X-ray diffraction studies of *Acacia* and *Eucalyptus* wood chars

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Acacia and *Eucalyptus* wood chars, prepared at various temperatures in the range 400–1200 °C, have been studied by X-ray diffractometry. The objective was to investigate the changes in structural ordering in relation to carbonization temperature and time. For both the *Acacia* and *Eucalyptus* wood chars, the apparent interlayer spacing (d_{002}) decreased slightly while the apparent microcrystallite diameter, L_a, increased markedly with increasing carbonization temperature. The trend was, in general, similar with increased soaking time at carbonization temperatures of 800 and 1000 °C, but these X-ray properties (i.e. d_{002} and L_a) were found to be more susceptible to carbonization temperature than to time. The results also showed that both the wood species, when carbonized under identical conditions, yielded chars with practically similar diffraction profiles.

1. Introduction

With the increasing interest of metallurgists in the utilization of wood char (a renewable and non-polluting energy source) for iron-making, it seems to be necessary to know those characteristics of wood char which are influential in controlling its reactivity, porosity, strength, etc. The literature reveals that these properties of carbonaceous materials will be sensitively dependent on their structural parameters. Haga and Nishiyama [1, 2], in connection with their studies on coal chars, found that a crystalline structure parameter sensitively reflected the reactivity of the char. Sahu *et al.* [3], during their study on oxidation rates of bituminous coal chars, also considered structural ordering of the coal chars (as affected by carbonization factors) an important parameter in controlling their reactivities. This shows that knowledge of the structural ordering in wood chars, as affected by the carbonization conditions, is of the utmost importance in order to use them more effectively for iron-making.

Warren (referred to in [4, 5]) was one of the first to recognize the significance of the diffraction characteristics for disordered carbons and he formulated the turbostratic model, which is continuing to be a very useful concept for consideration of the structure and many of the characteristics of disordered carbons. In Fig.1 the structure of a graphite crystal is compared with that of a turbostratic crystallite. The turbostratic model assumes that the layers present in disordered carbons are arranged roughly parallel and equidistant but with no correlation between adjacent layers. The X-ray diffraction (XRD) parameters which have been used in graphitization kinetic studies include the apparent crystallite dimensions L_c (height) and L_a (diameter). Though the accurate determination of L_c, L_a and d_{002} for materials giving very broad profiles is a difficult and time-consuming task with many pitfalls, the apparent L_c and L_a obtained from the widths of (0 0 2) and (1 0) profiles and d_{002} are the most frequently used parameters for describing the structural ordering.

Many research papers [6–21] have been published in the graphitization study of a variety of carbonaceous materials, using the XRD technique and other methods. As a result of heat treatment, these carbonaceous materials become more ordered in structure to an extent dependent on the nature of the precursor. On the other hand, very limited studies [22, 23] on the graphitization behaviour of wood chars have been reported in the literature. Emmerich *et al.* [22] studied the X-ray diffraction patterns of heat-treated endocarp of *Babassu* nut at various heat-treatment temperatures in the range 400–2200 °C, and developed an expression to calculate the volume fraction of the conducting phase in them.

Acacia and *Eucalyptus* are wood species known for their rapid growth and high biomass yielding capacity under Indian conditions. The aim of the work described in this paper was to carry out XRD investigations of *Acacia* and *Eucalyptus* wood chars to study their graphitization behaviour (i.e. structural ordering) in relation to the carbonization temperature and time. The XRD patterns of coal (procured from Dhanbad Colliery, India) char made at 800 °C and pure graphite were also taken in order to have a comparison with the XRD results of wood chars.
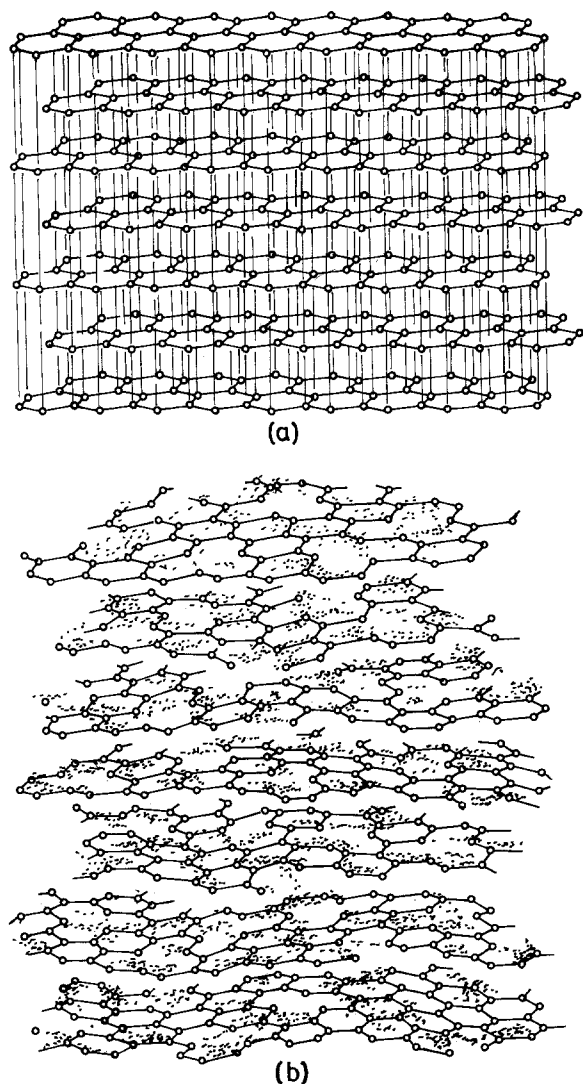
(a)

(b)

Figure 1 Schematic diagram comparing (a) a three-dimensional graphite lattice with (b) a turbostratic structure [5].

2. Experimental procedure

2.1. Preparation of wood char

In this work the chars were obtained by carbonization of *Acacia* and *Eucalyptus* woods at temperatures of 400, 600, 800, 1000 and 1200 °C. The carbonization was carried out by heating the wood samples (contained in a stainless steel retort) from room temperature to the final temperatures at the rate of about 4 °C min^{-1}. After reaching the final carbonization temperature, the samples were soaked for 1 h at this temperature and then allowed to cool in the furnace itself. To examine the influence of soak time, some chars were produced by soaking these wood samples for increased periods of 2, 3 and 5 h at carbonization temperatures of 800 and 1000 °C. The wood chars thus obtained were further processed for their XRD studies.

2.2. X-ray diffraction studies

XRD studies of powdered specimens (−170 mesh size) of wood chars were carried out on a Iso Debye-flex 2002 diffractometer (Germany) X-ray unit in the angular (2θ) range of 6–90° at a scanning speed of 3° min^{-1} in 2θ. Nickel-filtered Cu$K\alpha$ radiation (λ = 0.1541 841 nm) was used and the tube was operated at 30 kV with a filament current of 20 mA. Other

operating parameters like chart speed, counts per second and time constant were 30 mm min^{-1}, 200 s^{-1} and 10 s, respectively.

3. Results and discussion

The X-ray diffraction patterns of almost all the *Acacia* and *Eucalyptus* wood chars prepared in the present
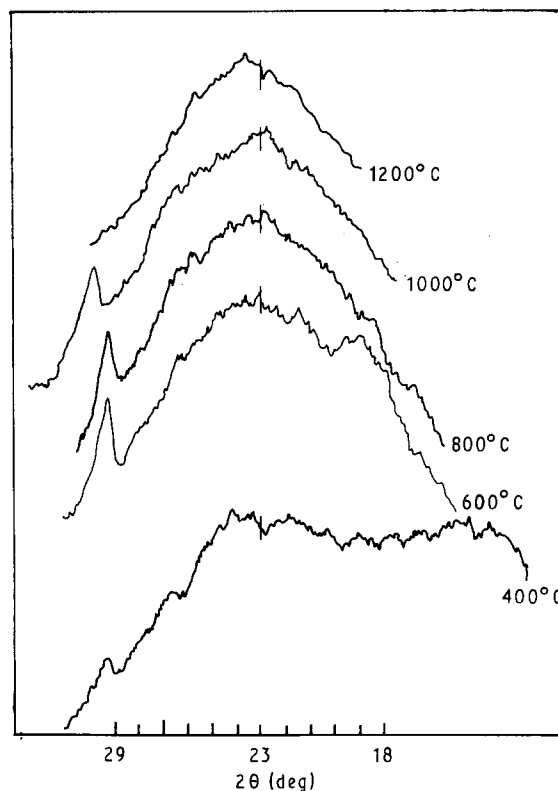

Figure 2 Changes in (0 0 2) diffraction profile of *Acacia* wood char with carbonization temperature (soaking: 1 h).
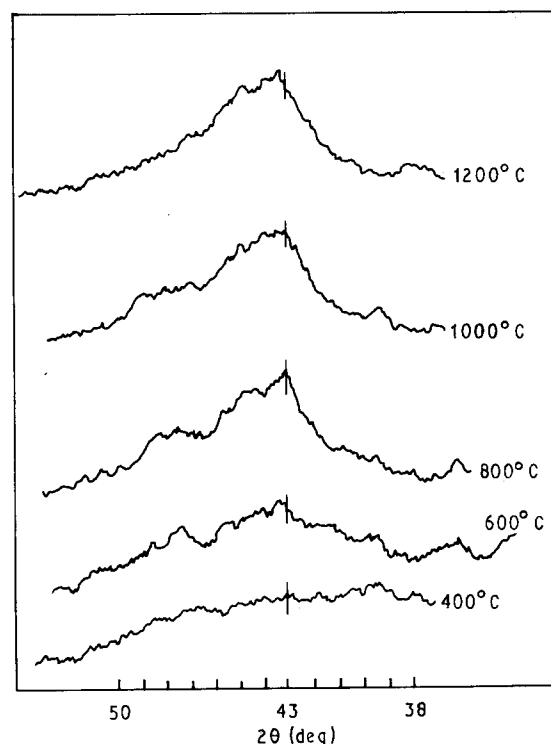

Figure 3 Changes in (1 0) diffraction profile of *Acacia* wood char with carbonization temperature (soaking: 1 h).

Figure 4 Changes in (0 0 2) diffraction profile of *Eucalyptus* wood char with carbonization temperature (soaking: 1 h).
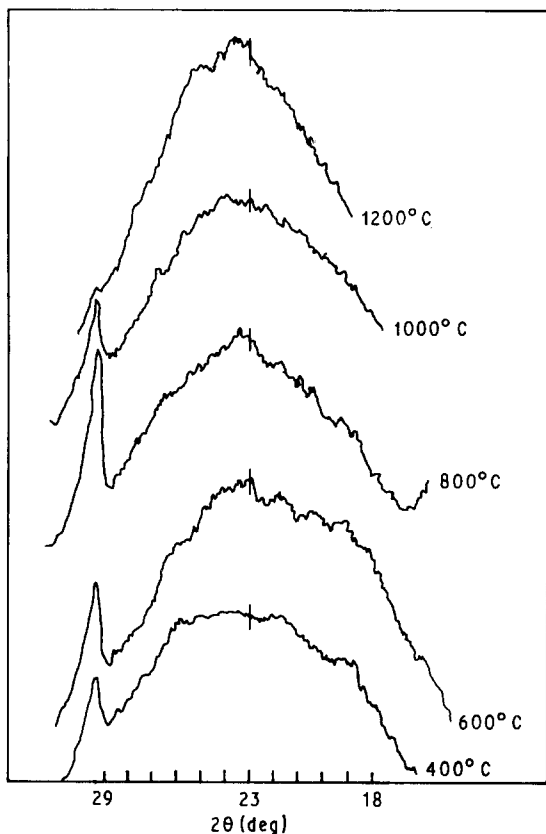

Figure 5 Changes in (1 0) diffraction profile of *Eucalyptus* wood char with carbonization temperature (soaking: 1 h).

investigation present broad profiles (containing only 0 0 2 and 1 0 bands) centred in angular positions near those of graphite (Figs 2–5), which is characteristic of a hard carbon. This indicates that the wood chars contain microcrystalline particles of the order of a few tenths of a nanometre, composed of graphite-like planes arranged turbostratically (Fig. 1), as suggested by Emmerich et al. [22]. The graphitizability in these systems was monitored through measurements of apparent interlayer spacing (d_{002}) and microcrystallite diameter, L_a. The interlayer spacing (d_{002}) indicates the packing density of carbon layers and has been estimated by the equation $n\lambda = 2d_{002} \sin\theta$. The apparent microcrystallite diameters, L_a, of wood chars were calculated from the breadths at half-maximum intensity of the (1 0) profiles by using Warren's formula [5, 21]

$$L_a = \frac{1.84 \, \lambda}{B \cos \theta}$$

where λ is the X-ray wavelength, θ is the Bragg angle and B is the breadth at half-maximum intensity in radians. Because of the breadth of the maximum, the peak position is difficult to determine precisely. This gives some error in the measured d_{002} values. Similar difficulties are encountered in the measurement of L_a. However, these apparent values of L_a and d_{002} essentially reflect the crystallographic parameters of the matrix. The L_a and d_{002} values for some of the low-temperature chars could not be determined due to excessive broadness and the diffuse nature of their
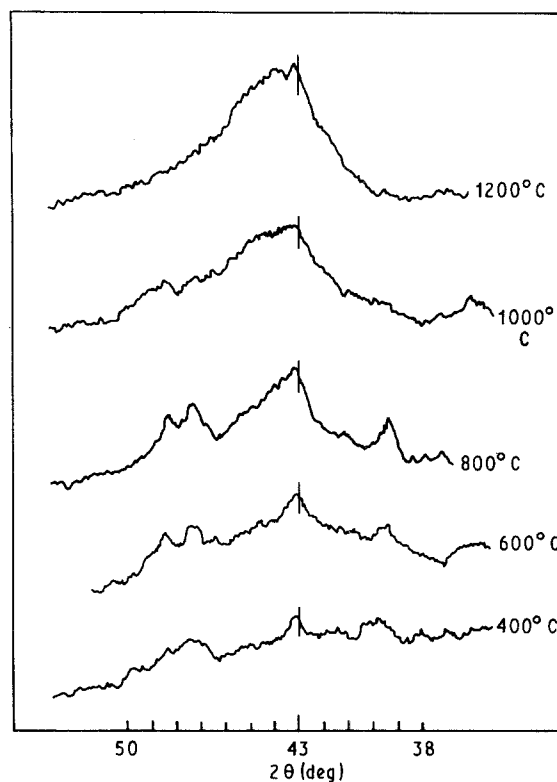
diffraction profiles. The structural ordering in wood chars, as affected by carbonization conditions, is described below.

3.1. Carbonization temperature

The change in (0 0 2) and (1 0) diffraction profiles for *Acacia* and *Eucalyptus* wood chars, prepared at various temperatures in the range 400–1200 °C (1 h soak), with increase of carbonization temperature is shown in Figs 2–5. The relative structural ordering in these wood chars, in relation to their carbonization temperature, was evaluated not only by the most advantageous lattice parameters d_{002} and L_a but also qualitatively by comparing the broadening/sharpening of their (0 0 2) and (1 0) diffraction profiles. As seen in Figs 2–5, these broad profiles sharpened and showed some angular shifting of the lines in the direction of the graphite characteristic values with increase of carbonization temperature. This infers the evolution of material towards a more ordered structure with increase of carbonization temperature.

The variations in apparent d_{002} and L_a values for *Acacia* and *Eucalyptus* wood chars with their preparation temperature are illustrated in Figs 6 and 7. As can be seen in these figures, d_{002}, in general, decreases slightly while L_a increases with increase of carbonization temperature. The increase in L_a is more rapid up to the carbonization temperature of 1000 °C, where volatile matter is lost. These results are in good agreement with the findings of Emmerich et al. [22] working on heat-treated endocarp of *Babassu* nut. As referred to by Emmerich et al. [22], the above increase in L_a appears to be produced by a thermally activated
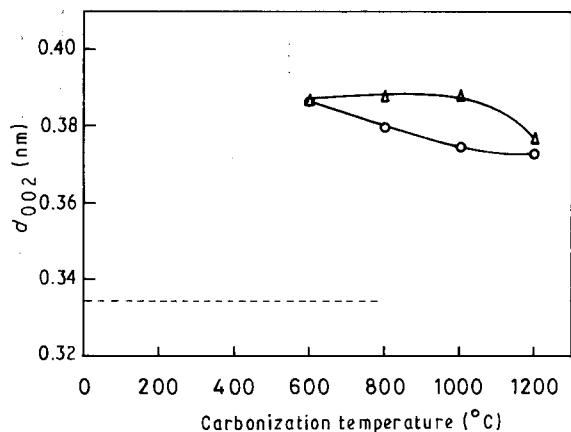
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Figure 6 Effect of carbonization temperature on apparent interlayer spacing (d_{002}) of resulting wood char. Slow carbonization, soaking 1 h: ($\bigcirc$) *Eucalyptus*, ($\triangle$) *Acacia*. (———) d_{002} for graphite, 0.335 nm.

Figure 8 Effect of carbonization temperature on wood char true specific gravity: (a) Slow carbonization, $\sim 4\,^\circ$C min^{-1}, soaking 1 h: ($\bigcirc$) *Eucalyptus*, ($\triangle$) *Acacia*. (b) Rapid carbonization, $\sim 100\,^\circ$C min^{-1}, soaking 1 h: ($\bullet$) *Eucalyptus*, ($\blacktriangle$) *Acacia*.
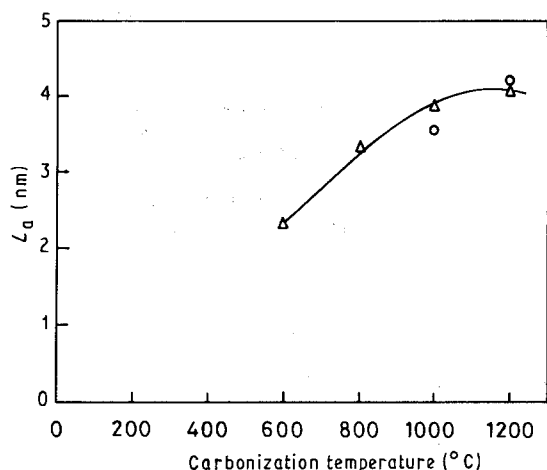

Figure 7 Effect of carbonization temperature on apparent microcrystallite diameter (L_a) of resulting wood char. Slow carbonization, soaking 1 h: ($\bigcirc$) *Eucalyptus*, ($\triangle$) *Acacia*.

carbonization process involving dehydrogenation, polymerization and condensation that effectively implies growth of the planes by the addition of carbon atoms originating from the aromo-aliphatic organic compounds responsible for the cross-links.

The above phenomenon is further supported by the increase in true specific gravity of wood char with carbonization temperature, as shown in Fig. 8 [24]. Though the values of L_c (apparent microcrystallite height) could not be determined quantitatively due to occurrence of some background in (0 0 2) diffraction profiles, the sharpening observed in these (0 0 2) profiles (Figs 2 and 4) with increase of carbonization temperature clearly reveals the growth of microcrystallites (i.e. L_c). The net result is that with increase of carbonization temperature, the improvement in structural ordering was accelerated but not sufficiently because of the difficulty of the rearrangement of C–C bonds.

The successive improvements of texture in wood chars, as heat treatment (carbonization) temperature increases, are most probably produced by the steps sketched in Fig. 9, as outlined by Oberlin [25] for materials like anthracene-base carbon. For wood chars there may be some variation in the temperature
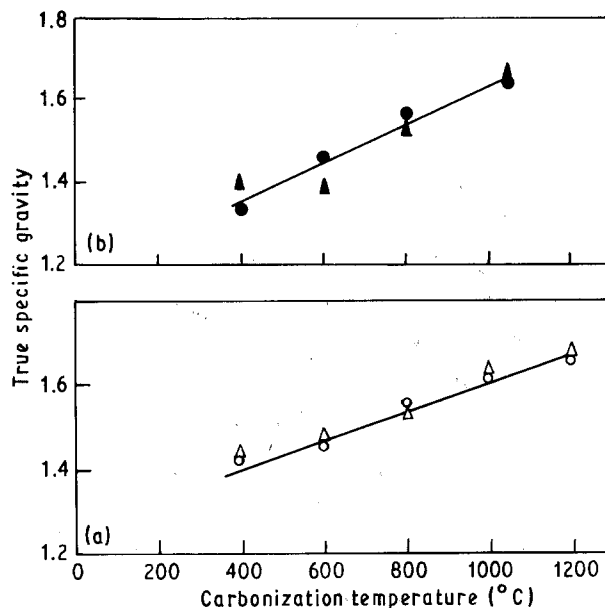
range, but the basic principle of improvement in texture with heat-treatment temperature appears to be the same. Initially, single basic structural units (BSUs) are present (stage 1); then they associate face to face into distorted columns (stage 2) and tend to pile up approximately parallel but independently. BSUs arrange in piles when they get close to each other. This closeness is caused by the release of heteroatoms (hydrogen) which ends at 800 °C. Fig. 9 also clearly shows that at heat-treatment temperatures above 1500 °C, the BSUs disappear and adjacent columns coalesce into distorted wrinkled layers (stage 3). At temperatures above 2100 °C, dewrinkling of the layers occurs rapidly and the turbostratic structure disappears (stage 4), i.e. the structure becomes perfect. The present work, limited to the heat-treatment temperature of 1200 °C, seems to represent stages 1 and 2 only.

3.2. Soaking time
Figs 10 and 11 represent the change in apparent interlayer spacing and microcrystallite diameter with soaking time for *Acacia* and *Eucalyptus* wood chars made at temperatures of 800 and 1000 °C. Unlike carbonization temperature, an increase in soaking time (at carbonization temperatures of 800 and 1000 °C) from 1 to 5 h did not produce an effective change in the structural ordering of wood chars. As evidenced by these figures, the apparent microcrystallite diameter, L_a, increases very slightly whereas the apparent interlayer spacing (d_{002}), in general, decreases with increase of soaking time. However, some fluctuations in data were observed.

The increased value of L_a with carbonization temperature and time indicates that the carbon plane is becoming wider, and this would affect the reactivity of wood char. As suggested by Kashiwaya and Ishii [26],
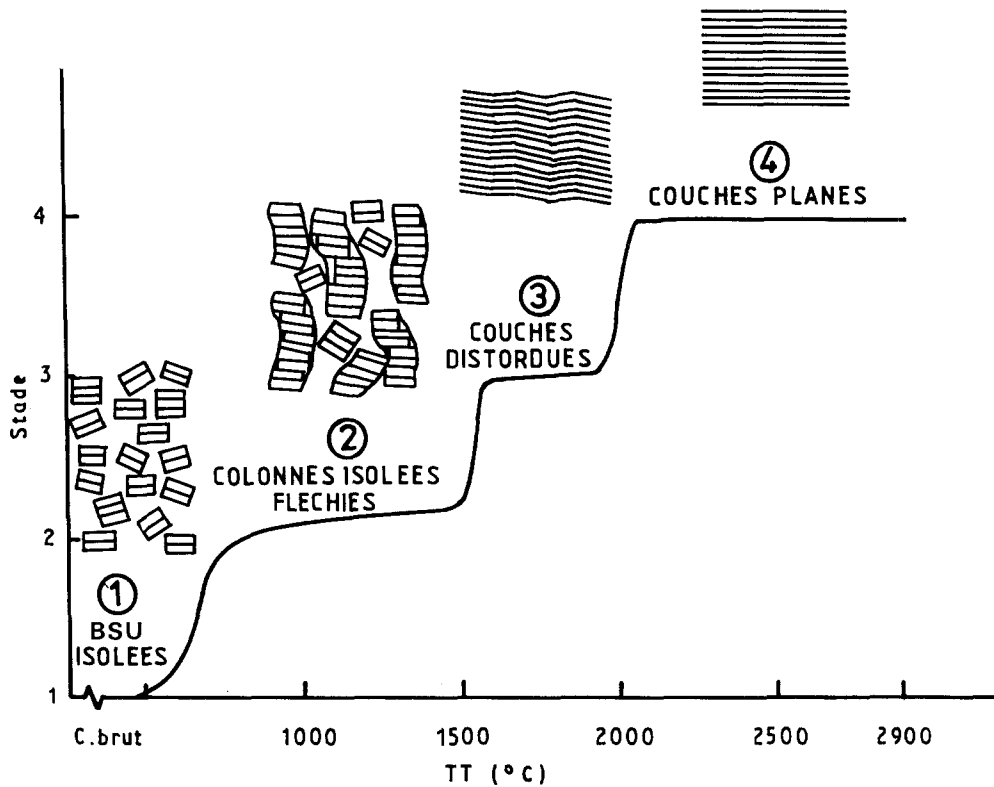
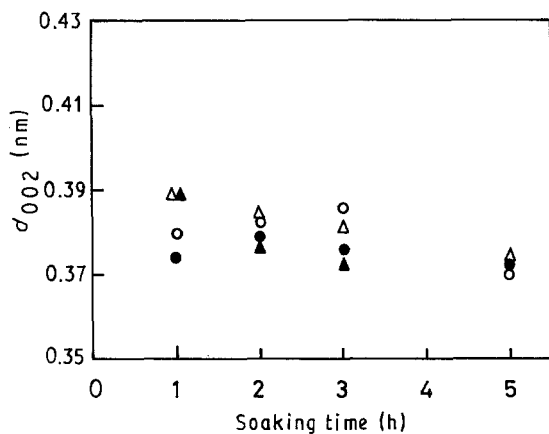*Figure 9* Various steps of graphitization and sketches of the process [25].

Figure 10 Effect of soaking time on apparent interlayer spacing (d_{002}) of resulting wood char. Slow carbonization of *Eucalyptus* at (○) 800 and (●) 1000°C, and of *Acacia* at (△) 800 and (▲) 1000°C.

Figure 11 Effect of soaking time on apparent microcrystallite diameter (L_a) of wood char. Slow carbonization of *Eucalyptus* at (○) 800 and (●) 1000°C, and of *Acacia* at (△) 800 and (▲) 1000°C.

the number of adsorption sites per carbon atom for reacting gases like CO_2, O_2 etc. (sites which exist at the periphery of the carbon net) decreases as the value of L_a increases. This results in a decrease of carbon reactivity. The decreased CO_2 reactivity of wood char with increased carbonization temperature and time was confirmed and is being reported separately. The decrease in apparent interlayer spacing (d_{002}) is indicative of an increase in carbon layer packing density.

wood chars, prepared under identical carbonization conditions, were similar. This indicates that the chars prepared from these two wood species under the same carbonization conditions are similar in their structure and graphitization characteristics.

3.3. Wood species

In the present investigation, XRD patterns of wood chars were found to be unaffected by a change in the type of wood. The broad X-ray reflection curves (characteristic of hard carbon) of *Acacia* and *Eucalyptus*
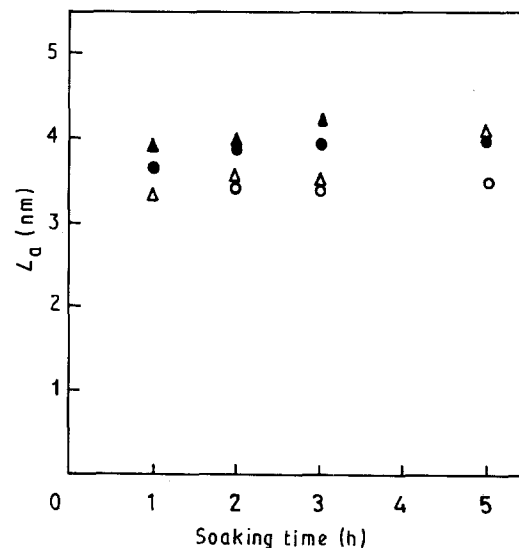
3.4. The nature of carbon in wood char, coal char and graphite

The (0 0 2) X-ray diffraction profiles of *Acacia* and *Eucalyptus* wood chars, as shown in Figs 2 and 4, can be compared with those of 800°C coal char and pure
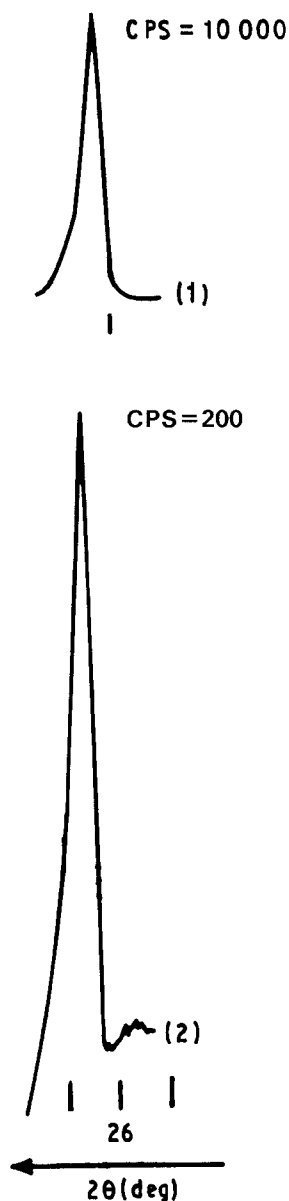
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CPS = 10 000

(1)

CPS = 200

(2)

26

$2\theta(deg)$

Figure 12 The (0 0 2) diffraction profiles of (1) graphite and (2) 800 °C non-coking coal char.

graphite (Fig. 12, curve 1), which reveals the very high concentration of carbon crystallites in graphite. The above observations indicate that the amount of crystalline (perfectly ordered) carbon is maximum in graphite followed by coal char, while the wood chars contain non-graphitized (i.e. hard) carbon.

4. Conclusions

The present work has given valuable information on the structural ordering in wood chars through measurements of the crystalline parameters d_{002} and L_a. Though the wood chars did not show any sharp peak for graphite, the structural ordering was still progressing with increasing carbonization temperature and soak time, the d_{002} values being less sensitive to these carbonization conditions than the values of L_a.

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graphite in Fig. 12. The wood chars were found to have a high value of interplanar spacing (d_{002}), usually greater than 0.37 nm (Figs 6 and 10), which was significantly larger than those observed for 800 °C coal char (0.335 nm) and graphite (0.335 nm). The increased interlayer spacing in wood chars is attributed to stacking disorder and weak Van der Waals bonding between the layers. Examination of the spectra in Fig. 12 (curve 2) shows that in 800 °C coal char, a well-developed graphitic reflection corresponding to an interlayer spacing of 0.335 nm (equal to that of graphite) can be seen. An extensive increase in intensity and sharpness of this reflection (0 0 2) is observed for pure