

ACTIVATED CARBONS BY H₃PO₄ ACTIVATION OF HARDWOODS: EFFECT OF PRECURSOR PRETREATMENT

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INTRODUCTION

Steam explosion is a process that is used to alter the structure of wood and other biomass materials. Further compositional change can be effected by solvent extraction to produce fractions with different proportions of altered biopolymers¹. Hence the pretreatment of wood by these techniques offers opportunities to examine the effects of precursor composition on activated carbon synthesis, and could potentially lead to the identification of methods to produce activated carbons with new and controlled pore structures. In this paper we describe the results of studies to study the influence of steam explosion and solvent fractionation on the pore structures of activated carbons formed by H₃PO₄ activation of two hardwoods, white oak (*Quercus Alba*) and yellow poplar (*Liriodendron Tulipifera*).

EXPERIMENTAL

Fresh yellow poplar or white oak chips were processed at the Virginia Polytechnic Institute using a Stake Technology steam explosion machine, under the following ranges of conditions: temperature 215-228°C; pressure 281-395 psig; and reaction time 2.5-4.1 min. The calculated steam explosion severity, $\log R_0$, defines the net effect of the particular combination of time, temperature and steam pressure that is used². Materials were prepared at four levels of $\log R_0$ between 3.9 and 4.5. Subsets of the steam exploded fractions (SEF) samples were extracted with water (60°C), removing xylose, some hemicellulose and lignin, and producing water extracted fractions (WEF). Part of the WEFs were further extracted with NaOH solution, at 80 to 90°C for 30 minutes, to remove a fraction that is primarily lignin, leaving an insoluble product that is rich in cellulose (alkali extracted fraction, AEF). The lignin-rich fraction is recovered by HCl precipitation (alkali soluble fraction, ASF). Activated carbons were produced by techniques that have been described

previously³. Essentially, phosphoric acid solution (30 wt%) and the starting material were mixed (weight ratio of acid to precursor = 1.0) and first heat treated to below 200°C in nitrogen flow for 2h, to allow time for penetration of the reagent and for the initial reactions. The mixture was then heat-treated in flowing nitrogen to a final temperature of 350°C and held for 1 hr. The product, after cooling, was leached extensively with distilled water to pH 6-7 to recover the reagent, before drying. Information on the carbon pore structure was derived from nitrogen adsorption isotherms obtained at 77K on a Coulter Omnisorb 610 apparatus. Micropore volumes were determined by the D- R equation, and mesopore volumes by the BJH method.

RESULTS AND DISCUSSION

A comparison of the pore structure of activated carbons produced from the parent hardwoods showed that, when activated under similar conditions, the micropore and mesopore volumes developed in white oak are much smaller than those in yellow poplar [micropore volumes 0.51 and 0.65, and mesopore volumes 0.34 and 0.65 for white oak and yellow poplar respectively]. However, it should be stressed that the activation conditions are not necessarily optimum for either precursor.

Pretreatment by steam explosion caused some significant changes to the carbon pore structure. As $\log R_0$ represents a logarithmic scale, the range 3.9 to 4.5 essentially corresponds to the extremes of this treatment. At $\log R_0$ 3.9, coarse fibers are produced with little chemical or morphological change, whereas at $\log R_0$ 4.5 the product appears black and charred, indicative of significant modification. The yield of recovered material was always in the range 90-100%, but it decreased with increasing $\log R_0$, suggesting that there was some volatile loss at higher severities. There were some variations in the pore structures of the SEF-derived carbons with $\log R_0$, but they

were less dependent on this variable than might be anticipated. The general effects were: micropore volume increased by up to 50% for white oak, and was moderately reduced for yellow poplar (up to 17% decrease); with both hardwoods, the mesopore volumes were reduced by as much as 50%.

For both woods, the yields of the WEF fractions were in the range 70-77%, and similar at corresponding $\log R_0$. The carbon pore structures obtained from the WEF fractions were very similar to those produced from the SEFs. The only notable difference was that there was less scatter in the data, and the pore volume distributions were almost independent of $\log R_0$.

With increasing $\log R_0$, the yield of AEF increased for yellow poplar (from 46 to 58%), but passed through a maximum of 57% at $\log R_0$ 4.26 for white oak, decreasing to 44% at R_0 4.43. The yields of ASF were lower (14 to 25%), and of comparable value for both woods at corresponding $\log R_0$. Alkali extraction was found to exert the greatest impact on the pore structures of the activated carbons. For AEF carbons, while the effects on microporosity were small, there were large increases in mesopore volume, especially at $\log R_0$ above 4.2, and most particularly for white oak (compared to the parent woods, the largest increases in mesopore volume were 25% for yellow poplar and 130% for white oak). The inverse situation

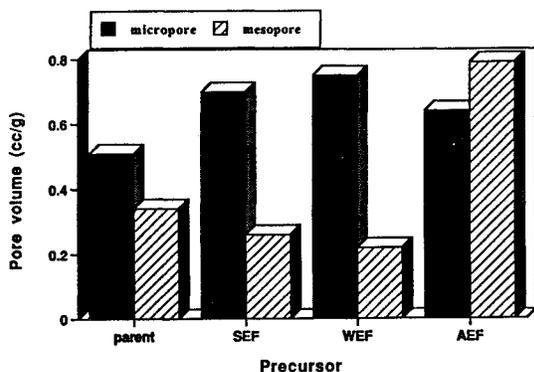


Figure 1: Carbons from White Oak fractions ($\log R_0=4.35$)

was found for the ASF - derived carbons, which possessed high micropore volumes and low mesopore volumes, especially at $\log R_0$ higher than 4.2.

Comparisons of the pore structures produced by the different pretreatments at high $\log R_0$ are given in Figures 1 and 2. It is known that steam explosion lowers the molecular weight of biopolymers, and that there is an abrupt enhancement of this process at $\log R_0$ above 4.2¹. At this stage, it is tentatively proposed that the lignin is most affected, and that the modified "amorphous" lignin is principally responsible for the increases in microporosity and/or reduction in mesoporosity in the SEF and WEF samples. It also accounts for the high microporosity in the ASF samples. The substantial removal of lignin from the AEF samples allows greater access of the acid to the cellulose, whose comparatively ordered structure is more conducive to the formation of wider pores.

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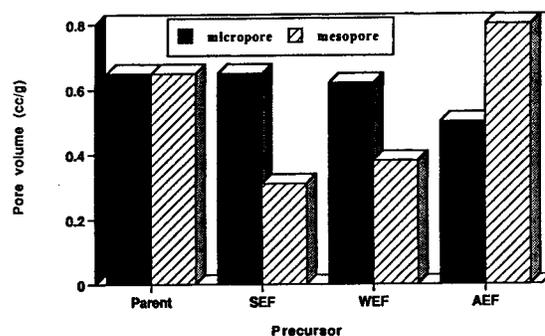


Figure 2: Carbons from Yellow Poplar fractions ($\log R_0=4.23$)