



## Full Length Article

## Effects of pyrolysis conditions on the structure of chars prepared from an Argentine asphaltite

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## HIGHLIGHTS

- Effect of pyrolysis conditions on an Argentine asphaltite char structure was studied.
- Experimental conditions investigated were temperature, heating rate and holding time.
- A significant reordering of the carbonaceous matrix was observed above 600 °C.
- Char aromaticity and crystalline carbon fraction were the most sensitive parameters.
- Appearance of a liquid phase during heating affected the char particle morphology.

## ARTICLE INFO

## Article history:

Received 15 December 2015

Received in revised form 24 May 2016

Accepted 28 May 2016

## Keywords:

Pyrolysis  
Gasification  
Char  
Asphaltite  
Reordering

## ABSTRACT

As gasification reactivity of carbonaceous solid material chars is known to be strongly dependent on their formation conditions, a comprehensive study was carried out on the effects of pyrolysis conditions on structure of chars prepared from an Argentine asphaltite. The study comprised qualitative and quantitative analyses of char structures by X-ray diffraction, complemented with the characterization of physical morphology of char particles by scanning electronic microscopy and high-resolution transmission electronic microscopy. Effects of pyrolysis temperature, heating rate and holding time at the peak temperature were investigated separately in a fixed bed tubular reactor. Additionally, the overall effect of variations in time-temperature history of individual char particles was evaluated using a drop tube furnace reactor. Experimental results have shown that pyrolysis conditions have a strong influence on the asphaltite-derived char structure, producing a significant reordering of the carbonaceous matrix at high heat treatment temperatures that is evidenced by increments in aromaticity and crystalline carbon fraction. The resulting physical morphology of asphaltite-derived char particles was found to be profoundly influenced by the heating rate at which the volatile matter is released, due to the appearance of a liquid phase during the heating process.

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## 1. Introduction

Coal and other carbonaceous solid materials have been historically used for power generation through direct combustion which is a highly inefficient and pollutant way of extracting the chemical energy stored in these natural resources. Improvements of the

overall efficiency and cleanliness of the energy production systems are currently an urgent demand since the global population growth and energy consume are steadily increasing while environmental protection standards become more and more stringent.

In this challenging framework, a renewed interest on gasification technologies has recently emerged worldwide since they offer the potential of a clean and efficient energy. One attractive characteristic of gasification technologies is the possibility of co-production of electricity, hydrogen, liquid fuels, and high-value chemicals that contribute to the improvement of power generation efficiency compared with conventional pulverized coal fired plants [1]. Gasification has also the additional advantage of accommodating a wide range of feed stocks, including low-cost fuels like petroleum coke, biomass, and municipal wastes [2].

*Abbreviations:* XRD, X-ray diffraction; SEM, scanning electronic microscopy; HRTEM, high resolution transmission electronic microscopy;  $T_d$ , active thermal decomposition temperature;  $f_a$ , aromaticity;  $L_{002}$ , average crystallite height;  $d_{002}$ , interlayer spacing;  $X_C$ , crystalline fraction of carbonaceous matrix;  $X_A$ , amorphous fraction of carbonaceous matrix; FB, fixed bed; DTF, drop tube furnace.

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Gasification process involves a set of exothermic and endothermic chemical reactions of feed solid particles with air or O<sub>2</sub>, steam, CO<sub>2</sub>, or a mixture of these gases at a temperature exceeding 700 °C, to yield a gaseous product suitable for use either as a source of energy or as a raw material for the synthesis of chemicals, liquid fuels or hydrogen. It is well-known that gasification is a two-step process. In the first step, pyrolysis or devolatilization, the volatile components of the feed solid material are rapidly released at temperatures between 300 °C and 600 °C, leaving a residual solid fuel or char and mineral matter as by-products. The second step, char conversion, involves the gasification of the residual char and it is much slower than devolatilization step, becoming then the rate-limiting step of the overall process [3].

Earlier studies demonstrated that reactivity of chars to gasifying agents depends strongly on their formation conditions, since very complex physical and chemical transformations occur during the solid particle heating while yielding volatile matter and generating solid residues. A good understanding of the behavior of solid feed particles during heating, when chemical and physical structure of chars is formed is then essential to the development of gasification kinetic models [4,5].

In this paper, a study on the effects of pyrolysis conditions on chemical and physical structure of chars prepared from an Argentine asphaltite is presented. Asphaltites seem to be an excellent raw material for the production of synthesis gas through gasification processes due to their low content of ashes and high percentage of elemental carbon [6].

The study comprised qualitative and quantitative analyses of the char structure by XRD, complemented with the characterization of physical morphology of char particles by SEM and HRTEM. Pyrolysis conditions investigated were temperature, heating rate, holding time at the peak temperature, and the overall effect of variations in the time-temperature history of individual char particles.

## 2. Theoretical background

Pyrolysis or devolatilization of carbonaceous solid materials refers to the release of volatile matter by thermal decomposition. Much evidence supports the hypothesis that devolatilization is a chemical decomposition reaction. As a solid particle is heated, the cross bonds are severed, the weaker ones rupture at lower temperatures and the stronger ones at higher temperatures. The resulting products consisting of carbon oxides, pyrolysis water, hydrocarbons and hydrogen, which are collectively referred as volatile, escape through the solid carbon matrix to the surrounding environment. Some of volatile species like tar, that is very reactive, may also undergo secondary reactions, i.e. cracking and repolymerization, as they are evolving [7,8].

As temperature is the most important parameter affecting pyrolysis, it is useful to divide the overall pyrolysis process into three main temperature regions with reference to  $T_d$ , beyond which the massive weight loss takes place [4,9]:

- (1) Temperatures below 300–400 °C, where limited thermal alterations of the original molecular structures occur, mostly by condensation reactions, prior to the massive release of volatile matter.
- (2) Temperatures between 400 °C and 600 °C, where the so-called primary pyrolysis takes place. It consists of a primary degradation as a result of which the weakest bridges may break to generate molecular fragments. The fragments subtract the hydrogen from the hydroaromatics or aliphatics thus increasing the concentration of aromatic hydrogen. These fragments are released as tar if they are small enough

to vaporize and be transported out of the solid particles. Functional groups also decompose to release gases, mainly CO<sub>2</sub>, light aliphatics and H<sub>2</sub>O.

- (3) Temperatures higher than 600 °C, where reactions that take place involve mainly the condensation of the carbonaceous matrix and the release of CO and H<sub>2</sub>. In this high-temperature range, a reordering of the char structure also takes place which results in a loss of the char reactivity toward further gasification or combustion. This char deactivation process is known in literature as thermal annealing [10].

Carbonaceous solid materials contain crystalline particles (crystallites) with diameters in the order of nanometers, which are composed by graphite-like layers arranged turbostratically. Heat treatments at high temperatures can enlarge these crystallites and make them more ordered, and this process can be characterized by XRD that is a well-developed technique for analyzing carbon matrices [11–13]. XRD is a non-destructive method that uses a relatively large amount of sample and collects most of the intensities scattered from the examined sample, yielding to average properties from the sample rather than local properties. This fact is very important for a material like coals and asphaltites which are inherently heterogeneous.

Fig. 1 shows a characteristic XRD pattern obtained from a carbonaceous char sample after subtracting the background intensity from the observed XRD diagram. Different structural parameters such as the amorphous and crystalline carbon fractions, aromaticity, crystallite height, interlayer spacing and other properties can be obtained from this XRD pattern.

Three two-dimensional bands are observed over the examined  $2\theta$  range. The band in the low angle region ( $2\theta \approx 25^\circ$ ) corresponds to the (0 0 2) peak of graphite which is generally accepted as the stacking of the graphitic basal plans of char crystallites. The other two bands in the higher angle region, which are indicated as (1 0) and (1 1), are attributed to hexagonal ring structure in char crystallites [11,12]. The asymmetric shape of the (0 0 2) diffuse peak suggests the existence of another band ( $\gamma$ ) in its left hand side. This  $\gamma$  band that usually occurs in the angular range of 16–23° ( $2\theta$ ) has also been observed by many other authors and it is associated with packing of the saturated structures such as aliphatic side chains [13,14].

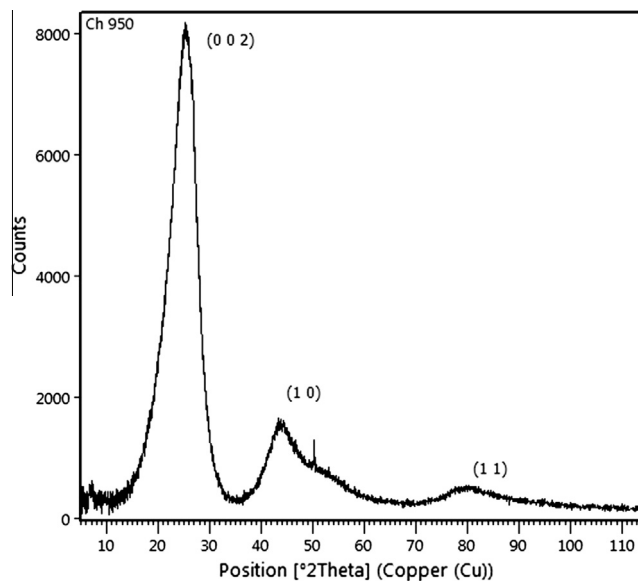


Fig. 1. Typical corrected XRD pattern of a carbonaceous material char sample.

The (0 0 2) graphite peak and the  $\gamma$  band can be separated as follows: it is assumed that the  $\gamma$  band would not contribute to the high angle side of the (0 0 2) peak due to its low intensity and, then, the high angle side of the (0 0 2) peak can be used as a guide to delineate the (0 0 2) symmetric peak. After (0 0 2) peak assumed as symmetric is resolved, the remaining intensity in the low angle side of this peak is hence attributed to the  $\gamma$  band [15].

After processing the measured XRD pattern, the following four structural parameters can be obtained from the resulting XRD diagram [16,17]:

**Aromaticity:** this parameter is usually used to describe the ratio of carbon atoms in aromatic rings vs. aliphatic side chains. Since the  $\gamma$  band is believed to be associated with the aliphatic side chains grafted on the edge of char crystallites, the area under the  $\gamma$  band should be equal to the number of aliphatic carbon atoms [15]. Similarly, the area under the (0 0 2) symmetric peak should be equal to the number of aromatic atoms;  $f_a$  in percentage is therefore defined as:

$$f_a = \frac{C_{ar}}{C_{ar} + C_{al}} \times 100 = \frac{A_{002}}{A_{002} + A_{\gamma}} \times 100 \quad (1)$$

where  $A$  is the area under the corresponding peak, and  $C_{ar}$  and  $C_{al}$  are the number of aromatic and aliphatic carbon atoms per structure unit, respectively.

**Crystallite Height:** each diffuse peak in the XRD pattern can be characterized by its peak position ( $\theta$ ), peak width at half-maximum intensity ( $B$ ), and the area under the peak ( $A$ ). For crystallites suffering no lattice strain or distortion,  $L_{002}$  can be expressed by the Scherrer's equation [18]:

$$L_{002} = \frac{K\lambda}{B_{002}\cos\theta_{002}} \quad (2)$$

where  $K$  is the non-dimensional Scherrer's constant and  $\lambda$  is the wavelength of the incident X-rays.

**Interlayer Spacing:** given the (0 0 2) peak position, the spacing between graphitic layers along  $c$ -axis,  $d_{002}$ , can be calculated according to the Bragg's law:

$$d_{002} = \frac{\lambda}{2\sin\theta_{002}} \quad (3)$$

**Crystalline and Amorphous Carbon Fractions:**  $X_C$  and  $X_A$  in chars can be determined by the method of full-pattern fitting which is based on the principle that the observed diffraction pattern is the sum of the individual phases that compose the sample [19]. This method involves comparing the intensity of one or more peaks of a phase (graphite) with the peak intensity of an internal standard like corundum or rutile which is added to the sample in a known amount.

The abundance of the crystalline and amorphous phases in the mixture is quantitatively determined by applying the Rietveld refinement method that comprises calculating diffraction patterns of individual components of a mixture using a crystal structure model [20]. The resulting simulated pattern is then fit to the observed pattern by varying the parameters of the model.

### 3. Experimental

#### 3.1. Asphaltite raw material samples

An asphaltite arising from a minefield located in Neuquén province, Argentina, was selected for this investigation [21]. This asphaltite, called Fortune IV, was chosen due to its relative abundance in Argentina and its low content of ashes that allows

to minimize the disturbances of mineral matter on the quantitative XRD analyses, as well as their possible effects on the gasification reactivity, since three mechanisms have been suggested for explaining the gasification reactivity discrepancies observed in chars prepared in different conditions from the same precursor: (1) changes in inherent reactivity of the carbon; (2) changes in physical structure of the carbon; and (3) changes in the amount, composition and distribution of catalytic mineral materials within the carbon matrix [22].

As-received asphaltite samples were firstly ground and sieved to a size fraction of 125–250  $\mu\text{m}$  and further chemically analyzed according to ASTM standard procedures. Composition and main physical properties of the asphaltite Fortune IV are summarised in Table 1. Fig. 2 shows SEM micrographs of the asphaltite raw material at: (a) low; and (b) high magnifications. It can be appreciated that asphaltite particles are rough and irregular in shape with sharp corners and rounded edges, and they present small crystals of mineral matter embedded on their surfaces.

#### 3.2. Char preparation

Most of asphaltite-derived char samples were prepared in a FB reactor that operates at atmospheric pressure under an inert atmosphere of flowing argon gas (99.99% purity). The experimental setup consists of a horizontal quartz tubular reactor, an electrical furnace, and a temperature and gas control panel. Asphaltite samples of about 200 mg were placed inside the tubular reactor on a flat quartz crucible forming a loose packed bed and subjected to a programmed temperature ramp while a constant argon flow of 3.2 L/h was maintained during heat treatments.

In order to investigate the effect of pyrolysis temperature on char structure, asphaltite char samples were produced at four different peak temperatures: 650, 750, 850 and 950  $^{\circ}\text{C}$ , using a constant heating rate of 20  $^{\circ}\text{C}/\text{min}$  and a holding time of 60 min at the peak temperature. Furthermore, for evaluating the effect of the heating rate during pyrolysis, asphaltite char samples were prepared at 650  $^{\circ}\text{C}$  using three different heating rates: 2, 20 and 200  $^{\circ}\text{C}/\text{min}$ , and zero holding time at the peak temperature. Finally, to evaluate the effect of the holding time at the peak temperature, asphaltite char samples were produced at 650  $^{\circ}\text{C}$  using holding times of zero, 15 and 60 min and a constant heating rate of 200  $^{\circ}\text{C}/\text{min}$ .

Additionally, pyrolysis experiments were carried out on asphaltite samples in a DTF reactor that is able to reproduce more realistically the conditions of char formation in large-scale gasification reactors, i.e. very fast heating of solid particles and gas convection around individual particles with definable intensity. These

**Table 1**  
Composition and physical properties of the raw asphaltite Fortune IV.

Analysis	Content [wt%]
<i>Proximate analysis (air dry basis)</i>	
Moisture	0.26
Volatile matter <sup>a</sup>	58.97
Ash <sup>a</sup>	0.46
Fixed carbon <sup>a</sup>	40.57
<i>Elemental analysis</i>	
C <sup>b</sup>	78.00
N <sup>b</sup>	2.92
S <sup>b</sup>	4.50
Density [g/cm <sup>3</sup> ]	0.412
Gross calorific value [MJ/kg]	39.47
Crystalline fraction, $X_C$ [%]	12.4
Amorphous fraction, $X_A$ [%]	87.6

<sup>a</sup> Moisture free.

<sup>b</sup> Dry ash free.

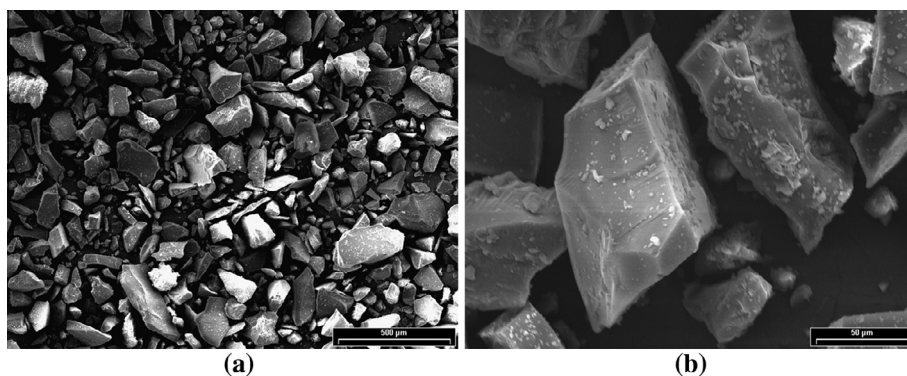


Fig. 2. SEM micrographs of as-received asphaltite samples at: (a) low magnification (60 $\times$ ); and (b) high magnification (500 $\times$ ).

additional tests were addressed to study the effect of variations in the time-temperature histories of individual asphaltite particles.

The DTF consists of an electric furnace able to operate up to 1100 °C which surrounds two concentric quartz tubes, having an effective zone of constant temperature of 70 cm length. Nitrogen inert gas is injected at the bottom of the outer cylinder and is preheated while flowing upwards; when at the top of the outer cylinder, the gas is forced onto the inner tube through a flow rectifier and the gas flows downwards and leaves the reactor through a water-cooled collection probe. Solid feed particles are entrained by a jet of non-preheated inert gas to a water-cooled injection probe placed on the top of the inner tube. The reactor operates in laminar fluid dynamic regime with an average gas velocity of 1.5 cm/s. At such conditions, the heating rate is expected to be about 800–1000 °C/s and the residence time of particles in the isothermal zone of reactor is of a few seconds [23]. Using this experimental setup, asphaltite-derived char samples were prepared at 950 °C, and the resulting char structure was compared with those of chars produced in the FB reactor at the same peak temperature but at much lower heating rates and longer residence times at high temperatures.

### 3.3. Char characterization

Structure of asphaltite-derived chars produced in different pyrolysis conditions was characterized by XRD, using a diffractometer Bruker D8 Advance that records the X-ray intensities scattered from the char samples. Copper K $\alpha$  radiation (40 kV, 30 mA) was used as X-ray source. Char samples for XRD analyses were packed into a silicon nanocrystal holder and scanned in a step-scan mode over the angular 2 $\theta$  range of 5–115°. Intensities were collected for 2 s at each step.

Observed XRD patterns were further corrected by subtracting the background intensity and, then, the  $\gamma$  bands were separated from the asymmetric (0 0 2) diffuse peaks by applying the procedure described above. From the resulting XRD patterns, several parameters like the area under peaks, the peak angular position and the peak width at half-maximum intensity were measured for calculating the structural parameters given by Eqs. (1)–(3). In order to quantify the crystalline fraction and the amorphous fraction of asphaltite-derived char samples, about 10 wt% rutile was added to the char samples and the Rietveld method-based TOPAS software [24] was used for matching the observed XRD pattern with the simulated XRD pattern obtained from the individual components of the mixture.

Physical morphology of asphaltite-derived char particles was characterized by SEM using a microscope Philips 515. Some selected samples of the raw material and produced chars were observed by HRTEM using a microscope Tecnai F20.

## 4. Results and discussion

### 4.1. Effect of pyrolysis temperature

Fig. 3 shows the corrected XRD patterns of asphaltite-derived chars pyrolyzed at 650, 750, 850 and 950 °C. For comparison, the XRD diagram of the asphaltite raw material is also given. It is clearly appreciated that heat treatments have produced some ordering in the carbonaceous matrix of asphaltite samples, evidenced by the significant growth of the (0 0 2) and (1 0) diffuse peaks when the heat treatment temperature was increased from 650 °C to 950 °C. Disappearance of reflection intensities at low angle compared with the XRD diagram of the asphaltite raw material indicates that volatile matter was released almost completely at temperatures below 650 °C (primary pyrolysis).

In Fig. 4, the decomposition of observed (0 0 2) diffuse peaks into (0 0 2) symmetric peaks and  $\gamma$  bands is presented for asphaltite-derived chars prepared at 650 °C (Fig. 4(a)) and 950 °C (Fig. 4(b)). It is seen that (0 0 2) diffuse peak becomes more symmetrical with increasing heat treatment temperature while the area under  $\gamma$  band progressively reduces in size. As  $\gamma$  band is associated with the aliphatic side chains grafted on the edges of crystallites [16], it is believed that more aliphatic side chains detach from crystallites at higher temperatures and they are

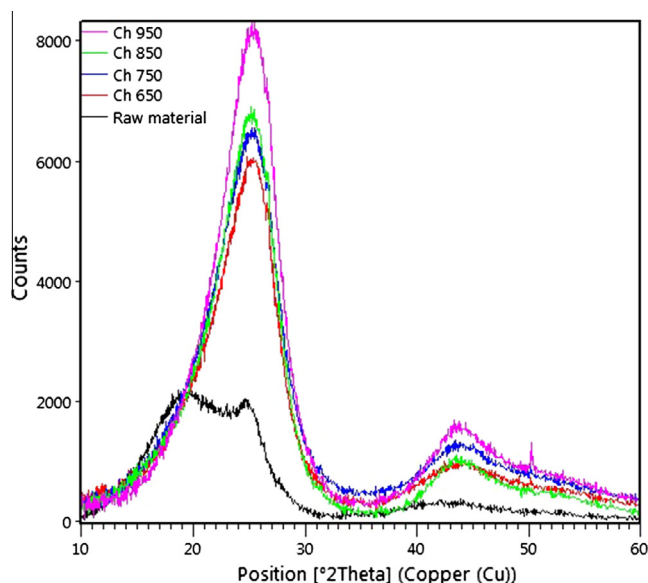


Fig. 3. XRD patterns of asphaltite raw material and chars prepared at different pyrolysis temperatures.



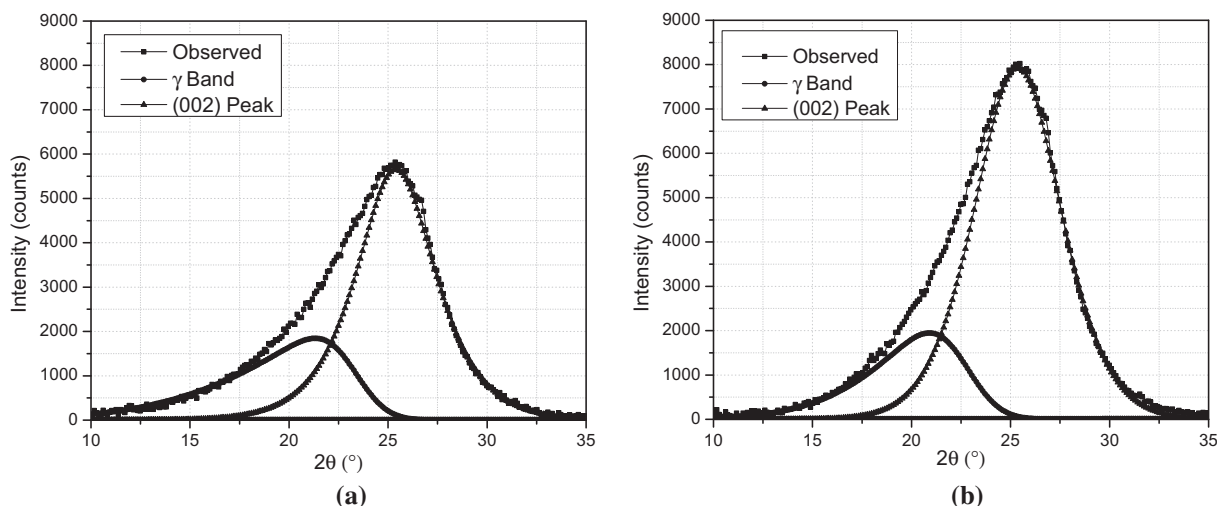


Fig. 4. (0 0 2) symmetric peak and  $\gamma$  band in asphaltite chars pyrolyzed at: (a) 650 °C; and (b) 950 °C.

transported out of the carbonaceous solid particles as volatiles, causing an increase of the aromaticity value, as it is discussed below (secondary pyrolysis).

Structural parameters of asphaltite-derived chars prepared at different pyrolysis temperatures were calculated using Eqs. (1)–(3), and results are given in Table 2. It is appreciated that both  $L_{002}$  and  $d_{002}$  remain almost constant with pyrolysis temperature within the temperature range studied. From calculated values, the average number of aromatic layers stacked along the  $c$ -axis in asphaltite-derived chars is expected to be 4–5 compared with around 70 layers for high purity synthetic graphite. These results are consistent with previous investigations [25] where it was observed that the  $L_{002}$  values did not grow at heat treatment temperatures below 1150 °C because the crystallite height growth is due to the coalescence of crystallites along the  $c$ -axis and this thermally activated process is not predicted to occur below 1200 °C [26].

On the opposite,  $f_a$  and  $X_C$  were observed to increase appreciably when the heat treatment temperature was augmented from 650 °C to 950 °C, making evident that the carbonaceous matrix of char suffers a certain structural reordering and condensation during heating at high temperatures. As was said before, the increment of  $f_a$  value is due to detachment of aliphatic side chains which are not strongly bonded to the carbonaceous matrix and their further transport out of the solid particles as volatile matter. According to Eq. (1), this process corresponds to a progressive reduction of the  $\gamma$  band size as observed in the corrected XRD patterns shown in Fig. 4. The increment of  $X_C$  can be explained by the combination of two different mechanisms: when char samples are heated at high temperatures, the associations between the amorphous carbon and the macromolecules are broken and this process is expected to release more amounts of amorphous carbon as volatile matter. On the other hand, the already existing graphite-like layers are predicted to grow in the  $a$ -direction through the incorporation of

non-organized carbon. This crystallite growth results in an increment of the in-plane crystallite size while  $L_{002}$  and the number of crystallites are not expected to change and, then, cannot be detected by XRD measurements [26].

Structural ordering of the asphaltite-derived chars at high temperatures was also confirmed by HRTEM observations in some selected samples. For each sample, many different areas were observed and no efforts were made to obtain the crystallite size from processing of the images. Fig. 5 presents the HRTEM fringe lattice images for the asphaltite raw material (Fig. 5(a)) and a char prepared at 950 °C, using a heating rate of 2 °C/min and a holding time of 60 min at the peak temperature (Fig. 5(b)). Significant amount of amorphous carbon was observed in both samples. Since this carbon is not periodic, it forms many vague areas in HRTEM images but it can be clearly appreciated that a layer structure is formed in the high-temperature processed char that is not observed in the raw material where the structure looks like distorted and not aligned.

#### 4.2. Effect of pyrolysis heating rate

Fig. 6 shows the corrected XRD patterns of asphaltite-derived chars pyrolyzed at 650 °C with different heating rates of 2, 20 and 200 °C/min and zero holding time at the peak temperature. For comparison, the XRD diagram of the asphaltite raw material is also given.

It can be observed that heat treatments at different heating rates also produced changes in the carbonaceous matrix of asphaltite samples, evidenced by the sharpening of (0 0 2) and (1 0) diffuse peaks when heating rate was reduced. The effect of decreasing the heating rate was similar to the increment of the pyrolysis temperature, as confirmed by structural parameters presented in Table 3: higher heating rates led to reductions in aromaticity and crystalline carbon fraction of asphaltite-derived chars, while crystallite height and interlayer spacing remained almost unmodified within the experimental error.

#### 4.3. Effect of pyrolysis holding time at the peak temperature

Fig. 7 presents the corrected XRD patterns of asphaltite-derived chars pyrolyzed at 650 °C with different holding times at the peak temperature of zero, 15 and 60 min, and a constant heating rate of 200 °C/min. For comparison, the XRD pattern of the asphaltite raw material is also given.

Table 2  
Effect of pyrolysis temperature on structural parameters of asphaltite chars.

Structural parameter	Temperature [°C]			
	650	750	850	950
Crystallite height, $L_{002}$ [nm]	1.80	1.60	1.58	1.60
Interlayer spacing, $d_{002}$ [nm]	0.348	0.350	0.353	0.350
Aromaticity, $f_a$ [%]	66.9	71.9	73.0	80.3
Crystalline fraction, $X_C$ [%]	49.9	50.5	56.5	62.2

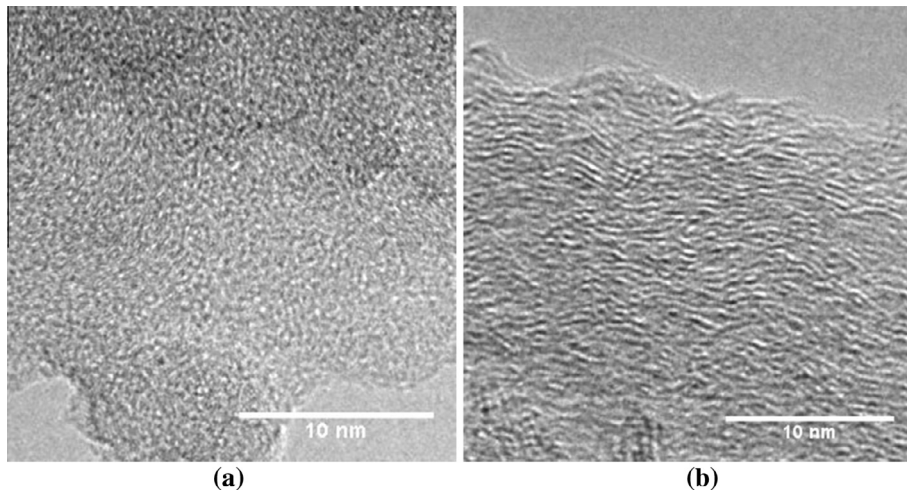


Fig. 5. HRTEM fringe lattice images of: (a) asphaltite raw material; and (b) asphaltite char prepared in the FB reactor at 950 °C.

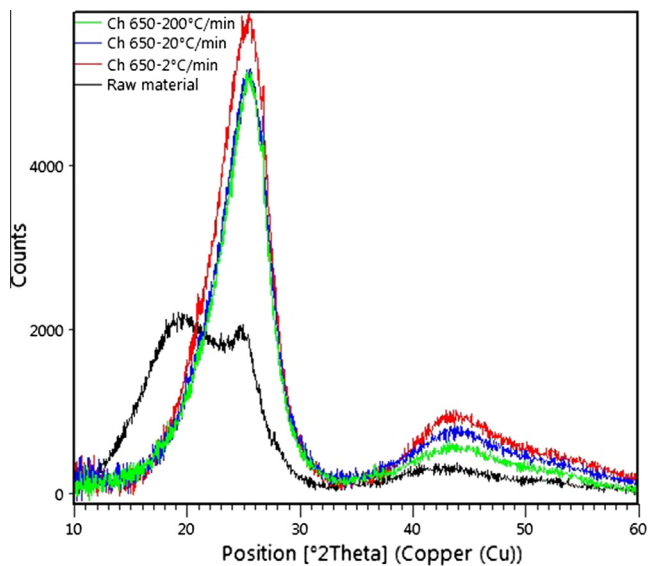


Fig. 6. XRD patterns of asphaltite raw material and chars prepared at different pyrolysis heating rates.

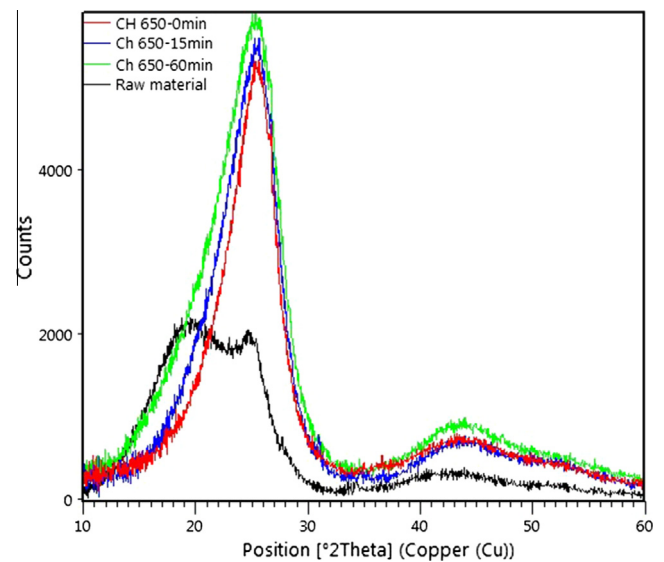


Fig. 7. XRD patterns of asphaltite raw material and chars prepared at different pyrolysis holding times at peak temperature.

**Table 3**  
Effect of pyrolysis heating rate on structural parameters of asphaltite chars.

Structural parameter	Heating rate [°C/min]		
	2	20	200
Crystallite height, $L_{002}$ [nm]	1.83	1.93	2.06
Interlayer spacing, $d_{002}$ [nm]	0.353	0.350	0.350
Aromaticity, $f_a$ [%]	80.9	77.8	76.2
Crystalline fraction, $X_c$ [%]	63.0	31.6	27.4

**Table 4**  
Effect of pyrolysis holding time at the peak temperature on structural parameters of asphaltite chars.

Structural parameter	Holding time at peak temp. [min]		
	0	15	60
Crystallite height, $L_{002}$ [nm]	1.80	1.80	1.80
Interlayer spacing, $d_{002}$ [nm]	0.348	0.350	0.348
Aromaticity, $f_a$ [%]	66.2	69.8	76.2
Crystalline fraction, $X_c$ [%]	27.4	40.4	42.4

Once again, it is seen that heat treatments at different holding times at the peak temperature also produced modifications in the structure of asphaltite raw material and these changes were in the same direction of an increment of the pyrolysis temperature: when the elapsed time at the peak temperature was increased, aromaticity and crystalline carbon fraction of asphaltite-derived chars also increased while crystallite height and interlayer spacing remained unchanged within the experimental error, as shown in Table 4.

#### 4.4. Effect of variations in the time-temperature history of char particles

While the separate effects of pyrolysis temperature, heating rate and holding time at the peak temperature on the structure of asphaltite-derived chars could be elucidated within a certain range of experimental conditions, experimental results have evidenced that the most relevant parameter for the resulting chemical and physical structure of chars is the time-temperature history of

each individual char particle above the temperature range where the volatile matter is mostly released and the structure ordering of carbonaceous matrix of chars begins to occur, i.e. 550–600 °C.

For evaluating the effect of different particle time-temperature histories, some of experimental results obtained in the FB reactor were compared with asphaltite-derived chars obtained in the DTF at the same peak temperature (950 °C) but at much higher heating rates (800–1000 °C/s) and shorter residence times at high temperature (a few seconds). These experimental conditions reproduce more closely the real conditions of char formation in large-scale gasification reactors and, then, they are more relevant for getting meaningful data about the kinetics of gasification reactions.

Fig. 8 presents the corrected XRD patterns of asphaltite-derived chars obtained at 950 °C in the DTF reactor (identified as Ch DTF 950) and in the FB reactor at two extreme experimental conditions of heating rates (2 and 200 °C/min) and holding times at the peak temperature (zero and 60 min). It is clearly seen that the particle time-temperature history has a strong influence on the asphaltite-derived char structure since the XRD patterns are significantly different. While asphaltite chars obtained in the FB reactor present XRD patterns with well-defined (0 0 2) and (1 0) diffuse peaks which become sharper when the elapsed time at high temperatures increases, the XRD pattern of asphaltite char produced in the DTF is very similar to that of the asphaltite raw material unless the disappearance of the high intensity reflections at low angle that corresponds to the release of volatile matter below 600 °C.

These qualitative results were further confirmed by quantitative XRD analyses using 10 wt% rutile for determining the fractions of crystalline and amorphous phases of carbon: while the crystalline fractions of the asphaltite raw material is 12.4% (see Table 1), it increased to only 19.9% after releasing all volatile matter in the DTF reactor. As opposed, the crystalline fraction in asphaltite-derived chars prepared in the FB reactor with much longer elapsed times at high temperatures was significantly higher, i.e. 67% for a heating rate of 2 °C/min and 60 min holding time.

Taking into account that the increment of carbon crystallinity and changes in the pore structure of carbonaceous solid materials are considered to be main responsible for the thermal deactivation process which results in a loss of reactivity during the subsequent char gasification, it is important to see that the chemical and

physical structure of asphaltite-derived chars can be profoundly changed through time-temperature histories at which the individual solid feed particles are subjected during the heating processes.

## 5. Physical morphology of asphaltite-derived chars

Physical morphology of asphaltite-derived chars was observed to depend strongly on the heat treatment conditions, in particular on the heating rate at which the volatile matter is released from the carbonaceous matrix. The effect of heat treatment heating rate has also been observed by several researchers in low-rank coals and it is attributed to the inhibition of low-temperature cross-linking reactions that occurs at high heating rates [4,27–29].

At the lowest heating rate tested, i.e. 2 °C/min, the asphaltite raw material behaved like a non-plastic or non-caking coal, retaining the original shape and the pore structure of particles during devolatilization, as shown in Fig. 9. Asphaltite-derived char particles obtained in such heating condition were dense, black metal in color and they presented high strength to grinding. It is considered that the mechanism of volatile release was similar to that observed in non-plastic coals [8]: even high pressure regions are expected to be formed within the particles, they could flow and hence the bubble growth was retarded; volatiles were then transported to the particle surface by diffusion and hydrodynamic flow.

On the opposite, the asphaltite raw material pyrolyzed at higher heating rates, i.e. equal or greater than 20 °C/min, behaved like the so-called softening or caking coals that melt at low temperatures to give a highly viscous liquid and, upon solidification, form a hard gray metal cellular mass like a cake. In such pyrolysis conditions, the mechanism of volatile release is assumed to be similar to that observed in caking coals [8]: melting of solid particles led to the collapse of pores, hindering the hydrodynamic and diffusional flow of volatiles; regions of high pressure gas are then expected to exist within the particles, forming gas bubbles that grew and coalesced as they moved to the particle surface; finally the movement of bubbles caused the particle swelling and bubbles burst as jets at the surface of particles.

Fig. 10 shows the typical morphology of asphaltite-derived char particles produced in the FB reactor at 20 °C/min and temperatures of 650 °C (Fig. 10(a)) and 950 °C (Fig. 10(b)). It is appreciated that char particles contain vesicles produced by degassing and show evidence of melting. Char particles obtained in such condition are brittle and easy to be grinded. In the case of asphaltite chars prepared in the DTF reactor at very high heating rates and short residence times, the behavior was similar to the caking coals with the difference that, due to the particular dynamic fluid conditions, the individual solid feed particles, which are surrounded by an inert gas stream while flowing downwards, undergo melting and, upon solidification, the liquid drops are transformed to very porous spheroidal chars. Resulting char morphology shown in Fig. 11 can be classified as thin-walled cenosphere, according to the classification system given by Benfell and Cloke et al. [30].

From a technological point of view, it must be pointed out that the appearance of a liquid phase during devolatilization process of asphaltite material could impair the proper operation of a large-scale gasification reactor since this flowing liquid upon solidification could form agglomerates that should be broken up by stirring to facilitate the counter-current flow of gases and solids.

## 6. Summary and future work

Effects of pyrolysis conditions on chemical and physical structure of asphaltite-derived chars were investigated by qualitative and quantitative XRD analyses, complemented with the characterization of physical morphology of char particles by SEM and

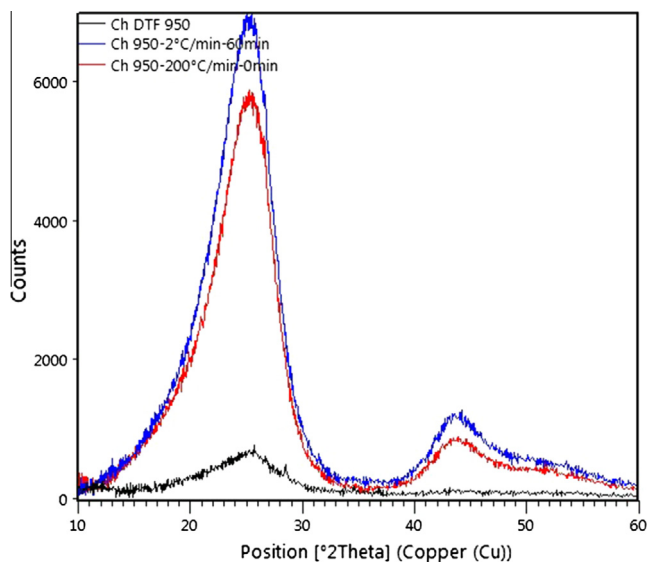
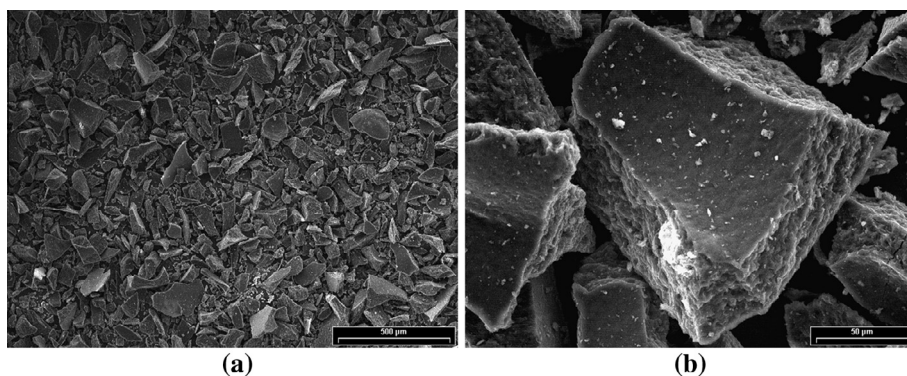
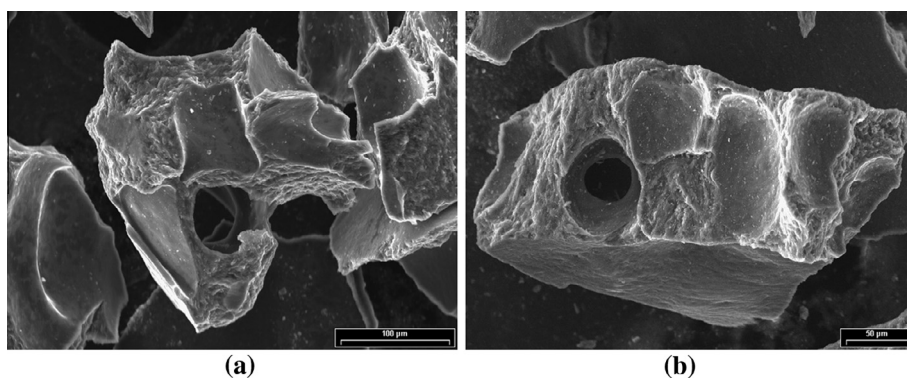


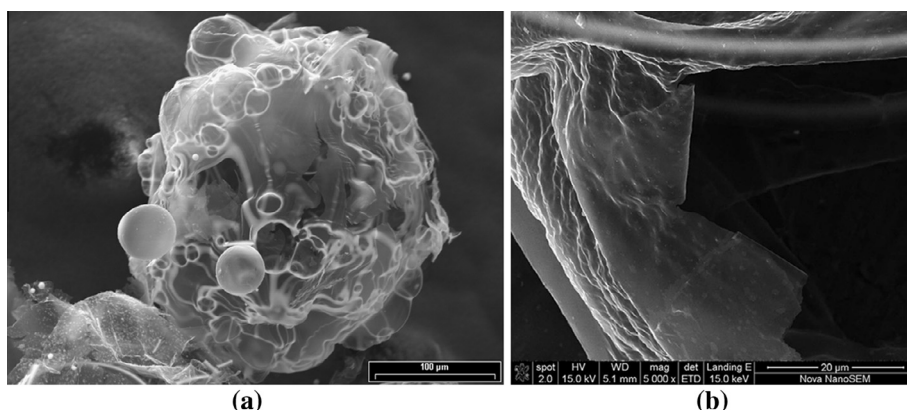
Fig. 8. XRD corrected patterns of asphaltite-derived chars prepared at different particle time-temperature histories.



**Fig. 9.** SEM micrographs of asphaltite-derived chars produced in the FB reactor at 950 °C and 2 °C/min, (a) low magnification (60×); and (b) high magnification (500×).



**Fig. 10.** SEM micrographs of asphaltite char particles produced in the FB reactor at 20 °C/min and: (a) 650 °C; (b) 950 °C.



**Fig. 11.** SEM micrographs of asphaltite char particles produced in the DTF reactor: (a) low magnification (300×); (b) high magnification (5000×).

HRTEM. Effect of temperature, heating rate and holding time at the peak temperature were studied separately through heat treatments produced in a FB tubular reactor. Furthermore, the overall effect of variations in time-temperature history of individual char particles was evaluated using a DTF reactor able to operate at very high heating rates and short residence times at high temperature.

Experimental results have shown that pyrolysis conditions have a strong influence on the asphaltite-derived char structure. A significant reordering of the carbonaceous matrix was observed to occur when the heat treatment temperature exceeded the temperature range where volatile matter is mostly released, i.e. 550–600 °C. This reordering process was evidenced by a systematic increment in aromaticity and crystalline carbon fraction of chars

when pyrolysis temperature and holding time at the peak temperature were increased, or when the heating rate was reduced.

The resulting physical morphology of asphaltite-derived char particles was found to be profoundly influenced by the heating rate at which the volatile matter is released, due to the appearance of a liquid phase during the heating process. When the heating rate was equal or greater than 20 °C/min, the asphaltite raw material behaved like a softening or caking coal that melted to give a highly viscous liquid and, upon solidification, formed a hard gray metal cellular mass like a cake. Partial melting of asphaltite material at low temperatures should be considered from a technological point of view, because the appearance of a liquid phase during devolatilization process could impair the proper operation of a



large-scale gasification reactor, forming agglomerates upon solidification that could impair the counter-current flow of gases and solids.

Effects of pyrolysis conditions on the asphaltite-derived char structure are expected to have strong influence on char reactivity under combustion or gasification conditions, since all physical and chemical transformations occurring during devolatilization process change significantly the original structure of the asphaltite raw material. These differential char reactivities to gasifying agents O<sub>2</sub> and CO<sub>2</sub> are being investigated and results of such investigations will be published soon.

### Acknowledgements

The authors would like to thank the Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional del Comahue, and International Atomic Energy Agency (IAEA) for the financial support of this research work. The authors also wish to thank to Dr. Sergio Moreno for his technical support in the processing and interpretation of HRTEM images.

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