INFLUÊNCIA DA ADIÇÃO DE ALCATRÃO NA QUALIDADE DO COQUE*

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Resumo

Métodos alternativos têm sido desenvolvidos para aumentar o uso de carvões semi-soft na produção de coque metalúrgico. Neste artigo, a influência da adição de alcatrão sobre a qualidade do coque foi analisada. Os testes foram executados em escala piloto com adição desse aditivo em 2 e 5%. Os resultados mostraram uma melhoranas principais propriedades (CSR, CRI e DI) e na fluidez da mistura.

Palavras-chave:Alcatrão; Piche; Coque metalúrgico; Resistência mecânica.

INFLUENCE OF COAL TAR ADDITION ON COKE QUALITY

Abstract

Alternative methods have been developed to increase the usage of semi-soft coking coal to produce metallurgical coke. In this paper, the influence of coal tar addition on coke quality was analyzed. The tests have been made in pilot-scale coke oven with the addition of 2 and 5% of the additive. The results have shown that the main properties (CSR, CRI and DI) and the fluidity of the blend have improved.

Keywords: Coal Tar; Pitch; Metallurgical Coke; Mechanical Resistance.

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1 INTRODUCTION

Coke is unavoidable raw materials for the blast furnace which could be attributed to many vital purposes. Coke plays triple roles in the blast furnace, namely physical, chemical and thermal functions. The physical role includes the supporting of burden descending, enhancement of gas distribution and gas permeability in the shaft, percolation of liquid iron and adsorption of dust. So far, there is no other material able to achieve the required permeable matrix and counter-current mechanism between gases and solids in the blast furnace. The chemical role includes a generation of reducing gas for indirect reduction, direct reduction of hard reducible oxides, and carburization of hot metal. The thermal role is mainly heat generation through the exothermic combustion of carbon with hot blast. About 80% of heat supply is coming from the combustion process of carbon while 20% is provided by the hot blast [1]. Therefore, coke cannot be totally replaced in a blast furnace due to many of these reasons. However, the production of metallurgical coke must face some challenges, such as the future depletion of hard coking coal (the worldwide reserve of prime coking coal is only 4%) and coke represents the most expensive feed material used in the blast furnace.

Consequently, it is of great importance to develop alternative methods to improve the characteristics of the coal blend, making it possible the use of semi-soft coking coal to reduce costs and, simultaneously, improve coke quality. Nonetheless, semi-soft coking coal is inferior in caking property such as dilatation and fluidity to hard coking coal. To improve these property, various technologies have been developed and commercialized such as measures to increase bulk density [2], optimum coal crushing [3-5] and additives for improving coal caking property [6-9].

In this paper, the mechanism investigated was the addition of coal tar on the coal blend to produce metallurgical coke.Figure 1 illustrates some of by-products obtained during the coke making process. Coal tar is one of them, it is an organic additive, formed by the union of polycyclic aromatic hydrocarbons, phenols and heterocyclic compounds of oxygen, sulfur and nitrogen, mainly aromatic substances, as shown in Figure 2.

Coal tar is a thermoplastic material, when subjected to heat treatments under suitable conditions, transforms itself into graphitized solid carbon, passing through an intermediary phase of the pyrolysis denominated mesophase. All those characteristics provides several applications, such as: binder, impregnator and sealant.

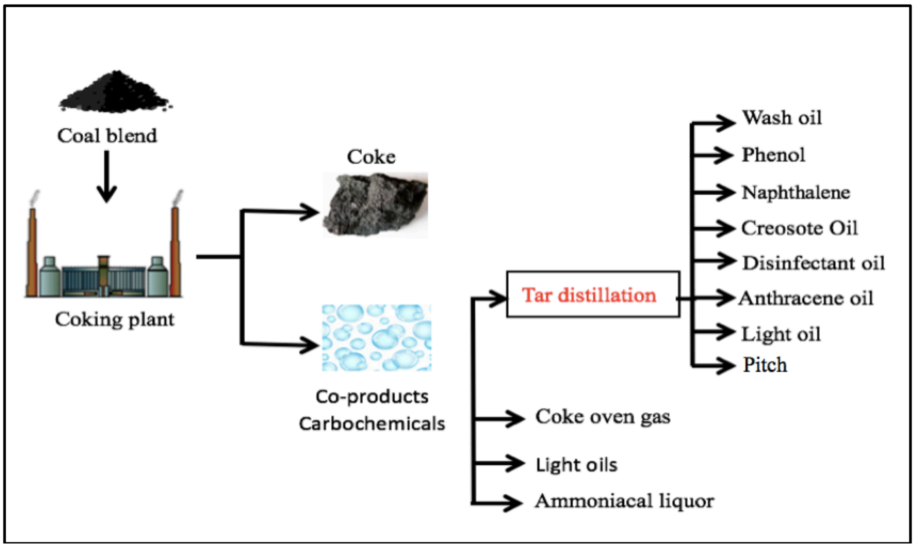

Figure 1. The main co-products of coke production.

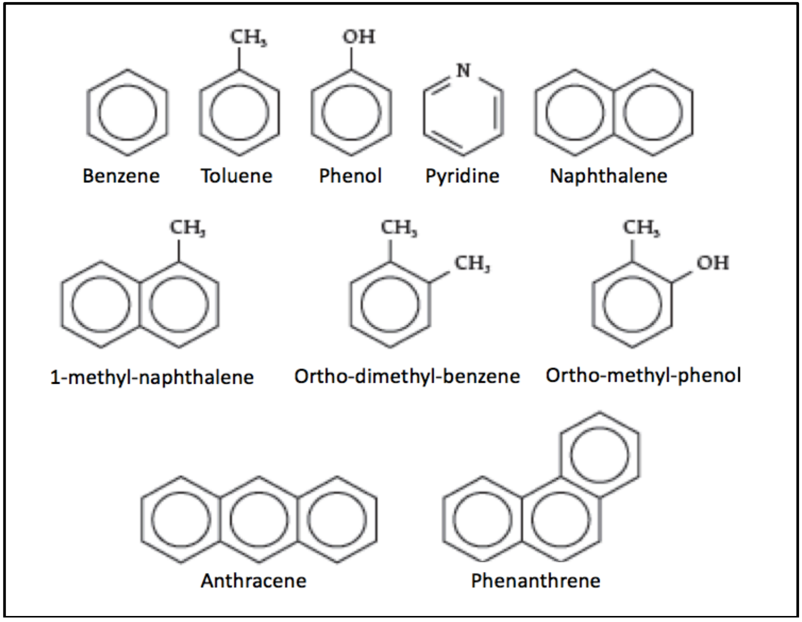

Figure 2. Composition of coal tar.

Many tests have been made with additions of the order of 2-6% of coal tar, and it has been shown that the caking property and coke strength can be increased [11-12]. The mechanism of how binder improves caking property is still unclear, however there are many studies on the interaction between them during heat treatment and how this interaction changes with the type of additive and affects the coal caking property [13-15]. The purpose of this paper is to investigate the influence of coal tar addition on coke main parameters (DI, CSR and CRI). The results obtained were compared with the standard values, making it possible to estimate the effects on coke quality according to the amount of additives added.

2 MATERIALS AND METHODS

The experiments required to realize this study were performed at Gerdau Plant Ouro Branco. The tests were made in a pilot coke plant. Figure 3 represents the flowchart of the process.

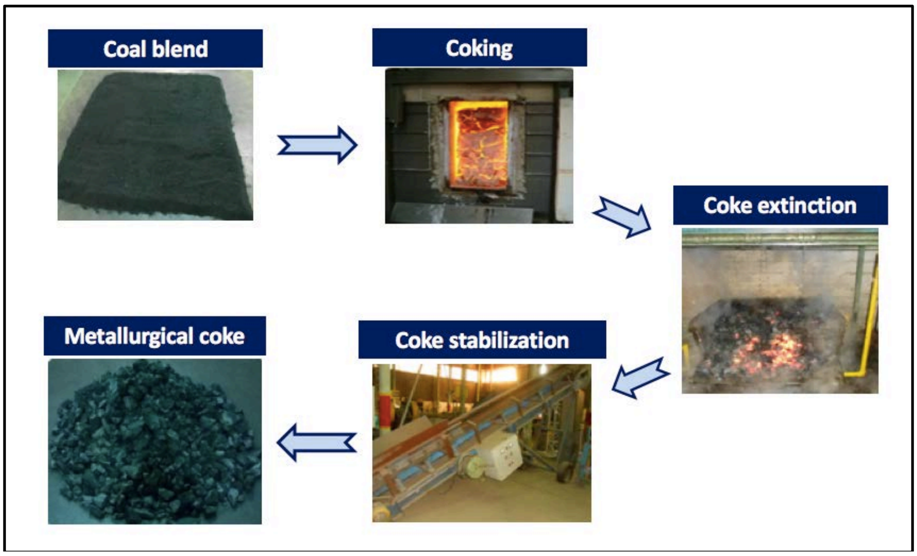

Figure 3. Flowchart pilot unit.

The first stage of this work was the collection and preparation of raw materials. The physical-chemical composition of the base coal blend used in this study is shown at Table 1.

Table 1. Physical-chemical metallurgical characterization of the base mix

Moisture (%)	**VolatileMatter (%)**	**FixedCarbon (%)**	**Ash (%)**	**Sulfur (%)**	**Fluidity [log (ddpm)]**	**Reactive (%)**
8,96	22,53	67	6,02	0,34	2,925	69,27
Na_2O (%)	**K_2O (%)**	**Al_2O_3(%)**	**CaO (%)**	**MgO (%)**	**Fe_2O_3(%)**	**SiO_2(%)**
0,35	1,4	25,45	1,35	0,71	5,9	60,75

Table 2 exhibits the main characteristics of the coal tar utilized in these experiments.

Table 2. Characterization of coal tar

	Ash (%)	**Density (g/cm^3)**	**H_20(%)**	**MIQ (%)**	**MIT (%)**	**Fluidity[log (ddpm)]**
CoalTar	0,18	1,211	0,2	4,47	8,47	16 (100°C)

An electrically heated pilot-scale coke oven was used for the carbonization process. The samples were charged in the oven with a bulk density of 850 kg/m^3 and humidity of 8%. They were carbonized for 20 h under heating conditions equivalent to a flue temperature of 1200 °C in an actual coke oven. Tests were performed in triplicate for each percentage of additive, 0, 2 or 5% of coal tar. A total of 9 experiment were carried out.

After the coking period, it was produced a mass of approximately 80 kg of coke for each sample. The CSR (Coke strength after reaction), CRI (Coke reactivity Index), DI (Cold mechanical resistance) and fluidity tests were performed in the Raw Materials Laboratory at Gerdau Ouro Branco. The current method adopted to obtain the CRI and CSR values is from Nippon Steel Corporation (NSC). Figure 4 shows a summaryofthemethodologyused.

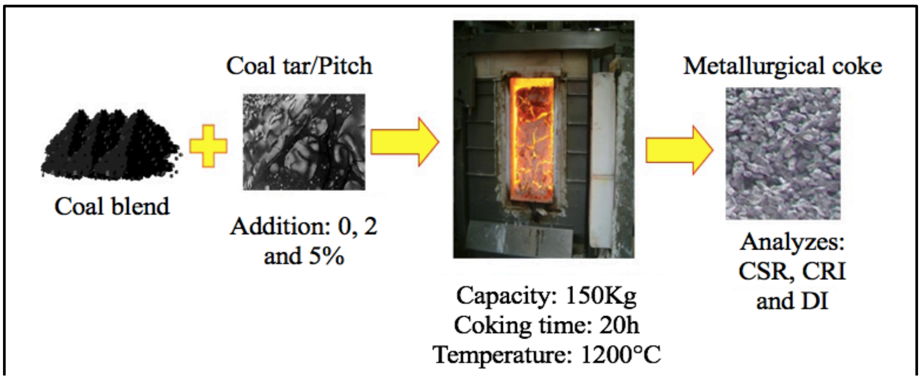

Figure 4. Illustration of the experimental methodology used in this work.

2.1 Mechanism

The main reason why coal tar improve coke quality is the development of liquid-crystal (mesophase) and optical anisotropic texture during co-carbonization of coal and additive [15-16]. The interaction between the additive and coal during heat treatment stimulates the formation of anisotropic cokes. This interaction works as a binder for coal particles, reducing and preventing cracks or fractures formation on coke particles (Figure 5). This phenomenon occurs due to hydrogen transfer reactions and the availability of donatable hydrogen of the additives to give high fluidity/low viscosity to the systems. In such conditions, aromatic molecular systems have enough mobility to stack parallel to each other resulting in a more ordered coke structure [17].

Among the characteristics of coal-tars, the thermal reactivity of their constituents is one of the most important because it determines the development of mesophase and, consequently, the structure of graphitizable carbons (cokes). The development of mesophase occurs due to increasing temperature or longer periods of heat treatment, allowing the spheres to grow and coalesce into large drops with anisotropic texture. Those areas transform later into a material known as apparent mesophase. This material is characterized by maintaining the properties of a liquid crystal.

Higher temperatures cause pyrolytic reactions of mesophase to become infusible, converting it into cokes of needle or mosaic textures. The possibility of producing mesophase with anisotropic structural features allows to obtain materials with highly oriented structure.

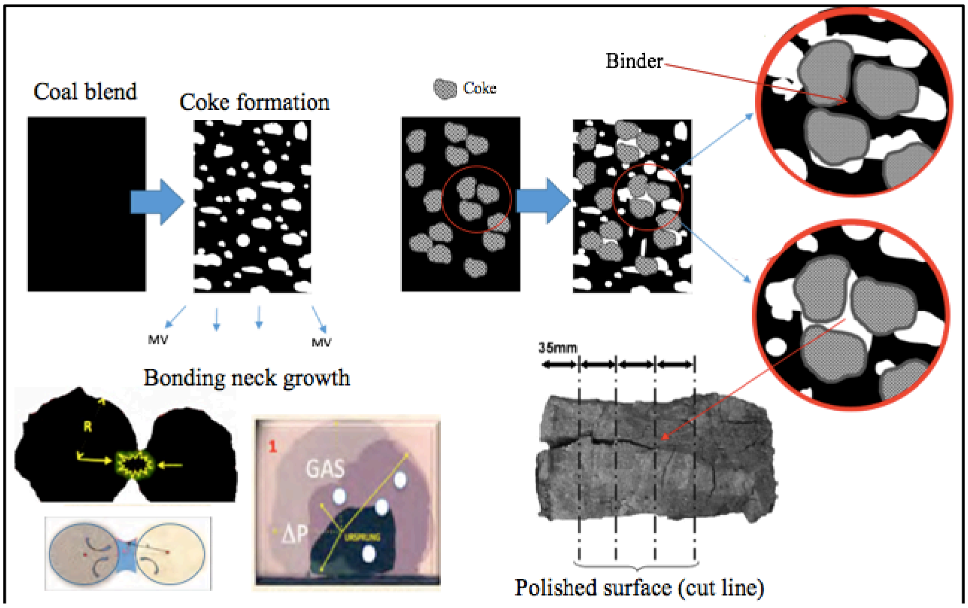

Figure 5. Representation of the additives working as a binder for coal particles.

The mesophase has a behavior of a discotic nematic liquid crystal, thermotropic and chemically reactive. It can be soluble or insoluble in organic solvents and it may also have a reversible character of dissolution or precipitation. The difference between mesophase and conventional nematic liquid crystal is the glass transition, the mesophase can maintain the anisotropic characteristic observed during fluid state in the vitreous state.

During the carbonization process, free radicals are thermally induced, when they are not stabilized by transferable hydrogen from the system, they may rapidly recombine with other species present in the high viscous system to form isotropic carbon and small-sized anisotropic carbon structures. However, when the radicals are stabilized, the growth and coalescence of mesophase takes place and an ordered anisotropic carbon structure is formed. When the system presents less donatable hydrogen available, intermediate free radicals may decompose into gaseous products and condense into coke. In such conditions, reactive free radicals can moderately be stabilized by the hydrogen donor compounds present and the condensation of aromatic molecules is accelerated because the additives cannot satisfy the demand of transferable hydrogen [17].

The formation and the effective stabilization of radicals by hydrogen transfer depend upon the chemical composition of the additives and the reactivity of its components. Their hydrogen donor and acceptor abilities can be associated with the amount of volatile matter released between 400 and 508C in the carbonization process.

A study was made to verify pitches ability to donate hydrogen and, accordingly to it, almost all types of pitches have shown good results, the highest being for petroleum pitches. For pitches derived from coal tars and those generated in the by-product plants as a residue, the contribution of ability to donor hydrogen accounts for more than 67% [17].

3 RESULTS AND DISCUSSION

Figure 6 represents the results obtained from the addition of 0,2 and 5% of coal tar in the coal blend on each coke quality parameter. A linear relation was made to estimate the impact of different percentages of addition. The expected values for the addition of 1% of coal tar also is shown in figure 6.

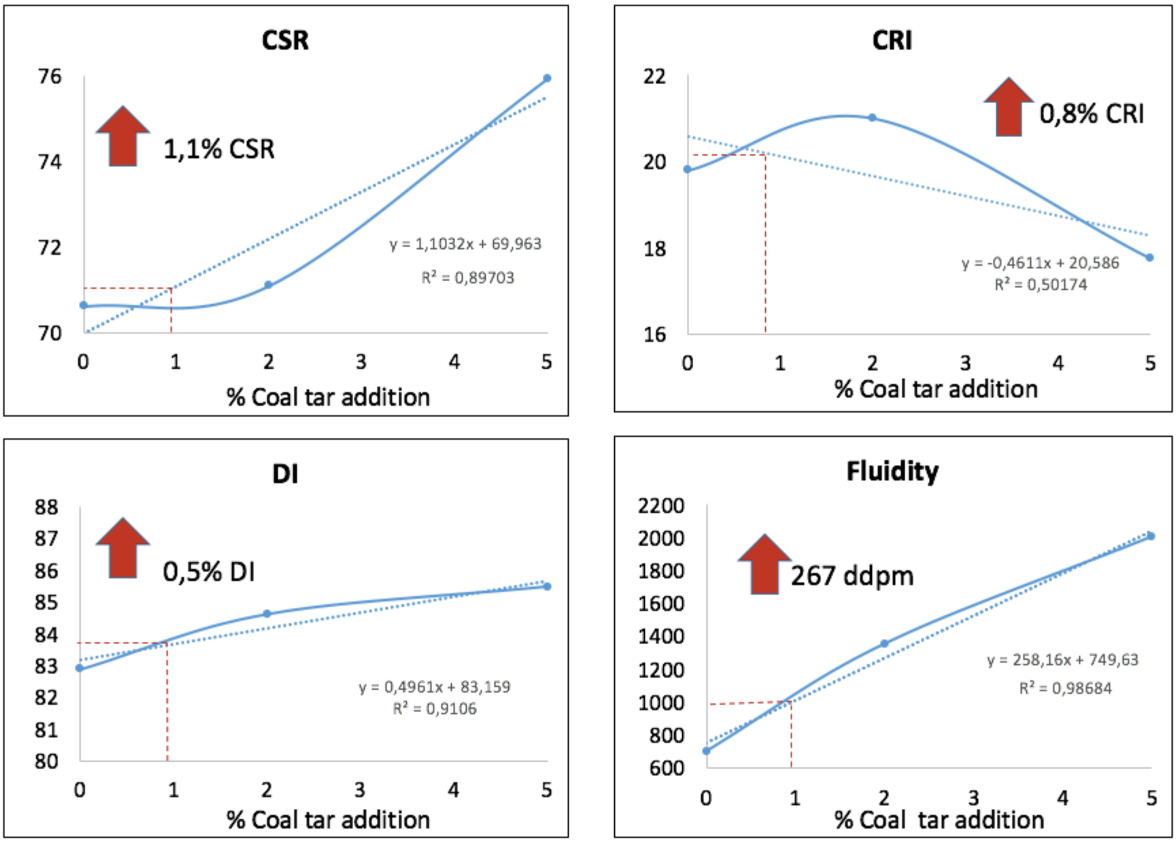

Figure 6. Influence of the coal tar addition in different percentage in each parameter of quality.

3.1 Fluidity

Fluidity is responsible for the cohesion of the coke structure. Insufficient cohesion of the carbonaceous matrix (low fluidity) results in a lower mechanical resistance and higher reactivity. Likewise, an excessively fluidity produces an extremely porous coke with inadequate properties. This indicates the existence of an ideal flow range, which promotes sufficient cohesion for the carbonaceous matrix and at the same time does not produce an exaggerated amount of pores.

One of the most important properties of coal in relation to coking is the plastic stage. Consequently, the influence of any additive on a coal's thermoplastic properties must be tested before it is used in the coal blends. A fluid phase is the requirement to produce graphitizable carbons. Fluidity measures how fluid the coal becomes when it is heated to the pyrolysis temperature. Fluidity is directly related to the ability of the coal blends to become plastic at a given moment of coking, and then, resolidify into a hard-porous material called semicoke at 500 ° C in an oxygen deficient atmosphere. In this study, it was observed an increase in the fluidity of the coal blend with the addition of coal tar.

Coal tar addition influences coke thermoplasticity because of its C-C chemical bond strength, the susceptibility to thermal degradation, the formation of oxygen-containing compounds during heating and the hydrogen transfer reactions to stabilize the macro radicals of the polymers, as explained above [18].

As can be noticed, the addition of coal tar tends to increase the coal blend fluidity as the addition content is increased, mainly due to the aromatic structures present, which play the role of C-C bonds stabilizers, which improves the density and carbon budget. The release of volatile matter in a larger volume before the start of the coke softening and plastification phase (around 400 to 500 C) also helps to increase fluidity. Moreover, the physicochemical phenomena of devolatization and polymerization forms the reactive compounds of influence [19].

The condensation of the free radicals, which will lead to the formation of semicoke, may be retardate by the presence of large quantities of polycondensed aromatic structures. This fact can help stabilize the free radicals formed, giving it more time to the system to organize and resolidify into a more oriented coke structure.

3.2 Coke reactivity Index (CRI)

It can be noticed that the reactivity of the coke increased when 2% of tar was added but the CRI values tends to decrease as the addition content of the coal tar increases. One of the main factors that influence the CRI of metallurgical cokes is the relation of the volume, location and types of pores present in the structure. The final porous structure of the coke is affected by the variations of the carbonized mixtures fluidities, the temperature range of the fluid and the volatile matter released before, during and after the fluid state of coal [18].

An increase in the micro pore volume (15 μm and 50 nm) over macro pores of several microns was verified when polymers were added to the coal blend, including coal tars [18]. These findings suggest that polymeric additives facilitate the formation of porosity due to the release of volatile matter near coke plastification temperatures. In addition, these additives prevent the enlargement and coalescence of pores resulting from higher viscosity. Both statements may justify the increase in coke reactivity with the addition of coal tar to produce coke.

To understand the decrease in the CRI values when 5% of coal tar was added it is necessary to evaluate the overlapping effects during pyrolysis, mainly, the growth and coalescence of the porous structure by the increase of viscosity and the presence of reactive compounds. This deleterious effect is a result of the final structure of coke, the forms of carbons organization and the structure of the pores. Coke with an oriented structure is less porous, provoking lower reactivity and higher resistance.

3.3 Coke strength after reaction (CSR)

The high strength coke is necessary to suppress the coke degradation and to keep the blast furnace skeleton permeable. Moreover, the blast furnace raceway and deadman zones retained the high-quality coke is applied. Overall, there was an increase in coke CSR values with the addition of coal tar. This fact is due to the binder property of the coal tar, producing a more organized and resistant structure of the coke due to the formation of mesophase and the transfer of hydrogen from the additives to the blend.

Even though there was increase in coke reactivity (CRI), the coke strength after reaction (CSR) also improved, generally, these two parameters are inversely proportional. The molecular orientation during the plastic stage and an anisotropic structure affects porosity considerably, as shown in figure 7. Figure 8 demonstrates the presence of coal tar on the coke surface working as a binder for the coal particles.

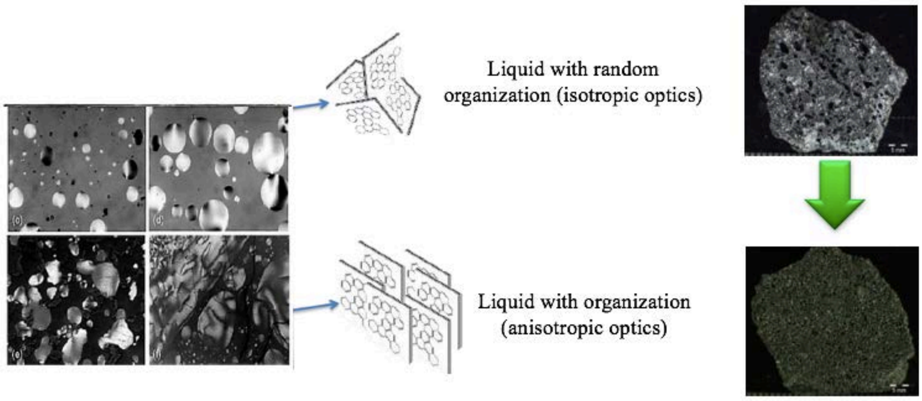

Figure 7. Representation of coke structures with different molecular orientations.

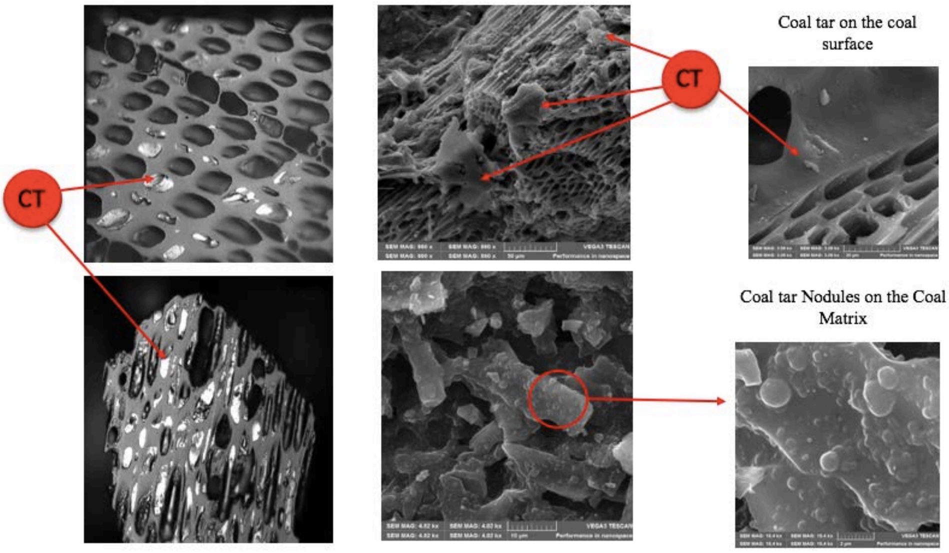

Figure 8. Coal tar on coke structure.

3.4 Drum Index (DI)

The mechanical strength or cold strength is defined as the coke ability to resist fragmentation by mechanical stress, impact and/or abrasion on a rotating drum. Coke resistance depends mainly on the average reflectance (rank parameter) and maximum fluidity (agglutination parameter) of the coal blend, also they have a direct effect on the texture and structure of the coke.

It can be observed that it occurred an increase in coke mechanical strength when coal tar was added. The increase of DI can be attributed to the interaction between the additive and the coal during the heat treatment. This interaction reduces and prevents the formation of cracks or fractures in the coke particles.

4 CONCLUSIONS

The development of the mesophase during carbonization is fundamental to form cokes with a more oriented structure (anisotropic). This structure allows reduction of porosity, increase mechanical resistance and prevents cracks or fractures formation on coke particles.

It can be concluded, from the results obtained in this work, that the addition of coal tar in the coal blend to produce metallurgical coke is an alternative method to reduce the costs and improve coke quality. The addition of 2% of coal tar increased 0.6 % of CSR, 1.2% of CRI, 1,71% of DI and 654 ddpm of fluidity.

The usage of coal tar as an additive improves coking properties of the blend, therefore, this fact allows to use higher levels of semi-soft coal on the mix. These type of coal is cheaper than hard coking, reducing costs of coke production. Nevertheless, this method has proved to be very useful to reduce costs and technically able to be tested in industrial scale.

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