EFFECTS OF SILICON CARBIDE FORMATION ON THE TRUE DENSITY OF A BIOMASS CARBON

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Introduction

Generally the true density (D_{tr}) of coals and other carbonaceous solid materials heat treated above 500°C increases monotonically with increasing heat treatment temperature (HTT) [1,2], and may reach the density of graphite (2.2 g/cm^3) at high HTT values.

In this work it was observed an anomalous behaviour in the values of D_{tr} of a biomass carbon (endocarp of babassu coconut) as a function of HTT above 1100°C HTT. This is correlated with a structural change that occurs in the material, characterized by the formation of a silicon carbide phase. The results of D_{tr} are discussed and correlated with those of previous experiments of X-ray diffraction (XRD) and electron spin resonance (ESR).

Experimental

Details about the endocarp of babassu coconut and heat treatments are given elsewhere [3,4].

The measurements of D_{tr} were made using the picnometer method, with helium as the displacement fluid. Since helium is the smallest atom available, it has the best chance of penetrating all the porosity in carbon materials [5,6].

Results and Discussion

The experimental values of D_{tr} as a function of HTT are shown in Fig. 1. It is observed that up to 1100°C HTT the behaviour of D_{tr} is similar to that found in other heat treated carbons [1,2]. However, above 1100°C HTT it shows a different behaviour, characterized by a reduction of D_{tr} that persists up to 2000°C HTT.

To analyze this anomalous behaviour of D_{tr} it is necessary to discuss some components of the mineral matter of the material. The endocarp of babassu coconut heat treated up to about 1100°C HTT naturally contains between 5 to 8% wt of mineral matter [3], 80% of it being silicon dioxide (SiO_2) [7,8]. This relative high fraction of SiO_2 is one of the principal causes of an important structural change that it undergoes at about 1100-1300°C HTT upon the heat treatment process. This structural change is characterized by the transformation of SiO_2 into crystalline β silicon carbide (β-SiC), as it can be observed in the XRD spectra [3,4] (cf. Fig 1 of ref [4]).

It is suggested that the observed decrease of D_{tr} above 1100°C HTT is directly caused by the formation of β-SiC, which precludes the penetration of the displacement fluid into the microporous phase of the carbon.

The main structural difference between the SiO_2 and the β-SiC in the material can be observed in the XRD patterns. Although the precursor and the heat treated material do contain SiO_2, as it is obtained from chemical analysis [7,8], the XRD spectra do not show any line corresponding to SiO_2. On the contrary, above 1200°C HTT the lines corresponding to a β-SiC phase are readily observed.

The non-existence of any line corresponding to the SiO_2 in the XRD spectra suggests that the SiO_2 content is dispersed through the carbon matrix and does not form appreciable three-dimensional structures; this explains why it could not preclude the penetration of the displacement fluid into the microporous phase of the carbon.

The situation is different in the case of the formed β-SiC, which has a diamond-like short-range structure and a three-dimensional crystalline structure with long-range order [9]. Since the carbon atoms of the crystallites of the material are in a state equivalent to that found in graphite (which is very different from that of β-SiC), it can be concluded that the formed β-SiC is not inside or directly mixed with the crystallites, but is mixed together with the non-organized carbon fraction. So,

this supports the present suggestion of the role played by β-SiC, that it may preclude the penetration of the displacement fluid into the microporous phase of the material.

In addition to the above discussion, a correlation between the results of D_{tr} and those of ESR [10] can also be established. A great similarity can be observed between the dependence with HTT of D_{tr} and that of the ESR linewidth of the free charge carriers (ΔH_{fc}) (cf. Fig 3 of ref. [10]). This similarity is not circumstantial but, as discussed in the previous work [10], can be attributed to the same origin: the transformation of SiO_2 into β-SiC.

Conclusions

It is suggested that the observed anomalous decrease of the true density D_{tr} above 1100°C HTT for the endocarp of babassu coconut is directly caused by an important structural change that it undergoes at about 1100-1300°C HTT upon the heat treatment process. This structural change is characterized by the transformation of its naturally present SiO_2 into crystalline β-SiC.

The SiO_2 , which does not shows any line in the XRD spectra, is dispersed through the carbon matrix and does not preclude the penetration of the displacement fluid into the microporous phase of the carbon. On the contrary, the formed β-SiC, which has three-dimensional crystalline structure with long-range order and is located together with non-organized carbons at the edges of the micropores, may preclude the penetration of the displacement fluid into the microporous phase of the material, thus decreasing the observed values of D_{tr}.

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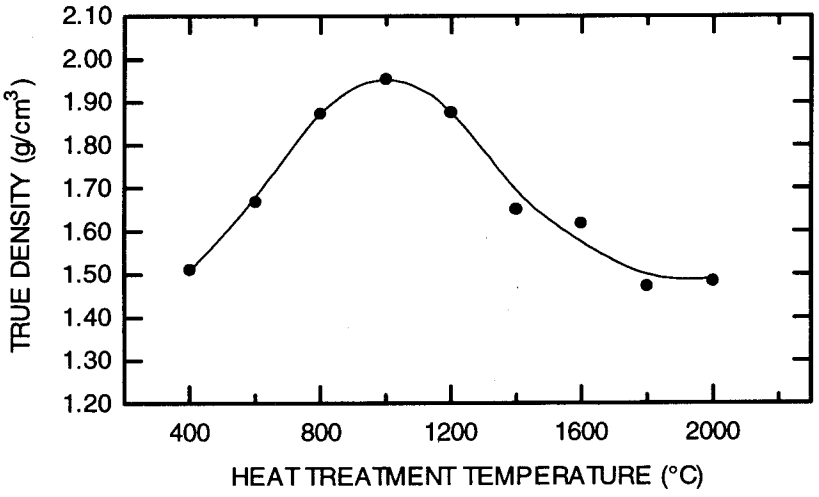

Fig. 1 - True density (D_{tr}) for endocarp of babassu coconut as a function of heat treatment temperature.