Effect of inertinite-rich coal on metallurgical coke strength and porous microstructure

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Abstract

The consumption of coals without coking properties in coal blends for coke production is a challenge, precisely because of their lack of coking properties, and in some cases, high contents of macerals from the inertinite group, which are known to contribute to a reduction in the mechanical strength of coke when present in high size dimensions. With the constant search for the use of non-coking coal in the coal blends, the main objective of the study was to investigate the effect of increase inertinite-rich coal content in multi-component coal blends. To achieve this, selective crushing was performed to obtain 1.5 mm as the critical inertinite size for the coke's mechanical strength, decreasing the amount of microcracks at the boundary between reactive maceral-derived components (RMDC) and inert maceral-derived components (IMDC). The microstructural characterization for the industrial metallurgical coke was studied using optical microscopy associated with image analysis (ImageJ software). It was established that a 25 % content of inertinite-rich coal addition in the blend caused systematic changes in the coke's microstructural features, decreasing the mechanical strength. Additionally, the segmentation between RMDC and IMDC was studied to achieve better correlation from the coke's microstructural parameters, predicting mechanical strength ($DI_{150/15}$). A new equation was proposed describing both microstructural features from reactive and inert components.

Keywords: inertinite-rich coal, coke strength, coal selective crushing, coke microstructure.

1. Introduction

1.1 Microstructure of coke

The mechanical behavior of coke is largely related to the microstructure or porous structure of the material and dependent on both the texture of the carbon matrix walls and the spatial arrangement of pores or void cavities in the material. Most cokes have a total porosity of around 50 % (Loison *et al*., 1989). Patrick & Stacey, (1972) initially used diametrical compression tests for coke samples to determine the effects of this stress by the fundamentals of the fracture mechanics of solids postulated by Griffith (1920). Since the pores in coke have different sizes and shapes, they can act as points of greater fragility to mechanical failure by the stress concentrator effect. Measurements of porosity and pore size have been the most interesting parameters associated with the coke microstructure by determinations of apparent density and mercury porosimetry (Patrick & Stacey, 1972; Nishioka & Yoshida, 1983). However, these techniques are not able to estimate the volumes occupied by voids relative to closed pores, and do not provide information on the shape of the pores. This limitation was overcome by the use of optical microscopy associated with advanced image analysis techniques with high processing capacity for greater representativeness of the heterogeneous structure of the coke, and has the advantage of obtaining all the parameters of interest in the study of the microstructure of the coke, such as porosity, shape and size of pores (open and closed) and thickness measurements of the walls of the matrix in order to establish relationships with the mechanical strength (Sato *et al*., 1998; Andriopoulos *et al*., 2003; Kubota *et al*., 2011; Hiraki *et al*., 2011; Nyathi *et al*., 2013; Saito *et al*., 2017; Meng *et al*., 2017; Donskoi *et al*., 2017; Ghosh *et al*., 2018; Agra, 2019; Xing, 2019, 2020; Agra *et al*., 2021).

1.2 Effects of inert particles on the porous microstructure of coke and mechanical strength

The inert particles do not show plastic behavior during the heating of the coal and the formation of coke, and if they are too coarse in size, they can become regions of crack formation and propagation as a result of the different contraction coefficients between the inert compounds and the carbon matrix. Patrick & Stacey, (1975) studied the dependence of the mechanical strength of coke on the level of participation and the size of inert particles of fine metallurgical coke (coke breeze) added to coal blends, with a view to interpreting possible changes in coke strength associated with modifications in the characteristics of the porous microstructure of the coke. Subsequently, Patrick & Stacey, (1978) furthered these investigations with inert additives in coal blends, working with metallurgical coke fines, petroleum coke and sand. The researchers concluded that mechanical strength is strongly influenced by the type of inert additive used in the blends and has as its major factor the ability of the additive to form a bond with the carbon matrix of the coke. Barriocanal *et al*., (1995) developed a quality indicator to identify, classify and measure the degree of contact of the interfaces formed between the carbon matrix derived from reactive coal constituents and inert particles from petroleum coke. Andriopoulos *et al*., (2003) studied the effect of heterogeneity in the carbonaceous matrix on the mechanical strength of coke and observed that regions derived from inert constituents (IMDC) have a higher hardness and Young's modulus than regions derived from reactive constituents (RMCD), and that the hardness of the carbon microtextures decreased as the rank of the parent coal increased. In the same study, using image analysis techniques to characterize the coke's microstructure, the authors observed that pore characteristics are particularly related to the percentage of inert macerals present in the coal used to produce the coke, suggesting that an increase in the inert content of the coal blend should produce coke with a smaller average pore size (Deq) and, consequently, tends to generate greater wall thickness (W) in the matrix. It also suggests that the overall strength of the coke is not significantly affected by the hardness or modulus of the individual microtextures but is more likely related to the porous structure of the coke, the fracture toughness of the carbon matrix wall and the adhesion between the microtextures of its components.

1.3 Effects of inert parent coal particle size on microstructure and mechanical strength of coke

Miura *et al*., (1981) discussed the effect of the particle size of inertinite-rich coal in coke production, reporting high values of the coke's mechanical strength for this coal size classification between 3 to 5 mm. Subsequently, Asada *et al*., (1994) reported a relationship between different particle size classifications (< 0.25 mm and between 0.5 and 1.0 mm) for coal with high inertinite maceral content used for coke production and the mechanical strength of the material. Until then, the relationships found were built considering the particle size of the coal with high participation of inert compounds, and not properly, the measurement of the size of the inertinite maceral contained in the coke microstructure. Kubota *et al*., (2008) advanced in this direction, measuring the size of the maceral inertinite constituent inserted in the carbonaceous matrix. These researchers used optical microscopy image analysis and examined the effects of inertinite size on the mechanical strength of coke. In this study, Kubota *et al*., (2008) evaluated the volumetric effect as a function of inertinite particle size in the carbonaceous matrix related to the mechanical strength of coke. The authors found that when the inertinite size was reduced to below or around 1.5 mm, the drum index did not decrease. Thus, a critical size for the inertinite group macerals was defined as the size from which these particles dispersed in the matrix, promoting the reduction of the mechanical strength of the coke. It was observed that as the size of the inert particle decreases, the size of the cracks found around it is also reduced. Donskoi *et al*., (2017) arrived at the same critical size relationship for inert particles (1.5 mm) by analyzing the correlation coefficients obtained between the results of tumbler test and IMDC segmented into various sizes, and expressed by diameter equivalent to the circle of equal area (Deq).

In this context, this article aims to evaluate the effect of reduced size of inert particles on the quality of the coke and to establish the relationship between the level of participation of this finely crushed material in the coal blend and the mechanical strength of the coke.

2. Materials and methods

2.1 Raw materials

The materials used in this study are classified according to the ASTM D388 standard, being A_1 and A_2 bituminous coals of high volatile matter, M_1, M_2 and M_3 bituminous coals of medium volatile matter. The medium volatile coal M_3 will be called inertinite-rich coal with high content of inert particles from the inertinite maceral group (52 % vol mmf) and reduced thermoplastic properties, showing maximum fluidity 4 ddpm, plastic range 44 °C and FSI 1.0. The properties of the individual coals are presented in Table 1, characterized by proximate analysis (ASTM D7582), total sulfur (ASTM 4239), petrography (ISO 7404/5), Gieseler plastometry (ASTM D2639) and FSI (ASTM D720).

Table 1 - Individual coal characterization.

Coals	Ash (%DB)	VM (%DB)	FC (%DB)	S (% DB)	Rr (%)	Vit (% vol mmf)	Lip (% vol mmf)	Ine (% vol mmf)	SF (% vol mmf)	MM (% vol)	R (%)	I (%)	R/I (-)	MF (ddpm)	PR (°C)	FSI (-)
A_1	6.27	35.74	57.99	0.98	0.80	65.05	9.95	25.00	13.27	2.00	79.42	20.58	3.86	59328	100	8.0
A_2	7.94	38.05	54.01	2.14	0.70	73.06	8.76	18.18	11.79	1.00	85.75	14.25	6.02	40927	94	8.0
M_1	10.00	22.40	67.60	0.54	1.26	68.48	0.00	31.56	22.83	0.67	76.09	23.95	3.18	540	80	8.5
M_2	8.10	21.10	69.20	0.26	1.27	57.58	0.00	42.42	34.21	1.00	68.98	31.02	2.22	80	62	7.0
M_3	10.40	20.70	68.90	0.44	1.29	48.09	0.00	51.91	40.97	1.75	61.75	38.25	1.61	4	44	1.0

VM: Volatile matter; FC: Fixed carbon; S: Total sulfur; Rr: Mean random reflectance of vitrinite; Vit: Vitrinite maceral group; Lip: Liptinite maceral group ; Ine: Inertinite maceral group; SF: Semifusinite maceral; MM: Mineral material; R: Reactives macerals (Vit + Lip + 1/3 SF); I: Inerts macerals (Ine - 1/3 SF); R/I: Ratio between reactives and inerts macerals; MF: Maximum fluidity; PR: Plastic range; FSI: Free-swelling index; DB: Dry basis; vol: Volumetric; mmf: Mineral material free.

2.2 Coal blends and carbonization procedure

MB, MC_{15}, MC_{20} and MC_{25} are identified, respectively, as reference coal blend and blends of coals with medium volatile matter content and participation of 15 %, 20 % and 25 % of inertinite-rich coal. Table 2 shows the percentage composition of the coal blends studied with different levels of participation of inertinite-rich coal (M_3), being (a), the percentage composition of the reference blend (MB) with regular grain size for all coals (83 % < 3.36 mm), and (b), the test blends with different levels of participation of inertinite-rich coal (M_3) of reduced grain size (88 % < 3.36 mm).

Table 2 - Relative wt % proportion of coals in the blends and grain size.

(a) Coal	MB	< 3.36 mm
A_1	24%	83%
A_2	10%	
M_1	30%	
M_2	30%	
M_3	6%	
Coke	C_{MB}	

(b) Coal	MC_{15}	MC_{20}	MC_{25}	< 3.36 mm
A_1	24%	24%	24%	83%
A_2	10%	10%	10%	
M_1	30%	30%	30%	
M_2	21%	16%	11%	
M_3	15%	20%	25%	88%
Coke	C_{15}	C_{20}	C_{25}	

Figure 1 shows the schematic flow of the blending and crushing preparation lines at ArcelorMittal Tubarão, with one of the three existing lines being used exclusively for the individual crushing of inert coal (M_3) under the most severe conditions in order to reduce the particle size (88 % < 3.36 mm). The other two lines processed the reactive coals (A_1, A_2, M_1, M_2) under the original crushing conditions. After crushing on the three lines, the test blends were produced.

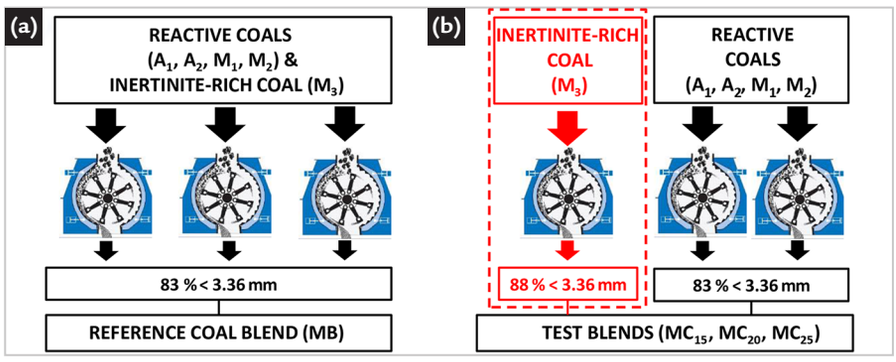

Figure 1 - Schematic flows of the crushing and preparation lines for (a) reference coal blend with regular crushing and (b) test blends with selective crushing of inertinite-rich coal (M_3) added in the blends studied.

The properties of the test blends are presented in Table 3, characterized by proximate analysis (ASTM D7582), total sulfur (ASTM 4239), petrography (ISO 7404/5), Gieseler plastometry (ASTM D2639) and FSI (ASTM D720). The participation of coal M_2 was reduced in the test blends with substitution by coal M_3 which rises in the same proportion. As planned in the study, a reduction in the ratio between reactive and inert maceral compounds (R/I) was observed and consequent reduction in fluidity to a value (133 ddpm), being below the range considered suitable for coke production, which is defined between 200 and 1000 ddpm (Miyazu *et al*., 1974; Miura *et al*., 1981; Loison *et al*., 1989; Díez *et al*., 2002).

Table 3 - Tested blend characterization.

Blends	Ash (%DB)	VM (%DB)	FC (%DB)	S (% DB)	Rr (%)	Vit (% vol mmf)	Lip (% vol mmf)	Ine (% vol mmf)	SF (% vol mmf)	MM (% vol)	R (%)	I (%)	R/I (-)	MF (ddpm)	PR (°C)	FSI (-)
MB	8.55	26.38	65.07	0.73	0.95	56.70	6.19	37.11	23.71	3.00	70.79	29.21	2.42	393	72	6.5
MC_{15}	8.74	26.52	64.75	0.76	0.98	55.10	5.10	39.80	28.57	2.00	69.73	30.27	2.30	409	68	6.5
MC_{20}	9.07	26.29	64.63	0.78	1.02	55.10	3.06	41.84	28.57	2.00	67.69	32.31	2.09	329	69	6.0
MC_{25}	8.86	26.69	64.70	0.81	1.01	54.08	2.04	43.88	29.59	2.00	65.99	34.01	1.94	133	67	6.5

VM: Volatile matter; FC: Fixed carbon; S: Total sulfur; Rr: Mean random reflectance of vitrinite; Vit: Vitrinite maceral group; Lip: Liptinite maceral group ; Ine: Inertinite maceral group; SF: Semifusinite maceral; MM: Mineral material; R: Reactives macerals (Vit + Lip + 1/3 SF); I: Inerts macerals (Ine - 1/3 SF); R/I: Ratio between reactives and inerts macerals; MF: Maximum fluidity; PR: Plastic range; FSI: Free-swelling index; DB: Dry basis; vol: Volumetric; mmf: Mineral material free.

The coking tests were carried out at the ArcelorMittal Tubarão industrial plant, with a nominal capacity of 1.7 Mt/y, consisting of 3 Carl Still-type batteries with 49 ovens each, totaling 147 top-charge ovens with a height of 6.5 m, a length of 15.2 m and a width of 0.42 m. The useful volume of the ovens was 39.5 m^3 and an average load of 32 t of coal with a moisture of 10 % and a granulometry of 83 % below 3.36 mm to obtain a charge density of 750 kg/m^3. The total duration of the tests was 19 hours (gross coking time), reaching temperatures of over 1100 °C. The process temperature was monitored using a thermocouple located in the gas ascension pipe. After carbonization, the coke produced in all coke ovens was cooled in a nitrogen atmosphere in the dry quenching unit (CDQ). The series of tests had at least a minimum time sequence of three days of coke production at the industrial plant for each level of inertinite-rich coal content (C_{MB}, C_{15}, C_{20} and C_{25}), which made it possible to take a single representative sample of each coke produced on the third day after the complete renewal of the coal tower load and the conclusion of the previous production cycle of all the coke oven batteries, thus discarding the results of the coke produced on the first two days, which represent the transition period between each of the mixtures tested. Coke samples representing the qualitative results of the coke plant's daily production were prepared by taking increments, every eight hours of production, collected on a conveyor belt (cross-section) and produced throughout the day in accordance with established industrial routine procedures. The samples of metallurgical coke were recovered after sieving (> 25 mm).

2.3 Coke microstructural image analysis

Coke observations were performed on polished surfaces using a Leica DM6000 optical microscope having the reflected light set at 50x magnification (10x and 5x for ocular and objective lens, respectively) resulting in images of 2500 x 1800 µm size and 0.8819 pixels/µm resolution, associated with image analysis treated by the public domain software ImageJ, developed at the National Institutes of Health with the possibility of implementing programming language for macro execution using identification patterns of the studied parameters in the coke microstructure. For this study, the experimental methodology developed by LaSid - UFRGS Iron and Steelmaking Laboratory was used, which consists of defining the experimental parameters (number of samples, analyzed sample area, particle size), capturing microscopy images and image analysis routine to obtain the microstructural parameters (Agra *et al*., 2021). After obtaining parameters related to the porous microstructure of the cokes, relationships were determined between the level of inert additives in the coal blend and the mechanical strength of the coke.

3. Results and discussion

3.1 Coke mechanical strength

The indices of cold mechanical strength were assessed by a drum test ($DI_{150/15}$), according to JIS K-2151, and the results for the industrial cokes ranged from 85.20 % (C_{MB}) to 84.40 % (C_{25}), showing a reduction in the absolute value of the index as the M_2 coal was replaced by M_3 in the series of test blends, according to the reduction in the R/I ratio indicated in Figure 2. This behavior can be attributed, in part, to the changes in fluidity and rank of the test blends, since the addition of M_3 coal reduces the fluidity of the blends, promoting less agglomeration of the coal particles during the carbonization process. This weakens the coke by the appearance of defects in the porous structure and consequent reduction of mechanical strength. The addition of selectively crushed inertinite-rich coal (M_3), under more severe conditions than the rest of the blend and average coal particle sizes close to 1.5 mm, resulted in suitable cokes (C_{15} and C_{20}) that remained with values close to the reference coke (C_{MB}). A significant reduction in the mechanical strength property is observed for the inert saturated coke (C_{25}).

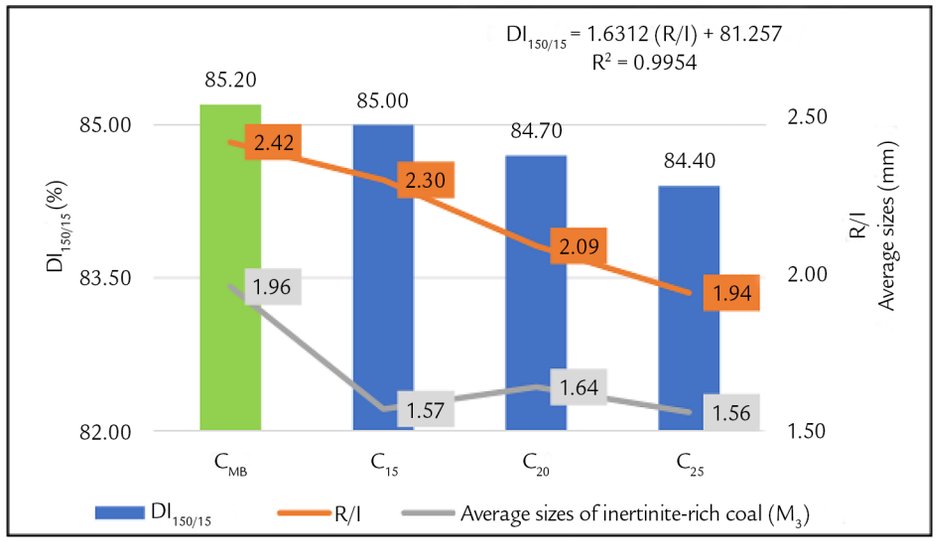

Figure 2 - Tumbling test ($DI_{150/15}$) for industrial cokes and ratio (R/I) and average sizes of inertinite-rich coal (M_3) added in the blends studied.

Considering the analytical variation of the JIS K2151 standard, which admits a standard deviation (σ) of 1.5 %, the $DI_{150/15}$ index was maintained for the cokes tested. However, in a more restrictive way, this study considered the reference adopted based on historical data from the industrial plant, with possible variability of results of up to 0.4 % in the index for cokes from the same blend. As a result, it was found that the coke with the highest proportion of inert coal (C_{25}) shows a significant drop in the index, with a value below the lower control limit, when compared to the coke produced by the reference coal blend (C_{MB}), as shown in Figure 3.

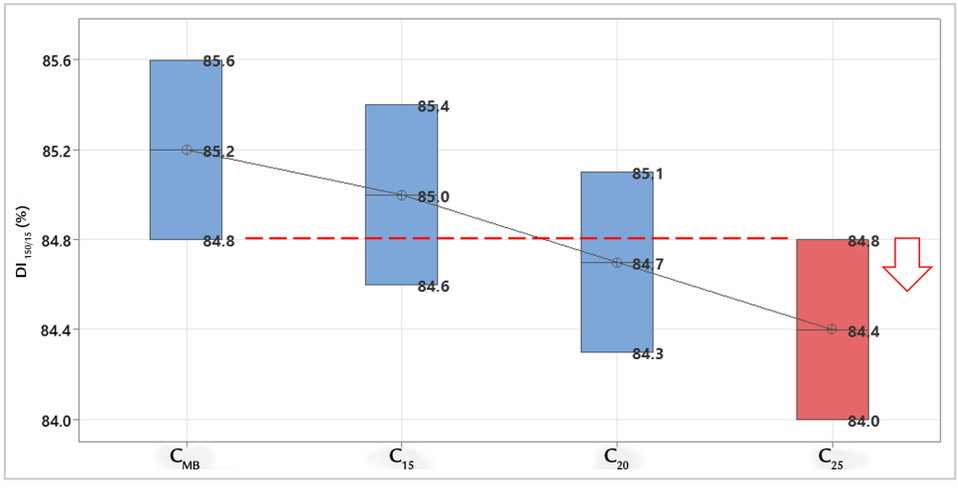

Figure 3 - Drum index results ($DI_{150/15}$) considering historical variability accepted in the industrial process of the coke plant studied.

3.2 Coke microstructural characterization

The microstructures of the industrial cokes were characterized, and the microstructural parameters: number of pores per square millimeter (N), porosity (P), average equivalent pore diameter (Deq), average wall thickness of the carbonaceous matrix of the coke (W), average roundness (C), maximum Feret diameter (Fmax) and Feret ratio (F) were extracted, as presented in Table 4.

Table 4 - Microstructural characterization of the studied industrial cokes.

Coke	N (Pores/mm²)	P (%)	Deq (µm)	W (µm)	C (-)	Fmax (µm)	F (-)
C_{MB}	11.56	45.90	225.64	341.07	0.64	271.12	1.54
C_{15}	12.41	46.12	217.57	355.62	0.63	269.55	1.60
C_{20}	12.65	41.26	204.83	397.72	0.59	262.07	1.58
C_{25}	11.13	49.54	238.22	325.49	0.66	281.46	1.55

N: Number of pores per mm²; P: Porosity; Deq: Equivalent diameter; W: Wall thickness; C: Circularity; Fmax: Maximum Feret diameter; F: Feret ratio

The parameter number of pores per area in mm² (N) ranged from 11.13 to 12.65 for cokes C_{25} and C_{20}, respectively. These same cokes presented extreme values for the parameters porosity (P) and the pore size (Deq). Sample C_{25} was characterized as the coke with the highest porosity (49.54 %) and largest pores (238.22 µm). It is reasonable to assume that the parameters: number of pores per area, porosity and pore size are strongly related. Therefore, it is assumed that the larger the pore size, the higher the total porosity. However, this condition is not always observed, as one must also consider the number of pores per area and the thickness of the walls in the carbon matrix. For example, the number of pores per area for coke C_{15} and C_{20} are similar, 12.41 and 12.65, respectively, however they have different porosities. This is due to the larger pore size and smaller wall thickness in coke C_{15}. Thus, it is found that it is not possible to describe the porous microstructure of coke by considering only an individual microstructural parameter, as described previously (Patrick *et al.*, 1980; Agra, 2019). Other parameters of the coke microstructure presented in Table 4 are related to the shape of the pores, being considered more suitable those with shapes that approximate to a circle. The parameters of circularity (C), equivalent diameter (Deq), maximum Feret (Fmax) and Feret ratio (F) measure how far the pore is from the shape of an ideal circle. The circularity of the cokes ranged from 0.59 for coke C_{20} to 0.66 for coke C_{25}. Considering the other shape factors, Feret ratio (F) and the difference between Deq and Fmax, it was also verified that the pores of coke C_{25} present the most appropriate shapes. Based on these parameters, therefore, coke C_{25} outperformed coke C_{20}, which presented worse shape factors for pores, characterized by a higher Feret ratio and a higher difference between Deq and Fmax. The circularity is calculated by the ratio between the area and the perimeter of the pores, with the circularity being lower for pores with more sinuous contours. The Feret ratio considers the ratio between the largest and smallest pore dimensions. Also, the difference between Deq and Fmax is used to measure the difference between the largest dimension of a pore and the diameter of a circle equivalent to the area of this pore. All shape measurements are used to quantify the pores in relation to the ideal circular shape that is associated with the highest mechanical strength.

The coke with the highest participation of inertinite-rich coal (C_{25}) presented a high number of critical pores, quantitatively indicated on Table 5, being considered more susceptible to rupture and failure of the material, classified by equivalent diameter (Deq) greater than 300 µm and circularity (C) less than 0.2 (Kubota *et al.*, 2011; Meng *et al.*, 2017).

Table 5 - Percentage distribution of pores in industrial cokes classified by size (Deq > 300 µm) and shape (C < 0.2) critical to mechanical strength.

Coke	Percentage distribution of pores		
	Deq > 300 µm (%)	C < 0.2 (%)	Total critical pores (%)
C_{MB}	51.11	1.75	52.86
C_{15}	49.03	1.19	50.22
C_{20}	39.65	0.67	40.32
C_{25}	57.44	0.77	58.21

Coke C_{MB}, C_{15} and C_{20} present less porous and more regular microstructures composed of smaller pore sizes and greater wall thickness of the carbon matrix. On the other hand, coke C_{25} has higher porosity (P) and lower number of pores per area (N), with larger pore sizes (Deq, Fmax) and lower wall thickness (W). This result does not agree with previous studies described in literature, since typically, the pores from the IMDC (macerals of the inertinite group) have small dimensions, and for this reason, the contribution of these pores to the critical areas should be minimized with the greater participation of these inerts in the blends. Thus, possibly, the effect of the addition of inerts on the porosity of C_{25} coke is not related to the pores of the inertinite maceral but may be associated with changes caused by interface problems between inert particles and the RMDC (Barriocanal *et al.*, 1995). There may also be other contributions of defects on the coke surface associated with deficiencies in the boundaries of non-adhered grains of low-quality coal (Arima, 2001), and that with the inadequate dilation of these particles will form voids or connected pores in the structure after resolidification (Nomura *et al.*, 2004; Kubota *et al.*, 2011). According to Nomura *et al.*, (2004), pores characterized by low circularity or high Feret ratio, originate from connected pores, due to insufficient expansion during carbonization or pores from regions derived from inert components (IMDC). Thus, it is expected that cokes with high porosity microstructures, larger pore sizes and more suitable shapes (lower Feret ratio and higher circularity) are produced by blends of coals with a higher fluidity and R/I ratio.

Figure 4 presents images of the microstructures of the cokes in three forms: as analyzed under the microscope, binarized (segmentation of pores and matrix) and a mapping of critical pores, the areas in white being the carbon matrix, in blue, the pores classified as suitable (non-critical pores) and in red, the pores critical to mechanical strength. The critical pores were defined by pore size and shape criteria, evaluated in previous research, and compiled by the LaSid methodology (Agra *et al.*, 2021). Identified in black are the regions of edge pores cut off by the image borders that have not been completely revealed. If edge pores are taken into account in the analysis, then average measurement of pore size and shape would be wrongly determined, as the software does not have the correct size and shape of these pores (Agra *et al.*, 2021).

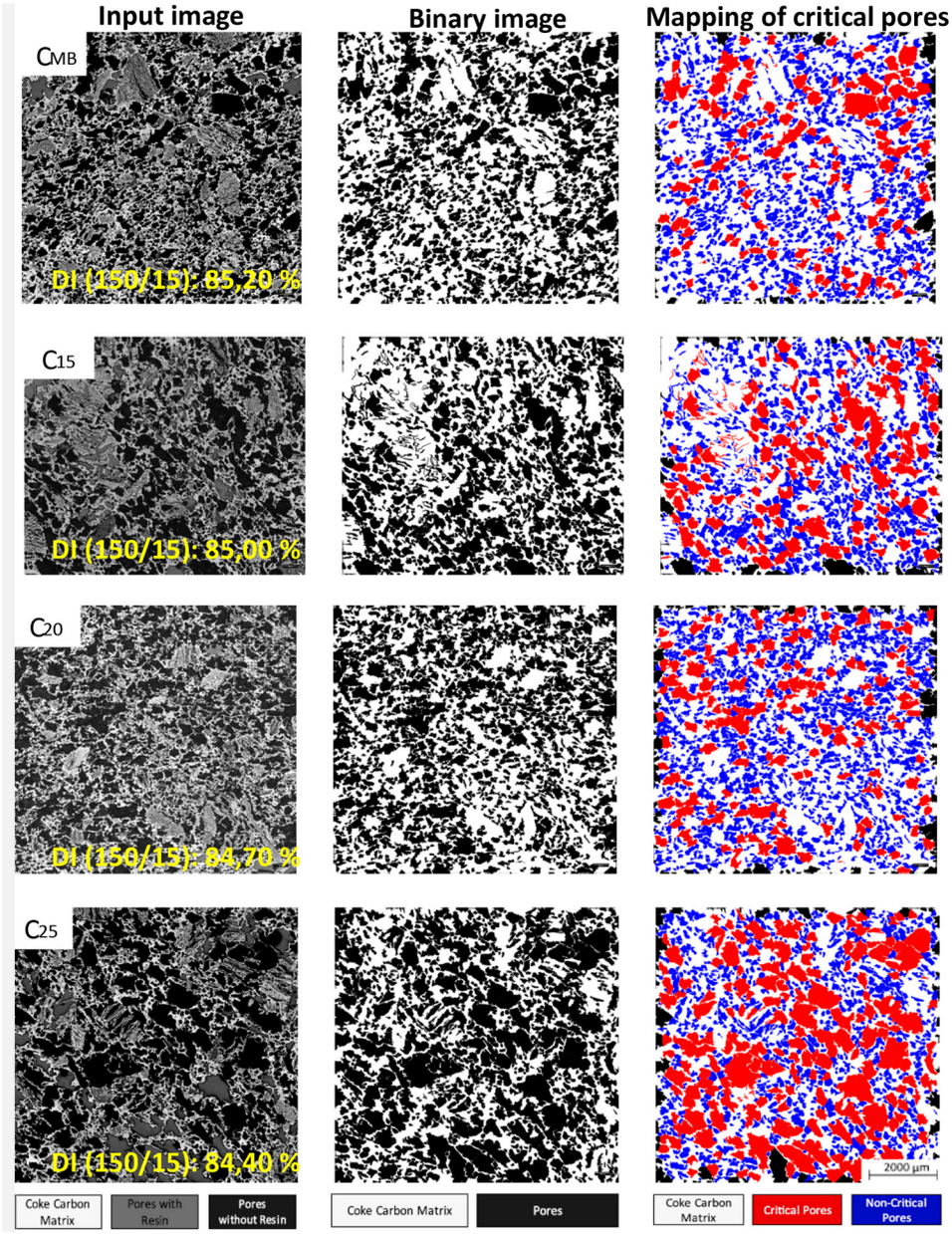

Figure 4 - Porous microstructure of cokes studied with as analyzed images, segmented binary images and pore mapping by size (Deq > 300 µm) and shape (C < 0.2) critical to mechanical strength and $DI_{150/15}$ results. 50x magnification.

3.3 Characterization of RMDC and IMDC

The carbon matrix of the coke is divided into a reactive compound derived region (RMDC) and inert compound derived region (IMDC). Table 6 presents the microstructural parameters related to RMDC for the industrial cokes studied, excluding IMDC areas that were removed from the analysis.

Table 6 – Characterization of the porous microstructure of cokes (RMDC) for industrial cokes studied with inert segmentation.

Coke RMDC	N (Pores/mm²)	P (%)	Deq (µm)	W (µm)	C (-)	Fmax (µm)	F (-)
C_{MB}	10.38	43.58	233.16	391.63	0.68	277.05	1.53
C_{15}	11.91	47.15	224.94	356.97	0.65	274.54	1.58
C_{20}	11.94	41.22	210.89	404.16	0.60	265.99	1.56
C_{25}	10.12	48.99	248.23	359.28	0.69	287.71	1.52

N: Number of pores per mm²; P: Porosity; Deq: Equivalent diameter; W: Wall thickness; C: Circularity; Fmax: Maximum Feret diameter; F: Feret ratio

In all cokes, a reduction in the number of pores per area (N) was observed, compared to the characterization of the cokes without the segmentation of the inerts indicated in Table 4. This change is due to the removal of the pores of the IMDC, which have small sizes and acicular shapes. With this, we also observed an increase in

the equivalent diameter (Deq) and circularity (C) of the pores measured only in the RMDC. The evaluations of the microstructural parameters of the cokes without and with inert segmentation, indicated in Tables 4 and 6, respectively, show that the cokes maintain similar characteristics due to the influence of the RMDC which are found in greater proportion in the microstructure of the materials.

The IMDC contributes with several deleterious effects to the porous microstructure of the coke with potential impact on the mechanical strength of the material, such as stress concentration within the microstructure, mainly dependent on the volume of the IMDC (Kubota *et al.*, 2008; Donskoi *et al.*, 2017), heterogeneity of mechanical properties (Andriopoulos *et al.*, 2003) and interface problems, usually caused by deficiency of agglutination of the inert particles by the RMDC (Barriocanal *et al.*, 1995). As described above, the size and shape of the inert particles are important factors for the depreciation of the mechanical strength of the coke and contribute to potentiate the effects on the microstructure of the coke. Therefore, these regions are the preferred sites for the formation and propagation of cracks as a result of the interaction between the inerts (IMDC) and the carbon matrix (RMDC) that have different thermal coefficients of contraction and expansion (Loison *et al.*, 1989).

Table 7 presents the microstructural parameters related to the IMDC for the industrial cokes studied.

Table 7 - Characterization of IMDC for studied industrial cokes.

Coke RMDC	AIMDC (%)	Deq-I (mm)	P (mm)	Fmax-I (µm)	F-I (-)
C_{MB}	10.2	4.028	5.220	1710.1	1.92
C_{15}	5.6	2.859	3.773	1348.8	2.15
C_{20}	14.4	3.293	3.820	1289.3	1.82
C_{25}	13.6	2.701	3.078	1033.1	1.98

AIMDC: IMDC Area; P: Porosity; Deq-I: Equivalent diameter; P: Perimeter; Fmax-I: Maximum Feret diameter; F-I: Feret ratio

According to Table 7, the cokes with the highest contents of inertinite-rich coal, respectively 20 % and 25 % in the C_{20} and C_{25} coke blends, present the highest IMDC areas in relation to the reference coke (C_{MB}). For coke C_{15}, this relationship was not confirmed, and a reduction in the percentage of IMDC area was observed when compared to C_{MB}. The size of the IMDC is smaller in coke C_{15}, C_{20} and C_{25} than in the reference coke (C_{MB}), presenting lower values for equivalent diameters (Deq-I), maximum Feret diameters (Fmax-I) and perimeters (P), confirming the expected effect due to the reduction of the particle size obtained in the selective crushing of the coal with the highest content of macerals of the inertinite group (M_3). The lower Feret ratio of the IMDC for C_{20} coke indicates the best shape for the inerts of this coke.

Figure 5 visually shows that C_{MB}-coke has larger inert particles due to denser areas of straight contours at the interface with the carbon matrix, typical of unmelted material from regions derived from inert components (IMDC). On the other hand, cokes C_{15}, C_{20} and C_{25}, which had an increase in the participation of inertinite-rich coal, show an increase in the volume of these regions and smaller particle size, as expected with the change in the crushing process and consequent particle size reduction of the inert particles.

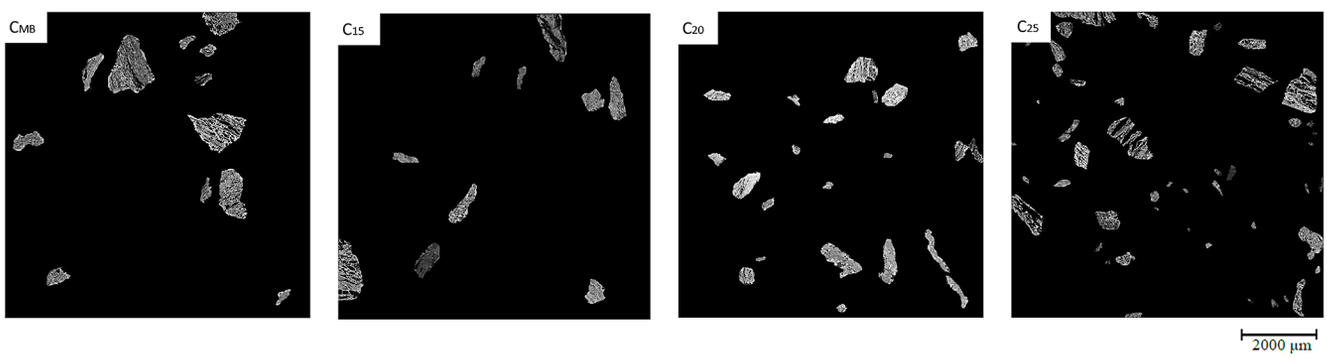

Figure 5 - Inert particles (IMDC) in coke samples. 50x magnification.

Tumbling tests ($DI_{150/15}$) for industrial cokes studied with the addition of selectively crushed inertinite-rich coal (M_3), under more severe conditions than the rest of the mixture and average coal particle sizes close to 1.5 mm resulted in suitable cokes (C_{15} and C_{20}) that remained with values close to the reference blend coke (C_{MB}).

Figure 6 shows cracks observed in (a) the microstructure of the reference blend coke (C_{MB}) due to the deficiency of agglutination at the interface of the larger inertinite with the carbon matrix. Also, transgranular cracks formed at various points of the IMDC, including branching inside the particle, generally caused by stress concentrator effect in the coke microstructure, and the positive effect resulting from the size reduction of the inertinite-rich coal in the (b) porous microstructure of the C_{20} coke, which presented the lowest Feret ratio of the IMDC. If these inert particles are small enough, the elasticity of the coke should relieve the stress formed. However, these points will still be preferred

sites for fracture on mechanical impact (Loison *et al.*, 1989). C_{20} was the coke with the highest content of inertinite-rich coal in the study (20 %) which still maintained the strength index result ($DI_{150/15}$) in the permissible control range. The average size of inertinite-rich coal (M_3) in MC_{20} blend of 1.64 mm corroborates with results of Kubota *et al.*, (2008) and Donskoi *et al.*, (2017).

Table 8 shows the relationships between the coke's microstructural properties and the mechanical strength determined by the diametral compressive stress (S), according to the equations in the literature. The low correlation obtained for the R1 equation agrees with the results initially tested for different cokes (Patrick & Stacey, 1975, 1978; Patrick *et al.*, 1980; Patrick, 1983), demonstrating that coke porosity alone is not enough to describe mechanical resistance behavior. In this relationship, it is also necessary to consider geometric factors relating to pores, such as shape and size, according to equations R2 to R6 proposed later, since at that time these structural characteristics were already considered highly significant (Brown *et al.*, 1964).

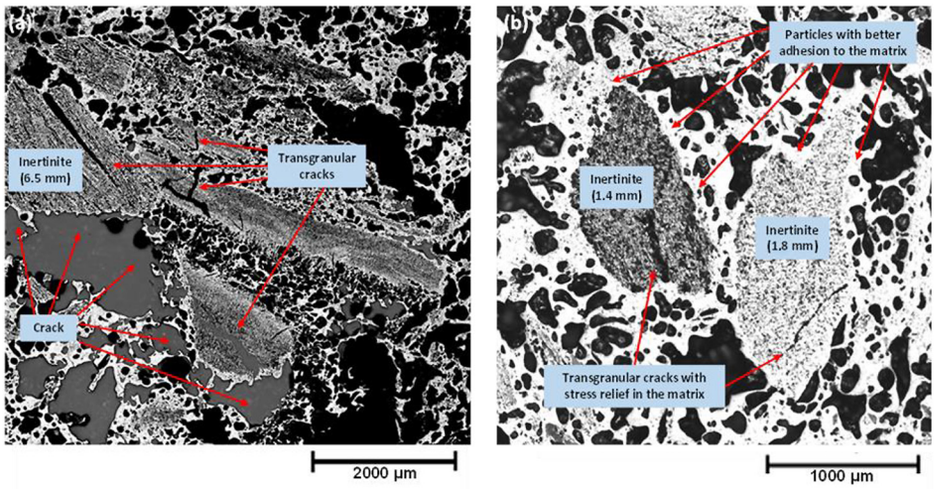

Figure 6 - Cracks observed in microstructure (a) developed radially from larger size inertinite in reference coke (C_{MB}) and microstructure (b) with agglutination of smaller inert particles by RMDC and transgranular cracks with stress relief in the coke matrix of lower Feret ratio of the IMDC (C_{20}). 50x magnification.

The relationships tested by equations R1 to R6, adapted for the $DI_{150/15}$ drum tests, showed low coefficients of determination (R^2). However, all the equations only consider the microstructural parameters relating to the regions derived from the reactive components (RMDC), and the effects of the regions derived from the inert components (IMDC) are not attributed. Since the aim of this work is to maximize the inert content in the industrial blend of coals to produce coke, it is necessary to confirm the hypothesis that the coke with the highest proportion of inert coal (C_{25}), whose mechanical behavior differs from the other coals, probably does not satisfy the equations tested because it is considerably influenced by the high proportion of inert particles not considered by these models. New relationships were carried out, this time studying only the C_{MB}, C_{15} and C_{20} coke samples, showing a significant increase in the coefficients of determination (R^{2*}), which are significantly closer to 1 when compared to the initial relationships considering all the coke samples (R^2), including the C_{25} coke considered to be saturated in inerts. Thus, for coke considered to be unsaturated in inerts, only the parameters related to the RMDC seem to be sufficient to describe the mechanical behavior, assuming an approximation of these equations from the literature for modelling the industrial coke studied, the drum index and the porous microstructure characterization methodology used. However, for a complete description of the mechanical behavior of coke, including coke produced with a high proportion of inert coal (saturated in inert), it is necessary to include the contributions of IMDC in the equations.

Table 8 – Correlations obtained from equations proposed in the literature.

Equation	Relationship	Author	R^2	R^{2*}
R1	$S = Smax\ exp(-bP)$	Patrick and Stacey, 1975	0.125	0.77
R2	$S = K\ (Fmax)^{-0.5}\ exp[-2(Fmax/Fmin)^{-0.5}\ P]$	Patrick, 1983	0.065	0.92
R3	$S \times N = W / Deq$	Patrick, 1983	0.003	0.87
R4	$S \times N = 10^3 \times W/Deq^2$	Patrick and Walker, 1989	0.010	0.93
R5	$S = W / Deq$	Andriopoulos *et al.*, 2003	0.013	0.97
R6	$S+ = (W \times SF \times RF) / (P \times Deq)$	Meng *et al.*, 2017	0.012	0.94

R^2: Coefficient of determination considering all the cokes studied; R^{2*}: Coefficient of determination excluding coke with a 25% inertinite-rich coal content.

As can be seen in Table 8, equation R5, adapted for the $DI_{150/15}$ tumbling test, was the one that showed the best relationship between the microstructural properties and the mechanical strength of the coke, considering only the microstructural parameters related to the RMDC (R^{2*} 0.97), excluding coke saturated in inerts (C_{25}) from the tests. After characterizing the

IMDC, it was possible to use a new relationship proposed to incorporate the negative contribution of the inerts to the coke's mechanical resistance (- Deq-I x F-I). This suggested relationship, called R7, takes into account the size and shape parameters of the inert particles. In this way, a more complete equation was tested to describe the mechanical strength of coke ($DI_{150/15}$), considering the contributions of RMDC (R5) and IMDC (R7). The coefficient of determination of the revised equation from the literature (R^2), applied to the industrial cokes studied, was significantly improved from 0.013 to 0.82. A new regression given by equation (1) has a positive contribution of the RMDC (Table 6), described by the ratio (W/Deq), which contributes to the increase in the mechanical strength of the coke due to the greater wall thickness (W) and smaller pore size (Deq). This agrees with previous research (Patrick, 1983; Patrick & Walker, 1989; Andriopoulos *et al.*, 2003). There is also the negative contribution of the IMDC (Table 7) with the addition of the factor (- Deq-I x F-I) leading to the depreciation of the mechanical strength of the coke of a larger size (Deq-I) and the irregular shape (F-I) of the inert particle, corroborating previous research (Kubota *et al.*, 2008; Donskoi *et al.*, 2017; Agra, 2019).

$$DI_{150/15}\ (\%) = 83.96 + 0.120\ (W/Deq) - 0.0509\ (Deq\text{-}I \times F\text{-}I) \quad (1)$$

Figure 7 shows the relationship between the drum index determined in the test and the calculated value with the new equation describing both microstructural features from reactive and inert components. A test was carried out for each of the point shown in the figure, which represents the quality of industrial coke for a daily production of around 4 kt for each of the blends studied.

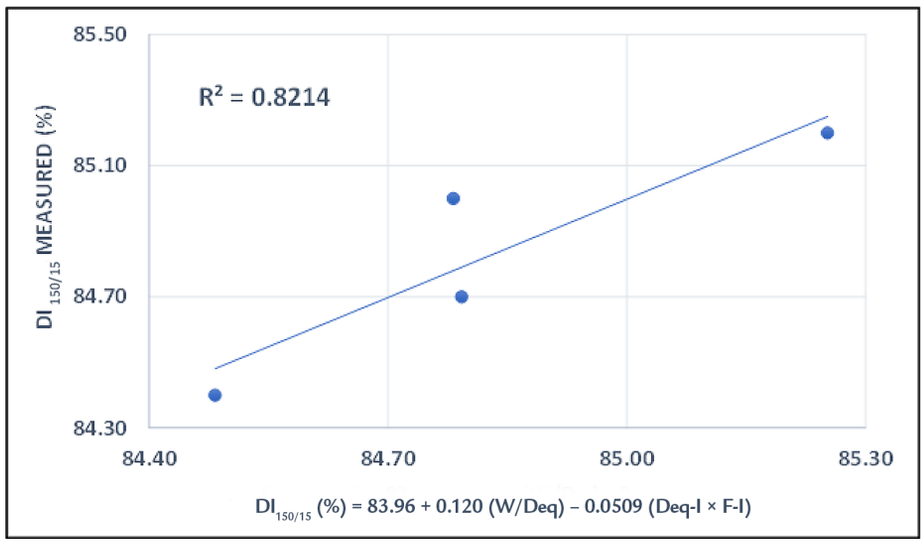

Figure 7 - Relationship between measured and calculated drum index with new equation.

4. Conclusion

The objective of this study was to maximize the addition of inertinite-rich coal in a blend for coking, from selective crushing with reduction of the size of maceral particles of the inertinite group. The results showed that:

The MC_{15} (R/I 2.30) and MC_{20} (R/I 2.09) blends with fluidity in the range of 200 to 1000 ddpm and the inertinite-rich coal with an average size of 1.55 mm generated cokes with satisfactory mechanical performances compared to the reference coke (R/I 2.42), whose inertinite-rich coal size was 1.96 mm.

The coke produced from the MC_{25} blend with low fluidity (< 200 ddpm) and high participation of inertinite group macerals (R/I 1.94), showed the worst performance in the tumbling test. This result was attributed to the unfavorable thermoplastic and petrographic properties with high concentration of inerts, saturating the carbon matrix, despite the size reduction of the IMDC.

The inert saturated coke (C_{25}) showed a high number (58.21 %) of pores critical to mechanical strength, classified by size (Deq > 300 µm) and shape (C < 0.2), considered more susceptible to rupture and failure of the material by mechanical stress. This result is not in line with previous studies described in the literature, since the pores of IMDC (inertinite group minerals) are typically small. Therefore, it is possible that the effect of the addition of inerts on the porosity of C_{25} coke may be associated with alterations caused by interface problems between the inert particles and the RMDC, defects in the coke surface associated with deficiencies in the boundaries of the non-adhered grains of low quality coal and related to the inadequate dilation of these particles, which will form voids or connected pores in the structure after resolidification.

This study of industrial application reinforced previous research on a pilot and laboratory scale, confirming a value of approximately 1.5 mm as the critical inertinite (or inert particle) size for the mechanical strength of coke. The maximum limit of 20 % in the participation of inertinite-rich coal in coking blends can be obtained on industrial scale application, without prejudice to the quality of the coke, from selective crushing of inertinite-rich coal aiming at reducing the average size to 1.5 mm.

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