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# Milling process of petroleum coke for sintered steel applications

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**Abstract:** The effect of milling on different properties of a petroleum coke has been evaluated. The material was subjected to planetary milling at two different rates (400 and 600 rev min<sup>-1</sup>) for different times up to 48 h. The milled material was characterised by scanning electron microscopy, X-ray diffraction, sieve analysis, thermal analysis, chemical analysis, specific surface area and compressibility has been undertaken. The results show that the milling produces a very quick loss of the crystal structure of the coke and a rapid comminution, which lead to large increases in specific surface area and compressibility losses. The coke has shown a high activity through the milling process, absorbing a great quantity of oxygen. The increase in milling time shifts its thermal decomposition to lower temperatures.

**Keywords:** Petroleum coke, Milling, Reactivity, Physical properties, Thermal properties

## Introduction

Generally, petroleum coke structure is described in terms of anisotropy (microstructural disorder). The degree of structural anisotropy has been evaluated through different techniques such as X-ray diffraction,<sup>1</sup> optical texture using optical microscopy techniques,<sup>2</sup> transmission electron microscopy and electron diffraction techniques.<sup>3</sup> All those techniques relate the physical chemical properties of carbon materials to their crystal structure and final microstructures. In literature, numerous works regarding microstructural descriptions (such as porosity, pore size and pore wall thickness) and microtextural descriptions regarding the nature of carbon in cokes can be found.<sup>4-6</sup> Physical and chemical structure of petroleum cokes influences many of their properties such as oxidation.<sup>7</sup>

There are different standardised methods which allow characterising carbon materials. The different tests or experiments used to characterise the coke structure are chosen according to their final application.<sup>8</sup> Specifically, there are characterisation standards such as those based on moisture, content of volatile compounds, ashes, chemical analysis, real density, porosity, specific electrical resistance, etc.

Mechanical milling is a process undertaken on particles in high energy mills, which implies a reduction in particle size and/or the presence of mechanically induced transformations. This kind of processes currently presents great technological interest.<sup>9</sup>

Works on coke milling are scarce. All of them point out that coke particle size diminution takes place through milling time, thus obtaining smaller powders, and also point out the existence of changes in powder morphology. However, there are discrepancies. Some researchers suggest that particle size diminution takes place, above all, at low milling times, from which particle size remains practically stable;<sup>10</sup> other researchers propose that such size reduction persists at high times.<sup>11</sup> Regarding final coke morphology, it might be either spherical<sup>10</sup> or elongated.<sup>11</sup> On the other hand, increase in specific surface area also takes place through milling time.<sup>10</sup> It has also been observed that the milling process destroys laminar structure and microcrystal orientation, and increases net distortion,<sup>11,12</sup> all of which improves coke sinterability.<sup>12</sup>

In the case of natural crystalline graphite, milling processes imply an increase in the interlaminar space d002 through time, while the average size of the crystallite domain decreases. Such changes are attributed to the introduction of interstitial carbon atoms into the structure of the original graphite<sup>13</sup> and also the introduction of structural defects.<sup>14</sup> Besides, the presence of oxygen in milling atmosphere<sup>15</sup> affects the mechanical deformation processes of graphite, decreasing fracture rate through the formation of brittle oxides in active centres created through the milling process and maintaining graphite crystallinity.

The present work attempts to evaluate the influence of milling on different properties of a petroleum coke. The main objective is to manufacture a carbonaceous

powder suitable for powder metallurgy (PM) applications, as sintered steels, that could be competitive with natural graphite. Previous results with carbonaceous materials from petroleum were very promising,<sup>16</sup> showing the feasibility of using these raw materials as carbon additions on sintered steels. Tailored properties can be obtained in the milled coke, and in some grades, oxygen uptake can occur. Anyhow, the presence of volatiles in milled coke can help reduction phenomena during sintering of carbon and low alloy steels. Research on this matter has taken place during this project,<sup>17</sup> and it will be published nearby.

## Experimental

A green petroleum coke from the company Repsol was used as raw material to study the influence of high energy milling process. Its composition is shown in Table 1. Before milling, the coke was ground and sieved at 800  $\mu\text{m}$ . Finally, it was dried in a furnace at 110°C for 30 min.

High energy milling process has been undertaken by using two high energy planetary mills, evaluating the influence of working rate. On the one hand, a planetary mill with one vessel was used at a constant rate of 600  $\text{rev min}^{-1}$ ; on the other hand, a planetary mill with two vessels was used at 400  $\text{rev min}^{-1}$ . In both cases milling vessels and balls media ( $\varnothing=10$  mm) was made of stainless steel. The mass ratio balls/powder was always 10:1. The vessel was maintained closed, so that a residual oxygen atmosphere remained, until such atmosphere got consumed. The milling process was evaluated at seven times (1, 2, 4, 8, 16, 32 and 48 h). Each condition was undertaken individually without opening the vessel.

The milling process of carbon powder was monitored by using different characterisation techniques and tests to study and evaluate the milling process and the behaviour of milled carbon powder. In all cases the authors have undertaken a minimum of five measurements. The following studies were carried out:

- (i) morphology study of the milled cokes by scanning electron microscopy (SEM)
- (ii) X-ray diffraction
- (iii) particle size distribution measured by laser wet diffraction
- (iv) specific surface area in particles, using the Brunauer–Emmett–Teller isotherm,<sup>18</sup> through nitrogen adsorption and desorption.<sup>19</sup> Specific surface area was calculated according to Dubinin method<sup>20</sup> and pore volume according to Horvath–Kawazoe method<sup>21,22</sup>
- (v) elemental analysis of carbon, hydrogen, nitrogen and sulphur content in the carbon material
- (vi) helium density
- (vii) compressibility of milled cokes. Milled cokes were pressed by cold isostatic pressing (CIP), applying a pressure of 200 MPa and maintaining such pressure for 15 min. Once green

compacts were obtained, the density was measured by the Archimedes' principle (buoyancy); and

- (viii) thermogravimetric analysis. The experiments were carried out in flowing air between 50 and 900°C, at a heating rate of 10°C  $\text{min}^{-1}$ .

According to literature, only the first three techniques have been applied to the study and characterisation of coke milling.<sup>10–12</sup> A natural graphite (EDM grade from ISMAF) typically used in PM applications was evaluated for comparison.

## Results

Figure 1 summarises how the evolution of the coke morphology observed by SEM. Micrographs are presented for coke milled at 400  $\text{rev min}^{-1}$ , as milling rate does not substantially alter the morphology. It can be observed that the particles have a very rounded morphology and high sphericity for low milling times. However, for high milling times, particles show a more angular morphology. Besides, when the material is milled for a long time (32 and 48 h), particle flattening occurs. In any case, at least apparently, a variation of the particle size cannot be distinguished with respect to milling time. Furthermore, insofar as milling time increases, small particles, gathering on the surface of higher size particles, can be observed.

In Fig. 2, the 002 X-ray diffraction band of the initial coke and the materials obtained at different milling times at 400  $\text{rev min}^{-1}$  are compared. Such band shows low relative intensity and a noticeable width for the raw material, indicating low crystallinity in the starting coke. It is observed that, insofar as milling time increases, material is progressively amorphised and, from 2 h of milling onwards, carbon derivatives show a completely amorphous structure as the 002 band (that usually most intense in the X-ray diffraction pattern of carbonaceous materials) completely devanishes.

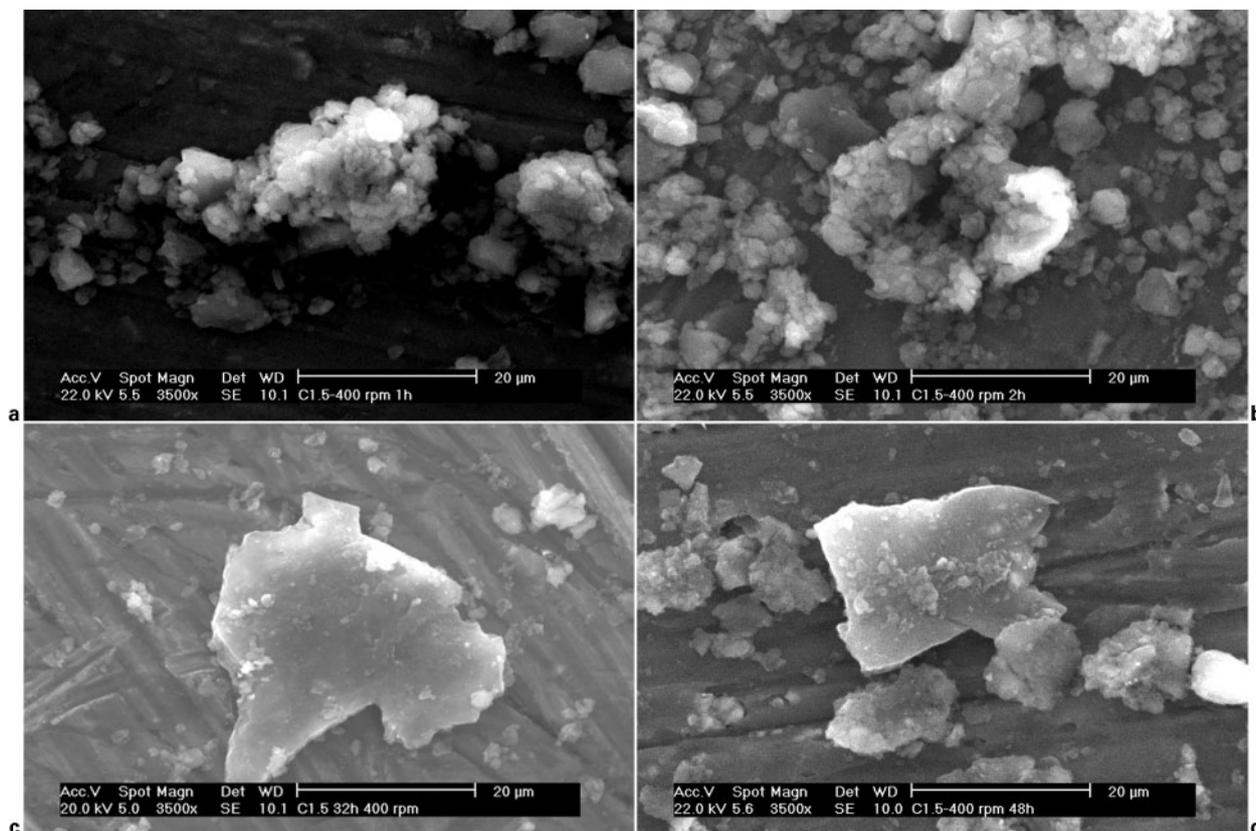
The D50 (particle size so that 50% of the particles are below such value) values for the raw coke and derived materials have been represented in Fig. 3a. It is observed that these values, for both milling rates and all times, are always lower than 15  $\mu\text{m}$ . In general, a pronounced decrease in D50 with milling time, until reaching values  $\sim 5$   $\mu\text{m}$ , can be observed. Figure 3b shows the evolution of the average particle size (D4.3) of milled coke versus milling time. In this case, it is not possible to suggest a clear tendency on the evolution of such parameter, although systematically the values for 600  $\text{rev min}^{-1}$  (about 14–15  $\mu\text{m}$ ) are almost a half of those correspondingly for 400  $\text{rev min}^{-1}$  ( $\sim 23$   $\mu\text{m}$ ). Nonetheless, analysing the values of both parameters, in general, higher milling rates promote lower particle sizes.

The grain size distributions are included in Fig. 4 for the coke milled at 600  $\text{rev min}^{-1}$  for 1 and 32 h. Figure 4a illustrates that whereas the coke milled for 1 h shows only a maximum at 12.2  $\mu\text{m}$  in the relative distribution curve, the coke milled for 32 h shows two maximums: one corresponding to 3.1  $\mu\text{m}$  and another to 30.3  $\mu\text{m}$ . Accumulated sieve size distributions (Fig. 4b) show once again that the D50 parameter is lower as milling time increases, thus particle size decreases.

Undertaking nitrogen physisorption analysis, different parameters such as specific surface area (Fig. 5) and micropore volume (Fig. 6) were obtained. The specific

**Table 1** Chemical composition of studied petroleum coke, wt-%

C	H	N	S	O	Volatiles	Ashes
95.2	3.73	0.15	0.23	0.68	6.9	0.03

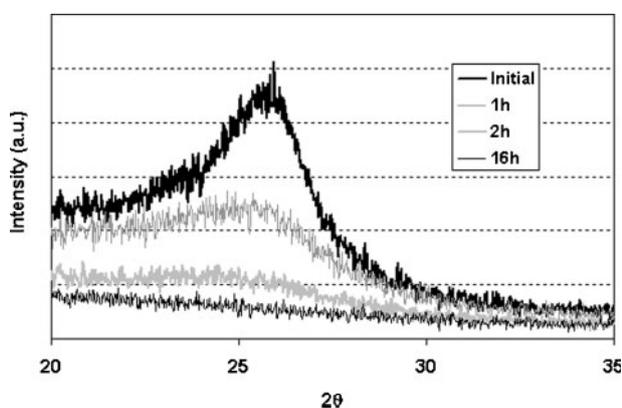


a 1 h; b 2 h; c 32 h; d 48 h

1 Scanning electron microscopy graphs showing morphological evolution of coke during milling at 400 rev min<sup>-1</sup> for different times

surface area (Fig. 5) increases with milling time, up to 16 h. From such milling time onwards, a slight drop takes place for both milling rates. In spite of that, the influence of the milling intensity in the textural properties is higher at the low intermedium milling times (4–8 h), as they are the conditions at which the corresponding samples show higher differences (much higher specific area for the samples milled at 600 rev min<sup>-1</sup>), whereas at milling times between 16–32 h the specific surface gets similar values for both conditions and evolving in a similar way. At the lowest milling times (1–2 h) the differences for both sets of samples are so low that, they are not significant.

Figure 6 shows the values for micropore volume versus milling time. The evolution of this parameter



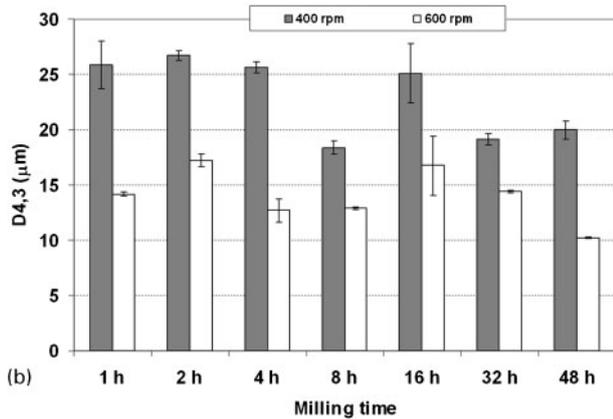
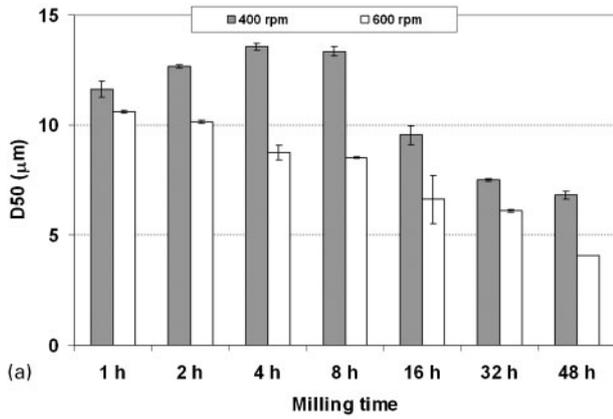
2 X-ray diffractograms of milled coke at 400 rev min<sup>-1</sup> for different times

for both milling intensities (400 and 600 rev min<sup>-1</sup>) is exactly the same that that observed for the specific area, which means that the surface value of these materials is a direct function of the micropore volume, i.e. the variations in specific surface is a consequence of the evolution of the micropores with the milling time and intensity.

In contrast with the results discussed above, the real density (helium density, Fig. 7) of the powders keeps practically constant for low milling times, but at times higher than 8 h a slight increase in the density can be observed, independently of the milling rate. There slight differences found between both coke milling rates do not show a clear tendency.

Green density of compacts after powder milling and subsequent pressing by CIP (technique applied for evaluation milled powder compressibility) was evaluated (Fig. 8). It is observed that the green density diminishes with milling time, especially at times higher than 8 h. Green densities obtained in powders milled at 400 rev min<sup>-1</sup> are slightly higher than those obtained for cokes milled at higher rate (600 rev min<sup>-1</sup>). For both milling rates, the highest green density values are obtained after 2 h of milling.

Figure 9 shows some thermogravimetric curves for raw coke and some selected milled cokes. Initially, a very small weight loss is observed for all samples, corresponding probably just to the desorption of moisture. After that, a plateau occurs until the combustion of the sample, which appears in the thermogravimetric curves as a sharp weight loss. Before combustion, it can be appreciated a slight weight gain, corresponding to the chemisorption of oxygen on the carbon. This weight

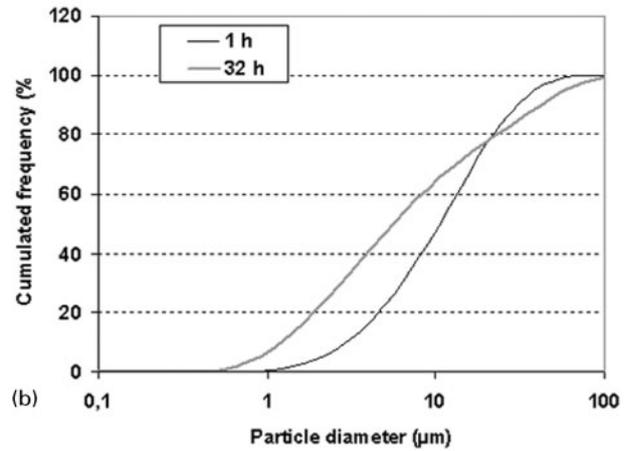
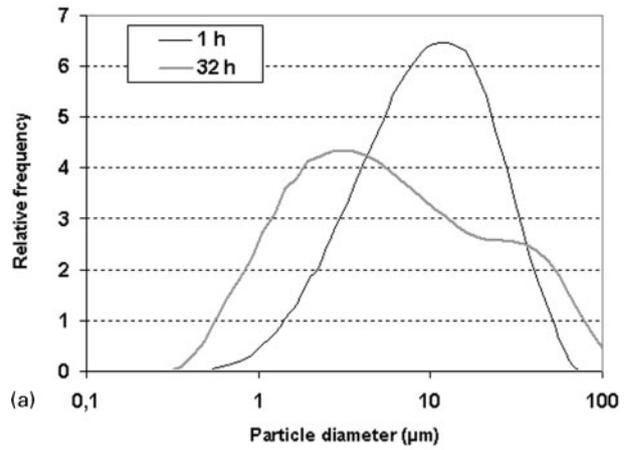


3 Evolution of *a* D50 and *b* D4,3 parameters in milled coke powders after milling at 400 and 600 rev min<sup>-1</sup> for different times

gain, in both cases (400 and 600 rev min<sup>-1</sup>), is maximum for the sample milled for 1 h, being lower as the milling time is increased, and completely absent at 48 h. At the same time, the temperature of the beginning of decomposition (onset temperature) is gradually reduced with milling time. Table 2 summarises the results, in terms of onset temperature, obtained after thermal analysis in air of coke milled at 400 and 600 rev min<sup>-1</sup> for different milling times. It is observed that, insofar as milling time increases, the initial decomposition temperature of the sample is lower. Related to the higher increase of the specific surface area of the milled powders observed at times higher than 8 h (Fig. 5), a very high decrease in the onset temperature takes place between 8 and 16 h milling time. On the other hand, comparing the results obtained in both studied milling rates, it is observed that the decomposition temperature is lower in powders milled at 600 rev min<sup>-1</sup> than at lower rates (400 rev min<sup>-1</sup>) and that, at 48 h of milling, the onset temperature is the same in both cases.

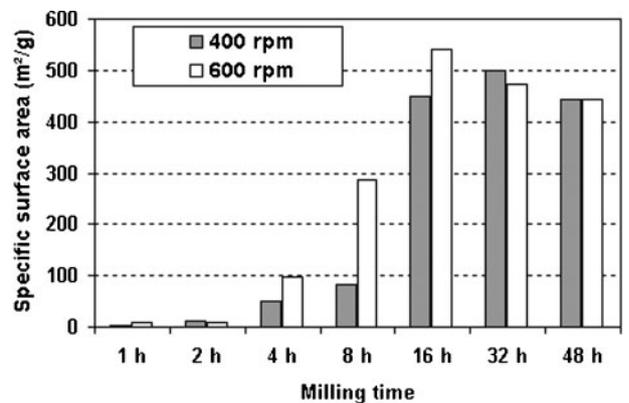
Table 2 Onset temperature (°C) of combustion of petroleum coke as received (unmilled, 0 h) and after milling at 400 and 600 rev min<sup>-1</sup> for different times

Milling speed, rev min <sup>-1</sup>	Milling time, h							
	0	1	2	4	8	16	32	48
400	582	565	552	547	529	408	412	370
600		539	522	507	477	390	373	370

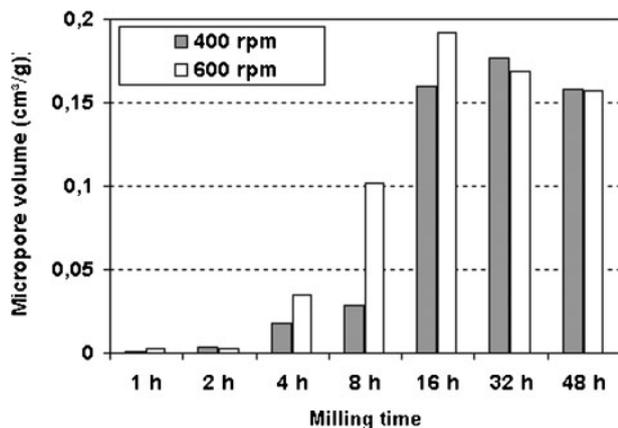


4 Sieve analysis of milled coke powders during 1 and 32 h at 600 rev min<sup>-1</sup>: *a* relative and *b* cumulated frequencies

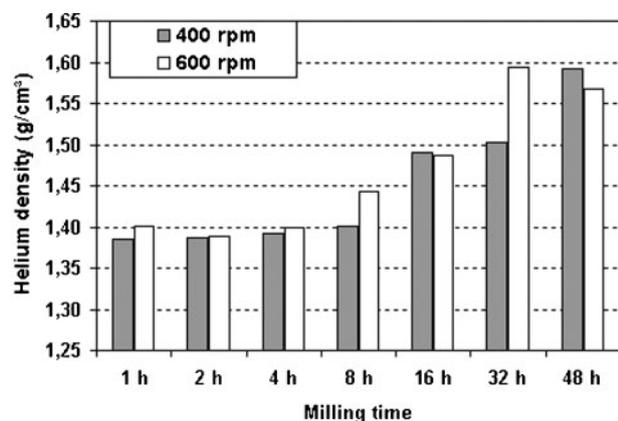
Figure 10 shows the results obtained from the chemical analysis of the milled cokes at different times including the values for the main constituents of the carbons (H, C, N, O and S). The first clearly noticeable aspect is that there is no substantial variation in hydrogen, sulphur or nitrogen for none of the cokes milled at 400 or 600 rev min<sup>-1</sup>. In both cases it is observed that, insofar as milling time increases, since the coke progressively becomes more reactive, the carbon content decreases and the oxygen content increases, showing stronger affinity towards oxygen. In fact, material was cooled down with liquid nitrogen during



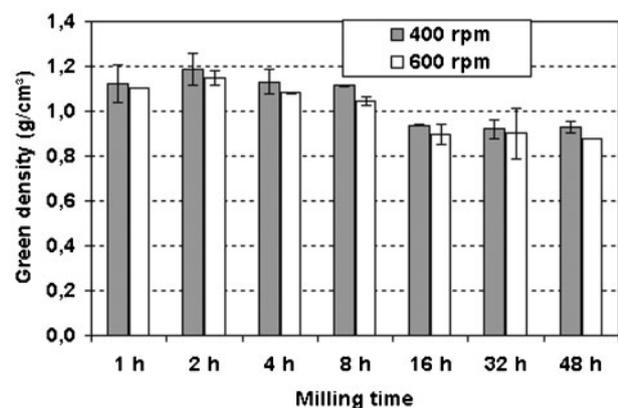
5 Specific surface area in milled coke powders after milling at 400 and 600 rev min<sup>-1</sup> for different times



6 Volume of micropores in milled coke powders after milling at 400 and 600 rev min<sup>-1</sup> for different times



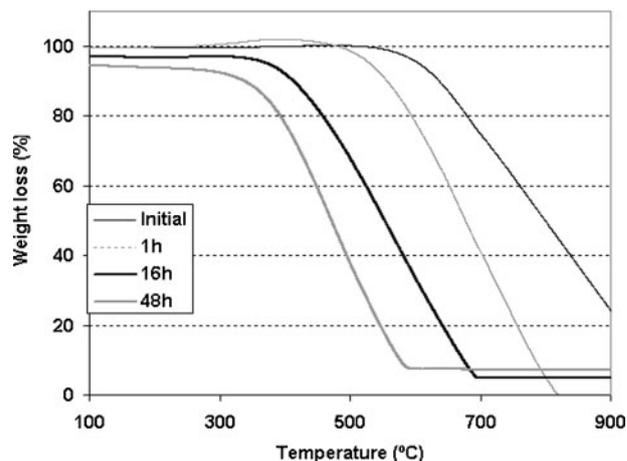
7 Helium density in milled coke powders after milling at 400 and 600 rev min<sup>-1</sup> for different times



8 Green density in milled coke powders after milling at 400 and 600 rev min<sup>-1</sup> for different times, and CIP processing

the opening of the milling vessel to avoid the spontaneous combustion that would happen if the milling vessel is open normally in air at room temperature. The oxygen content of the milled coke is that that has been chemisorpted from the air remaining in the vessel, and it does not show significant differences regarding milling rate.

Finally Fig. 11 represents the atomic ratios C/H (Fig. 11a) and C/O (Fig. 11b) of coke milled at 400 and 600 rev min<sup>-1</sup> for all studied milling times. As shown in Fig. 11a, the C/H variation of coke milled at



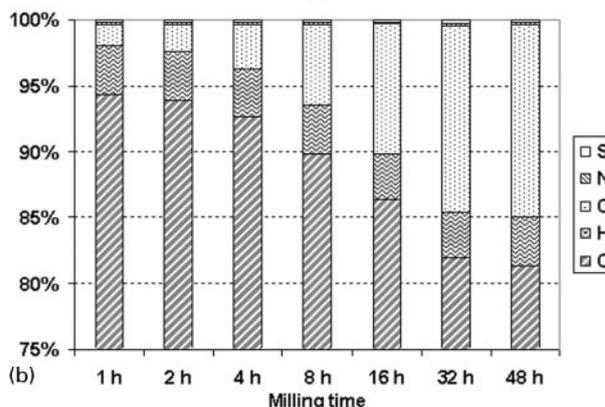
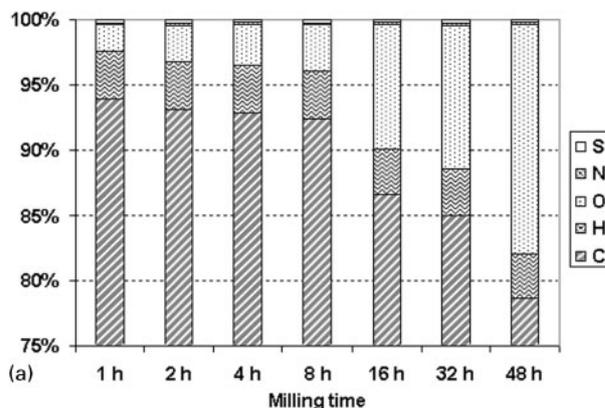
9 Thermogram in air of milled coke powders after milling at 400 rev min<sup>-1</sup> for different times

400 and 600 rev min<sup>-1</sup> is small and almost the same, diminishing after 16 h until completing 48 h of milling. However, the C/O ratio (Fig. 11b) diminishes markedly through milling time until reaching a near constant and very low value from 16 h of milling for both milling rates.

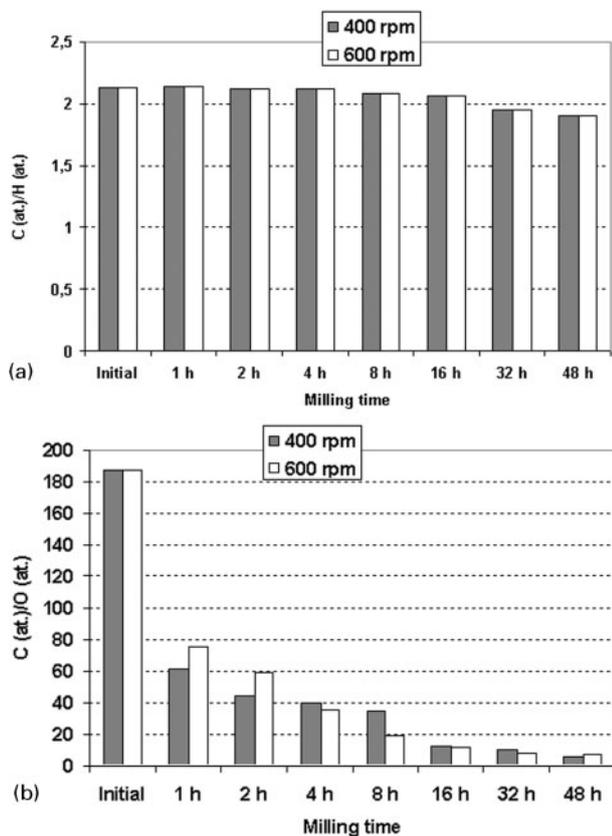
The main numerical results for natural graphite are shown in Table 3. Those results were measured in the same conditions than milled petroleum coke. Chemical composition is 100%C, without any other element.

## Discussion

In principle, the milling of a material might entail two basic effects: structure amorphisation and particle size



10 Chemical analysis of milled coke powders after milling at a 400 and b 600 rev min<sup>-1</sup> for different times



**11 Atomic a C/H and b C/O ratios in milled coke powders after milling at 400 and 600 rev min<sup>-1</sup> for different times**

reduction. Regarding amorphisation, increasing milling time, the material is progressively amorphised, even reaching complete amorphisation once the milling process is finished. Coke can be considered as a ceramic material but, in spite of such consideration, coke can be amorphised by milling. The initial coke studied in this work already shows only the broad diffraction peak corresponding to the (002) plane (Fig. 2). That is, coke structure is not much orderly, as it could be expected from a green coke. Such scarce order, just few ( $\sim 3$ ) extended planar aromatic molecules piled up, is broken indeed through the milling process. This indicates that coke has certain planar structure, which is broken through milling. These results can be contrasted with previous works mentioned in the literature,<sup>11</sup> where the plane (002) undergoes stretching through milling time and the coke structure gets gradually distorted, decreasing and amorphising crystal domain size due to the milling process.

However, when comparing with other carbon materials, softer and structurally different to petroleum coke, such as graphite, milling effects are different. Several studies of its milling at different times show that

graphite does not amorphise,<sup>13,14</sup> although some authors point out the contrary.<sup>23</sup>

On the one hand, the analysis carried out on the coke milled at 400 rev min<sup>-1</sup> (Fig. 1), shows that the morphology of the particles milled for low milling times is globular, it is observed that they are rounded particles. However, for high milling times, particle morphology is different, and more angular particles can be observed due to particle–particle and particle–ball impacts. Coke is a brittle material and, insofar as milling is developed, its particles break and, in turn, more flat and elongated particles are obtained. Constant impacts make that, insofar as milling is developed, breakage planes are found in particles, which give rise to more angular particles. This fact has been previously studied<sup>11</sup> and fits with the results obtained in the present work, thus justifying that increasing milling time gradually modifies particle morphology, flattening it through milling.

This analysis does not change when 600 rev min<sup>-1</sup> rate is used; that is, the same effect is achieved at lower times when a higher rate is used. Only a slightly more angular morphology is observed, which is a consequence of the higher milling rate, which is more aggressive, so that the particle boundaries are more pronounced.

Particle size considerably diminishes within the first milling hour (Fig. 3a). Such reduction is quite quick: from a maximum size of 800  $\mu\text{m}$  in the starting coke to 50  $\mu\text{m}$  after only 1 h. Since coke is a hard and brittle material, it undergoes strong particle diminution in the first times of the milling process. The data of the particle size obtained through laser diffraction (Fig. 3b) can be corroborated with size observed by SEM (Fig. 1). It should be taken into account that agglomeration problems may arise during particle size measurement by laser diffraction technique.

Regarding the influence of milling speed on the evolution of the particle size, Fig. 3 illustrates that an increase in milling speed produces a higher diminution in parameter D50 (Fig. 3a) and D4.3 (Fig. 3b). A higher energy is generated at higher milling rate, thus producing greater impacts between the powder and the balls, which results in greater particle breakages. In this sense, the percentage of particles lower than 40  $\mu\text{m}$  (100% for natural graphite), although, on the whole, is  $\sim 90\%$ , it is higher for the cokes milled at 600 rev min<sup>-1</sup> than for those treated at 400 rev min<sup>-1</sup>.

Regarding the influence of milling rate, an increase in milling time from 1 to 48 h at 600 rev min<sup>-1</sup> achieves diminution of parameter D50 from 10 to 5  $\mu\text{m}$  (Fig. 3a). Such behaviour is typical and has been contrasted with data found in numerous studies,<sup>9</sup> where particles of milled powders become smaller through time. Moreover, an increase in milling rate (from 400 to 600 rev min<sup>-1</sup>) diminishes D4.3 parameter (Fig. 3b), since an increase in the milling rate diminishes particle size and finer particles are obtained. Therefore, average size diminishes and, consequently, the percentage of particles smaller than 40  $\mu\text{m}$  increases.

Although the effect of milling time on the parameter D50 is very clear, specially for milling at 600 rev min<sup>-1</sup>, for D4.3 and the percentage of particles smaller than 40  $\mu\text{m}$ , such trend is not so clear. The reason for this behaviour is mainly related to the formation of agglomerates through the milling process, as can be observed in the sieve size curves (Fig. 4). From these

**Table 3 Properties measured on natural graphite**

D50, $\mu\text{m}$	18
Specific surface area, $\text{m}^2 \text{g}^{-1}$	11.0
Volume of micropores, $\text{cm}^3 \text{g}^{-1}$	0.004
Helium density, $\text{g cm}^{-3}$	2.25
Green density, $\text{g cm}^{-3}$	2.13
Onset temperature of combustion, $^{\circ}\text{C}$	560

curves the presence or absence of agglomerate formation can be analysed. In Fig. 4a, it is observed that the distribution curve of coke milled for 1 h only shows one maximum. However, coke milled for 32 h shows a bimodal distribution with two maximums. This means that, in the case of 32 h of milling, the agglomerates were not disagreed, in spite of using a dispersing agent, during size measurement by laser diffraction. Thus, it can be justified that, insofar as milling is developed, finer powders are progressively obtained. This can be inferred from the values of parameter D50, which is lower insofar as milling is developed, as it can be observed in Fig. 4b, where particle size with 50% of grain size distribution decreases. However, this is difficult to deduce from D<sub>4.3</sub> because of agglomerate (thicker particles) formation is taking place (Fig. 4a).

Agglomerate formation might be related to the structure of milled carbon materials. During the milling, the impacts give rise molecule rupture, causing the formation of free radicals, quite stable due to their aromatic nature. Besides that, the milling can induce the appearance of electrostatic charges. In general, all those effects would lead out to the formation of those agglomerates, specially at higher milling times.

Other parameter that evolves through the milling is the composition, specially regarding the oxygen concentration (Fig. 10), getting higher as the milling time increases. The origin of this oxygen uptake can be the residual air included in the vessel when this is close and that what reacts when the vessel is open after the milling process, as a consequence of the high reactivity of the coke developed during the milling. Possibly, very reactive free radicals are being formed during milling process as a consequence of the progressive 'destruction' of the coke. Those radicals would react with the oxygen in the vessel. After that, the left free radicals (if they are) will react with the oxygen in the air just when the material would be exposed to it, as it has already been observed in previous works.<sup>15</sup> The formation of such active centres should be related to side chains adjacent to aromatic rings, and not precisely on them.<sup>7</sup> The relation C/H ratio (Fig. 11a) scarcely varies, which implies scarce carbon loss, although some of it would become CO and CO<sub>2</sub>, whereas the C/O ratio diminishes through milling process (Fig. 11b), which confirms that the active centres formed are related to oxygen and not to hydrogen.

As it has been pointed out previously, parameter D50 diminishes through milling time, due to the formation of smaller particles, which results in an increase in specific surface area (Fig. 5), especially for 16 h of milling onwards. This has also been related to particle size distributions corresponding to Fig. 4. When increasing milling time, particle morphology suffers a radical transformation from globular to more plain and angular morphologies which is clearly reflected in the specific surface area (with variations of two orders of magnitude as long as particle size scarcely undergoes variation). The increase in specific surface area provokes increasing reactivity and, as a consequence, oxygen content through milling time. Values of specific surface area even reach 500 m<sup>2</sup> g<sup>-1</sup>, which is similar to that observed in graphite milling to obtain nanostructural graphite.<sup>24</sup> This trend can be generalised to micropore volume (Fig. 6), in such way that milling promotes the presence of higher quantity of micropores; giving rise a 'more

open' structure. In this way, the increase in the He density (Fig. 7) can be explain as a consequence of the opening by the milling of voids that there were close initially, thus developing a larger porous space.

Green density (Fig. 8) diminishes through milling time because compressibility is lower. The evolution of this parameter is in good agreement with the development of a micropore space throughout the milling, indeed considering that at the highest milling times (16, 32 and 48 h) in both cases (400 and 600 rev min<sup>-1</sup>) the density is stable. This fact is a consequence of the formation of progressively smaller powders (with less appropriate morphology), greater surface area and worse packing index when milling time increases. This, together with the intrinsic hardness of coke, provokes worse pressing. The fact that particle size distributions are progressively more open for high milling times (Fig. 6) might imply better particle pressing, although such effect seems to be lower than that of angular particles, especially since greater particles are actually agglomerated particles.

As a consequence of milling, an increase in active centres takes place, progressively forming finer and more reactive particles, as it can be ascertained from the high oxygen absorption (Fig. 11b), as well as the increase in specific surface area (Fig. 5) and particle size, especially D50 (Fig. 3). This set of parameters would give rise to an earlier decomposition of the coke with milling time, as it has established from the thermogravimetric curves (Table 2 and Fig. 9). The two effects found in thermal analysis, diminution of chemisorption of oxygen and onset temperature  $T_{o,c}$  as the intensity of the milling increases (higher milling time and rev min<sup>-1</sup>), are indicative that the milling process is causing a noticeable 'demolition' of the material, doing easier the and more immediate the reaction with oxygen. In this sense, the fact that the onset temperature is the same for the samples obtained after 48 h of milling at both conditions (400 and 600 rev min<sup>-1</sup>) means that at so long milling times the structure is so 'wrecked' that the milling intensity is of small influence, having reached a sort of 'wrecking' limit. On the other hand, it should be noted that a 'soft' milling treatment, i.e. for short milling times (1 h), the modification of the structure is not so dramatic as this treatment makes possible a higher chemisorption of oxygen, although the combustion begins at lower temperatures.

Comparing these results with those of natural graphite (Table 3), it is found the good performance of milled coke for low milling times. D50 values (Fig. 3a) are slightly lower for milled coke than for natural graphite, although coarser coke particles will appear, specially for high milling times (Fig. 4). Low milling times give specific surface area (Fig. 5) and volume of micropores (Fig. 6) results in the range of natural graphite ( $\sim 10$  m<sup>2</sup> g<sup>-1</sup> and 0.004 cm<sup>3</sup> g<sup>-1</sup>). Thermal decomposition also lies in the same temperature range (Tables 2 and 3), specially for 400 rev min<sup>-1</sup> milling rate. Higher milling times that promote a strong 'demolition' of the coke and its structure fall apart from graphite, highly crystalline. Although helium density of cokes (Fig. 7) are smaller than graphite (Table 3), taking into account relative green density values (green density versus helium density), compressibility results are quite adequate. Values of about 80–85% are obtained in low

times milled coke, while graphite shows 94%. The reason is the higher hardness of this coke, although other coke grades do not have this problem. Compressibility of steels manufactured with milled cokes is similar to that of graphite steels.<sup>17</sup> Sintering performance of those additions will be presented in further communications.

## Conclusions

1. The milling process destroys the basic structural units of the coke, the laminar structure and microcrystal direction, increasing net distortion.

2. Very quick comminutions are achieved in the first milling stages. Few milling hours are needed (maximum of 2 h) to reach average particle size lower than 15  $\mu\text{m}$ . More severe milling conditions (600  $\text{rev min}^{-1}$ ) provide lower particle sizes than softer conditions (400  $\text{rev min}^{-1}$ ).

3. Specific surface area increases through milling time due to particle size diminution and opening of the close porosity contained in the original material.

4. Thermal behaviour demonstrates that, insofar as milling time increases, the reactivity of milled powders is higher, given that decomposition temperature is progressively lower.

5. Strong variations in chemical analysis confirm coke reactivity when milled.

6. Low milling time coke present results close to those of natural graphite.

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