Porosity Development in Activated Carbons Prepared from Walnut Shells by Carbon Dioxide or Steam Activation

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The influence of carbon dioxide and steam as activating agents on the porosity development of activated carbons produced from walnut shells was investigated. The study was made covering a wide range of burnoff (12–76%) and employing different temperatures and times: in carbon dioxide activation, 850 °C varying the activation time in the range 60–480 min, and in steam activation, 700, 850, and 900 °C (for 30–120 min). It was found that the gasifying agent has a profound influence on the activated carbon porosity development. First, steam is more reactive and produces, in general, activated carbons with greater N_2 adsorption capacity. Second, the increase in the fraction of mesopores with activation time is more pronounced for steam. While steam generates micro-, meso-, and macropores from the early stages of the process, carbon dioxide produces highly microporous carbons, with broadening of the microporosity only for long activation times.

1. Introduction

Activated carbons (ACs) can be prepared from a large number of organic precursors. Among them, agricultural subproducts or wastes are currently being extensively studied because of their cheapness, availability in large quantities, and potential to create significant economic added value. Published studies have considered the use of such waste products as walnut shells,[1] peach stones,[2,3] olive stones,[4–6] almond shells,[7,8] and coffee endocarp,[9] to cite just a few. It is widely accepted that the porosity of ACs depends not only on the raw material used as precursor, but also on the manufacturing process. With respect to physical activation, it has been shown that the molecular size and reactivity of the activating agents play important roles in the porosity development of the resulting ACs. In this line, many researchers have established the differences between the way in which carbon dioxide and steam develop porosity in chars.[5,10,11]

Reactions of carbon dioxide or water steam with carbon are endothermic and require temperatures in the range 700–950 °C to eliminate carbon atoms. The reactions involved (see below) are (1) in the case of CO_2 activation and (1)–(3) for steam activation. The equilibrium (1) is present in both activations due to the large quantities of CO_2 generated during the process and the high temperatures involved:

$$C + CO_2 \rightarrow 2CO \quad (1)$$

$$C + H_2O \rightarrow CO + H_2 \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

These equilibria are favored by temperature to different extents. Most authors agree that, at a given temperature, the reactivity of steam is greater than that of carbon dioxide.[5,6,11–13] Also, these agents give rise to ACs with very different pore size distributions, and the impact of varying the activation conditions on the pore structure of the carbons also depends on the activating agent.

The present study was conducted with the objective of developing adsorbents from walnut shells that have similar features to the current commercially available ACs in terms of high surface areas and tailored pore size distributions to be used in a wide variety of adsorption applications. Walnut shells were selected as AC precursors because of their availability and suitability for AC production, as reported by previous studies. Earlier studies have investigated walnut shells as a raw material for AC production. However, most have centered on chemical activation with $ZnCl_2$,[14,15] KOH,[16] or K_2CO_3.[17] The few studies that have considered the physical activation of walnut shells were performed in the framework of a broader study of various lignocellulose materials[18,19] and investigated the effect of a single activating agent.[20]

2. Materials and Experimental

2.1. Materials. ACs were prepared from walnut shells, which were previously crushed, ground, and sieved to a particle size of 1–2 mm. The ultimate analysis was performed using a LECO CHNS 1000 analyzer. The proximate analysis was carried out following the procedure described elsewhere.[21–23] The results are given in Table 1. With respect to the proximate analysis, it can be seen that the walnut shells have a high content of volatile matter and low content of ash, which is clearly important for gasification and pyrolysis processes. On the other hand, from the ultimate analysis, we can highlight that this precursor also presents no sulfur and a low content of nitrogen.

Table 1. Proximate and Ultimate Analyses of Walnut Shell

proximate analysis (%)				ultimate analysis (%)				
fixed carbon	moisture	volatile matter	ash	C	H	N	S	O[a]
15.86	11.02	71.81	1.31	45.10	6.00	0.30	0.00	48.60

[a] Balanced.

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10.1021/ie801848x CCC: $40.75
Published on Web 07/28/2009