnace, at least 10% of charcoal fines in the blend, Macphee developed tests using charcoal fines in different quotas and particles size. The use of charcoal fines with particle size smaller than 0.250 mm produced high reactivity metallurgical coke. Although when was used charcoal fines with particle size between 0.250 to 0.375 mm, the results showed a metallurgical coke with reactivity smaller than metallurgical coke obtained from particle size smaller than 0.250 mm.

2. MATERIALS AND METHODS

The blends to produce metallurgical coke were composed by mineral coal (85% particles size smaller than 2.83 mm) and charcoal fines in two particles size (70% smaller than 2.83 mm and 100% smaller than 2.83 mm). The table 2 and 3 shows the physical-chemical characteristics of mineral coal and charcoal fines, respectively.

Table 2. Physical-chemical characteristics of mineral coal

Moisture (%)	**Volatile matter (%)**	**Fixed carbon (%)**	**Ash (%)**	**Sulfur content (%)**	**Fluidity [log(ddpm)]**	**Reactivity (%)**
8.96	21.71	67.00	9.62	0.34	1.43	69.27
Na_2O (%)	**K_2O (%)**	**Al_2O_3 (%)**	**CaO (%)**	**MgO (%)**	**Fe_2O_3 (%)**	**SiO_2 (%)**
0.09	0.52	25.69	2.55	0.39	3.92	58.36

Table 3. Physical-chemical characteristics of charcoal fines

Ash (%)	**Volatile matter (%)**	**Sulfur content (%)**	**Fluidity [log(ddpm)]**
5.47	22.31	0.017	0

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The table 4 shows the ash chemistry of charcoal fines.

Table 4. Results of ash chemistry of charcoal fines

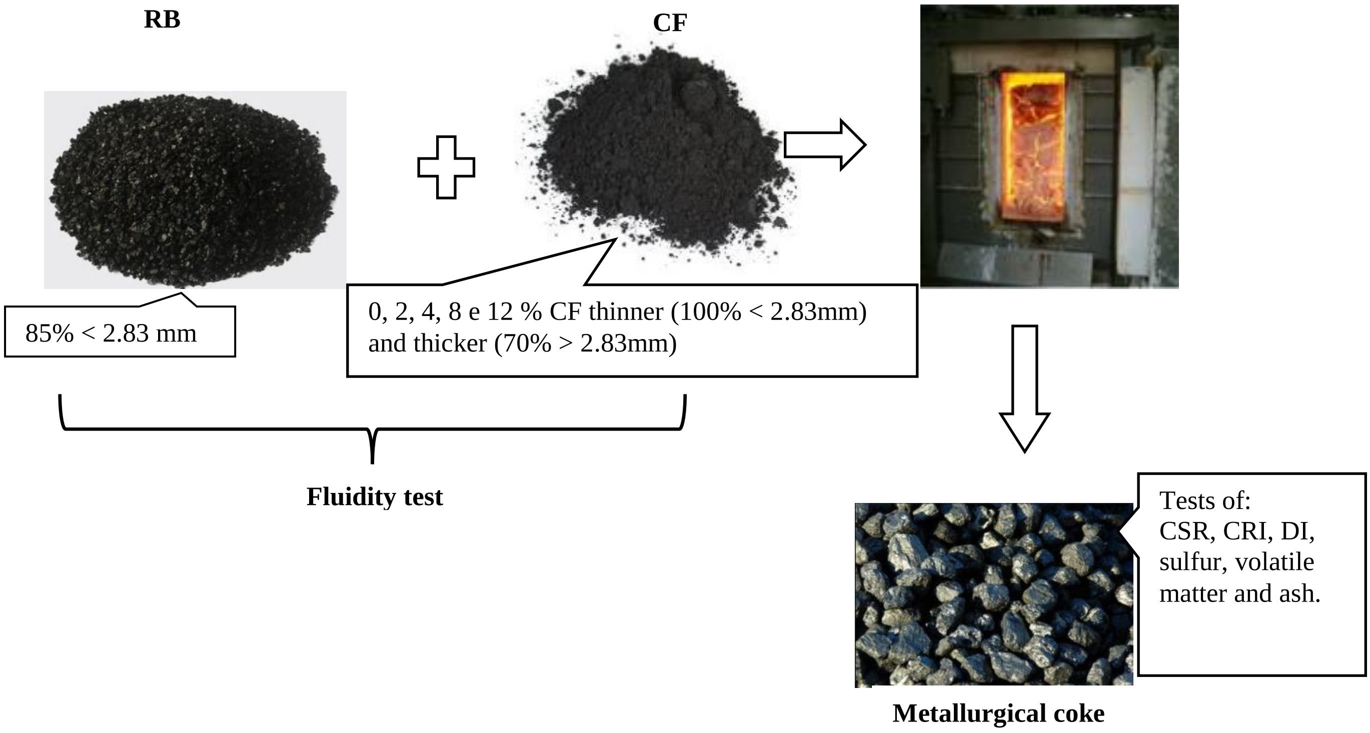
Fe_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	Na_2O (%)	SiO_2 (%)	Al_2O_3 (%)
4.47	15.91	3.19	0.79	0.49	48.17	8.28

Were developed ten (10) pilot oven tests composed by regular blend (100% mineral coal) and different fractions (2, 4, 8 and 12%) and particles size (70% smaller than 2.83 mm and 100% smaller than 2.83 mm) of charcoal fines, as showed in table 5.

Table 5. Composition of the pilot oven tests

Test	Particle size of charcoal fines	Charcoal fines (%)	Regular blend (kg)	Charcoal fines (kg)
1	-	0	250	0
2	100% smaller than 2.83 mm	2	245	5
3	70% smaller than 2.83mm	2	245	5
4	100% smaller than 2.83 mm	4	240	10
6	70% smaller than 2.83 mm	4	240	10
7	100% smaller than 2.83 mm	8	230	20
8	70% smaller than 2.83 mm	8	230	20
9	100% smaller than 2.83 mm	12	220	30
10	70% smaller than 2.83 mm	12	220	30

The tests were developed at 1200ºC and the cokemaking time were 20h for each test. After cokemaking period, the metallurgical coke was cooled by water and after that were sampled 80kg of coke for each sample composition. The collected materials were sent to lab where it was realized metallurgical coke analysis. There is a flowchart of process below.



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The tests followed the usual current standards as detail in table 6.

Table 6. Analysis standards for coals and blends

Analyzes and tests	Content	Method
Samples preparation	Lot Representation	JIS M 8811
Immediate analysis	Sulfur	ASTM - D – 2492
Ash chemical composition	Fe_2O_3, SiO_2, Al_2O_3, MnO_4, CaO, MgO, P_2O_5, ZnO, Na_2O, K_2O, TiO_2	Atomic Absorption
Sole heat oven	Contraction / expansion (pressure Coq. - psi)	ASTM - D – 2014
Optical microscopy	Maceral composition; Reflector power	Standards adaptation ASTM - D - 2798 e ASTM - 2799
Plastometry gieseler	Fluidity Log(DDPM)	ASTM - D – 2639

2.1. Coke reactivity index (CRI)

This test follows ASTM Standard D5341-99. In this test, a 200g coke sample dried with particle size between 19 and 21 mm were put in a reactor (under N_2 flow) and were introduced in an electric oven at 1100ºC. After temperature stabilization in the reactor center at 1100ºC, the coke is subjected by CO_2 flow at 5 l/min for 120 min. After reactor cooling until 40ºC, the weight lost percentage by the sample give the CRI.

2.2. Coke strength after reaction rate (CSR)

The remaining coke of the CRI test is subjected to 600 revolutions (20 rpm) in a spinning cylinder and then analyzed by particle size. The retained in the 9.52 mm sieve (percentage on the weight after reaction) gives the resistance index of the coke after reaction.

2.3. Drum index (DI)

In this test were used 10kg of coke with particle size between 25 and 100 mm. This sample were paced in a drum (MICUM) and were subjected to 150 rpm. After this step, the coke is sifted in 15 mm, the percentage of coke retained in the screen by initial coke mass gives DI.

2.4. Sulfur content

The sulfur content is determined by infrared radiation. A sample of 3.0g of coke with particle size smaller than 0.250 mm were placed in a pot then in an oven. The sample were heated in an O_2 atmosphere at 1137ºC. While this step, the sulfur is oxidized to SO_3 so measure by infrared detector.

2.5. Porosity

Five hundred measurements were performed using the optical microscope in the metallurgical coke matrix. At each measurement, it was analyzed whether the point was in the matrix or in the pore. At the end of the 500 measurements, the porosity was calculated by percentage, number of measurements that were found in the pores under total number of measurements.

2.6. Fluidity

This test followed ASTM D2639 standard. A 5g coal sample with particle size smaller than 35 mesh were put in pot. A small stirrer coupled to a motor with 300rpm and a dial with 100 divisions (Readings up to 30.000 ddpm) positioned in the middle of coal is subjected to a constant torque. The sample were heated in the absence of air at 3ºC/min between 300ºC and 500ºC. When the temperature reached a value in the range of 350°C to 420°C, the stirrer started to rotate

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very slowly. Its speed increased when increase temperature and reached a maximum between 430°C and 480°C. The speed decreased too fast and the stirrer finally stopped at a temperature below 500°C.

3. RESULTS

3.1. CSR

The figure 2 shows the CSR index when charcoal fines is added.

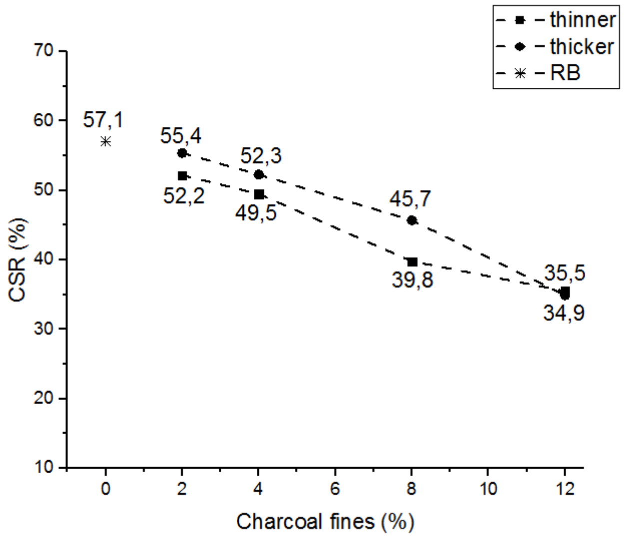

Figure 2. CSR as a function of charcoal fines added.

The tests showed that the CSR tended to decreased in all cases, and the results when are used charcoal fines thicker (70% smaller than 2.83 mm) are always better when compared with the charcoal fines thinner (100% smaller than 2.83 mm) results.

3.2. CRI

The figure 3 below shows the CRI index when the charcoal fines are added.

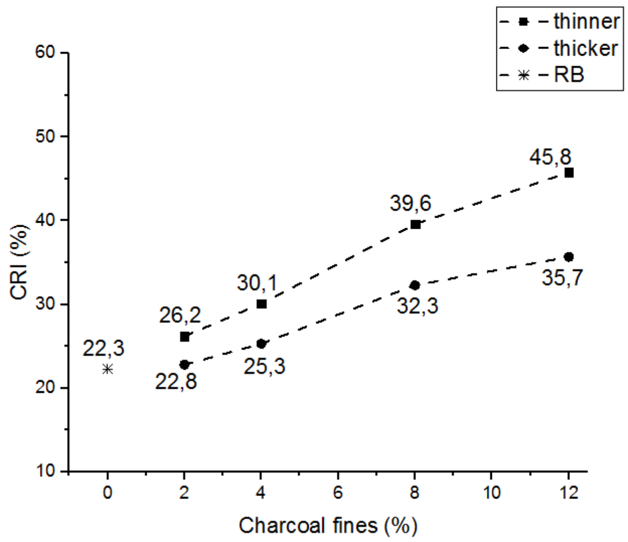

Figure 3. CRI as a function of charcoal fines added.

Was possible to observe from the results that the metallurgical coke reactivity tended to increase in all cases approximately linearly. The better results were obtained when was added 2 % of charcoal fines thicker, we can observe

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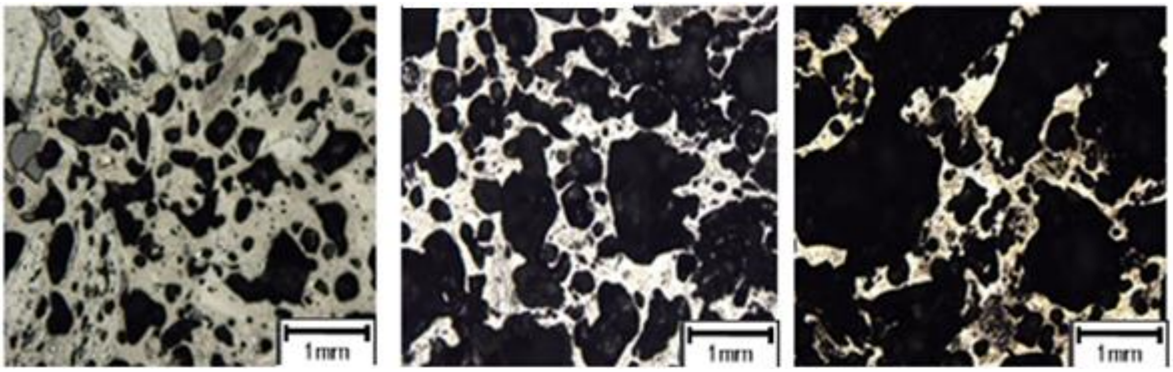
ether that the results when used charcoal fines thicker showed up always better when compared with charcoal fines thinner (It is important to remember that the increase of reactivity of metallurgical coke isn't desired). The thinner particles are more reactive because of its higher surface area and its smaller volume.

3.3. Porosity

The coke porosity was analyzed and the results are showed in table 7 and figure 4.

Table 7. Coke metallurgical porosity (500 measurement)

Blend	% Pores	Carbon matrix
Regular blend (RB)	35.50%	64.50%
98%RB + 4%CF	59.40%	40.60%
88% RB + 12%CF	78.00%	22.00%



(a) (b) (c)

Figure 4. Micrography of metallurgical coke with (a) 100% regular blend, (b) 98%RB + 4%CF and (c) 88%RB + 12%CF

The increase of porosity is directly related with the high pores volume of charcoal fines. The increase of metallurgical coke reactivity confers higher porosity to the metallurgical coke matrix, which in turn confers lower mechanical resistance to metallurgical coke.

3.4. DI

The figure 5 below shows the DI index when charcoal fines are added.

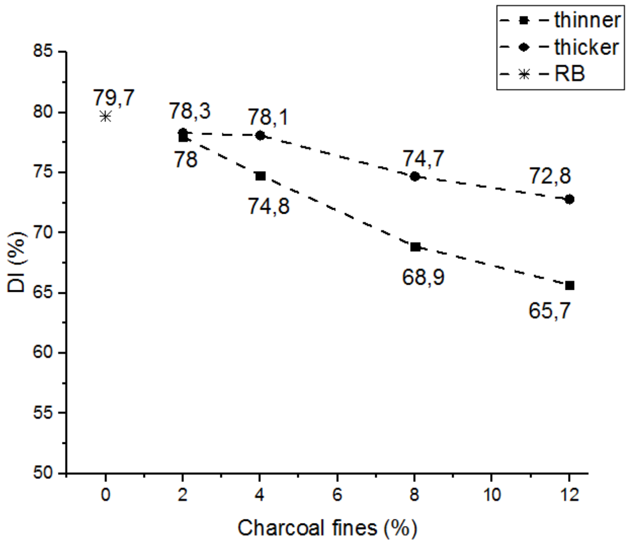


Figure 5. DI as a function of charcoal fines added.

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Was observed that the addition of charcoal fines tended to decrease the mechanical resistance of metallurgical coke. All results were lower when compared with regular blend, the additions of charcoal fines thicker presented showed up always better results when compared with charcoal fines thinner. Was possible to notice that the difference between charcoal fines thinner and thicker results always increase when the volume of charcoal fines in the blend increase.

3.5. Sulfur content

The figure 6 shows the sulfur content of metallurgical coke when charcoal fines are added.

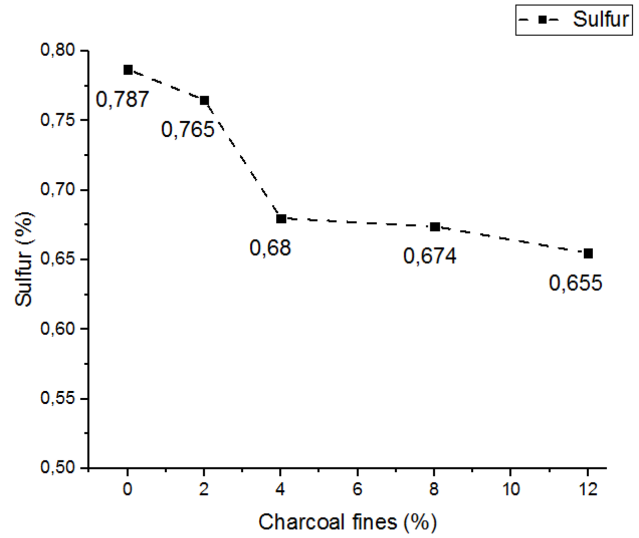

Figure 6. Sulfur content as a function of charcoal fines added.

The decrease of sulfur content in metallurgical coke was already expected, because the charcoal fines present sulfur content 20 times lower than mineral coal. Therefore, the use of charcoal fines in the blend allows the use of mineral coals with sulfur content higher preserving the metallurgical coke quality.

3.6. Fluidity

The figure 7 shows the fluidity of metallurgical coke when charcoal fines are added.

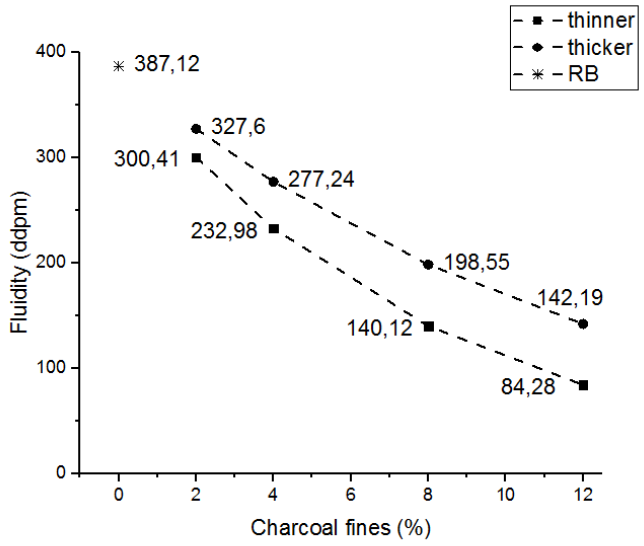

Figure 7. Fluidity as a function of charcoal fines added.

The metallurgical coke fluidity decreases exponentially in all cases and we can observe that charcoal fines thicker presented better results when compared to charcoal fines thinner. This phenomenon can be explained because the

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thinner particles has more surface area, because of that, it limits the interaction among the "walls" of particles of mineral coal when it are expanding during the test, reducing the plasticity (the ability to behave as a plastic phase).

3. CONCLUSIONS

The CSR, CRI, fluidity and DI index showed up worse when was used charcoal fines in the blend (although CRI index increased, this behavior decrease the metallurgical coke mechanical resistance). However, the use of 2% of charcoal fines (thinner or thicker) did not represents huge negative effects in metallurgical coke resultant, in this situation, this blend allows to produce a metallurgical coke with quality acceptable and also cheaper and environmentally friendly.

Was possible to show the reactivity affects directly the metallurgical coke porosity, with the reactivity increase, the porosity volume increases.

The sulfur content of metallurgical coke decreased with the use of charcoal fines, which was already expected, once that the sulfur content of charcoal fines is lower than the mineral coal.

In a scenario where companies are looking for solutions, profitable and green, for their processes, the use of charcoal fines proved to be an excellent alternative for this issue, even if used in small portions.

4. ACKNOWLEDGEMENTS

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