

# SHAPED ACTIVATED CARBONS BY H<sub>3</sub>PO<sub>4</sub> ACTIVATION OF WOOD MIXTURES

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## INTRODUCTION

This paper is concerned with the synthesis of high density, extruded activated carbons from hardwood through phosphoric acid activation. While powdered wood-based activated carbons are used in water treatment and other liquid phase applications, wood has essentially been excluded as a starting material for the production of granular activated carbon (GAC) because of the poor strength and friability of the products. The ability to produce wood-derived GAC with acceptable properties could greatly extend the range of applications for wood-sourced products, and allow them to compete in water treatment applications, and in other existing and growing markets that require the activated carbon to be in granular form.

Phosphoric acid is the most common reagent used for chemical activation of lignocellulosic materials. In previous papers we have described the results of studies to investigate the origins of porosity development in activated carbons from white oak (*Quercus alba*) and yellow poplar (*Liriodendron Tulipifera*)<sup>1,2</sup>. Among the processes that occur, phosphoric acid is found to effect the partial depolymerization of biopolymers, notably lignin, at temperatures below 150°C. The altered lignin is sufficiently mobile to redistribute through the wood structure. It appears that the lignin then repolymerizes upon heat treatment to higher temperatures. The low temperature phenomena have been utilized in a patent that describes the production of granular carbons by the phosphoric acid activation of wood, where the mixture is extruded while in a "plastic phase"<sup>3</sup>. It appears that sufficient binding action is induced between the wood particles to allow the formation of shaped carbons. Another patent describes the use of precursors with naturally high lignin content for the formation of granular carbons, in which the lignin acts a strong binder<sup>4</sup>.

Based upon our own findings and other reported results, we have initiated a study of the synthesis of

extruded activated carbons by the phosphoric acid activation of white oak, or *Quercus alba*. The intention is to explore the effectiveness of using high concentrations of lignin as a binder material.

This paper describes the results of a series of experiments, in which Kraft lignin was used as the binder, and the objectives were to determine its influence on the ability to form extrudates, and on their pore structure and hardness

## EXPERIMENTAL

### Activated Carbon Synthesis

The general synthesis procedure consists of first mixing an aqueous solution of phosphoric acid at 85% concentration and the white oak precursor [ground to a particle size below 50 mesh], together with a Kraft lignin binder in the form of finely ground solids. The concentration of binder in the mixture was varied from 0 to 100 wt%, and the ratio of H<sub>3</sub>PO<sub>4</sub> to the mixture of wood and binder was varied from 0.5 to 2.0 (based on combined precursor weight). The mixture was thoroughly blended at ambient temperature for about 30 minutes. Additional water was then added as necessary to form an extrudable paste, and the mixture was extruded using a high-pressure screw extruder, equipped with a multi-hole die. The continuous strands of product were then broken into shorter lengths for handling.

The extrudates were heat treated in a N<sub>2</sub> -purged tube furnace. Heat treatment was conducted in two stages: a low temperature stage, typically 130-170°C for 30-90 minutes, to allow the critical initial processes to take place; and a second heat treatment to a temperature from 350-650°C for a reaction time from 1-2 hours. After cooling, the product was extensively water washed to pH=6, to remove excess phosphoric acid, and dried.

### Characterization

Information on the carbon pore structure was derived from nitrogen adsorption isotherms obtained at 77K on a Coulter Omnisorb 100CX

apparatus. The micropore volume  $W_0$  was determined using the Dubinin-Raduskevich equation. The mesopore volume was calculated using the BJH method. The relative hardness, or abrasion resistance, of the activated extrudates was measured and compared to that of commercially available materials, by the Takeda microstrength hardness test method<sup>5</sup>. This procedure involves tumbling a known weight of sample pre-sieved to a particle size from 2.36mm to 600 $\mu$ m in a tubular container together with five 5mm steel balls for a specified number of rotations. The mass of carbon passing a 600 $\mu$ m screen is then measured and expressed as a percentage of the initial mass.

## RESULTS AND DISCUSSION

The hardness and pore structure of the activated carbons were found to be strongly dependent upon the concentration of binder used, as shown in Figures 1 and 2, respectively. It was possible to form extrudates at all binder concentrations, although at low and high values (below 15 wt% and above 20 wt%) they became very fragile after heat treatment.

As the binder concentration is increased up to 30 wt%, the micropore volume passes through a sharp minimum at 15-20 wt%. In contrast, the mesopore volume increases, and attains a shallow maximum in this same concentration range. The changes in porosity correspond to a dramatic increase in hardness. The activated carbons with binder concentrations of 15 and 20 wt% compositions were found to have comparable micropore and mesopore volumes to that of a commercial coal-based granular carbon, and were almost as hard. On the other hand, while a commercial wood-based granular carbon was found to possess over twice the total pore volume (due principally to a higher mesopore volume), it was much weaker. At still higher binder concentrations, the micropore volume again increases, before falling to a low value for the pure Kraft lignin. The mesopore volume, however, is small at all binder concentrations above 20 wt%.

The inverse relationship between pore volume and hardness, as reflected by the data in Figures 1 and 2, at binder concentrations below 30 wt% can be anticipated. Over this range, it is suggested that the added lignin supplements the action of the natural lignin. Low temperature depolymerization of both types of lignin will be promoted by reaction with phosphoric acid and allow a more fluid condition,

wherein mixing and flow of the biopolymers is facilitated, with the formation of bridges between individual wood particles - thus improving binding and hardness. As can also be seen, the pure Kraft

lignin develops much lower microporosity than the parent wood, which could explain the reduced microporosity as a dilution effect. However, the real picture appears to be more complex, and this proposition does not account for the changes in porosity at higher binder concentrations.

At binder concentrations of 30 wt% and above, it is conjectured that the lower concentration of wood particles reduces the extent of particle-particle contact, impeding any effective binding.

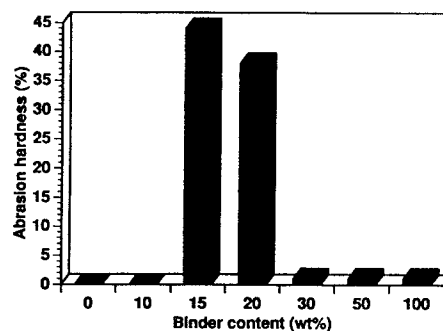


Figure 1: Abrasion hardness of activated carbons.

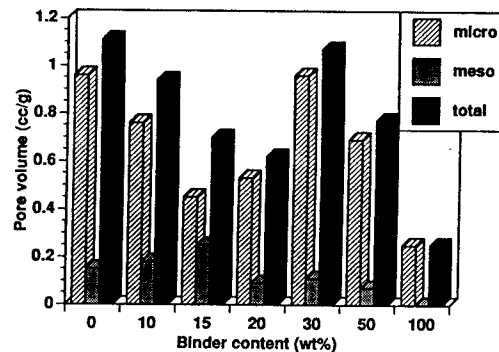


Figure 2: Pore volume of activated carbons.

## REFERENCES

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