

MODIFICATION OF PORE STRUCTURE OF WOOD BASED ACTIVATED CARBONS BY USE OF POLYMER ADDITIVES

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Introduction

High surface area carbons are produced commercially by phosphoric acid activation of hardwood at temperatures around 450°C¹. However, there is limited published information on the mechanisms of porosity development of these carbons. In earlier work a hypotheses was proposed for the development of porosity and the observed dilation of the wood structure over the temperature range 150-300°C¹. It was believed that the acid first promotes the breakdown of the wood biopolymers (at temperatures below 150°C) followed by repolymerization of the resulting molecular fragments at higher temperatures. The process of repolymerization generates a different, and larger space-filling conformation resulting in dilation of the structure and porosity development as the temperature is increased to 450°C.

Evidence of depolymerization can be found in the low temperature products of phosphoric acid activation by optical microscopy indicating that there is a redistribution of material. The amorphous lignin and hemicellulose polymers are assumed to be the main components that contribute to the formation of lower molecular weight products, since the morphological changes are most apparent in the non-crystalline region of the wood structure.

A series of patents by Westvaco also describe the formation of a plastic phase when heating wood in the presence of a chemical reagent such as zinc chloride or phosphoric acid to 100-200°C. It is also well known that acid catalysts promote bond cleavage as well as the formation of cross links in the reactions of organic compounds. Phosphoric acid is used as a catalyst in petroleum refining to reduce the molecular weight of the residua from petroleum distillation and also to initiate and promote polymerization reactions. It is therefore quite reasonable to

assume that phosphoric acid will catalyze the depolymerization and repolymerization of wood biopolymers.

A hypothesis is proposed suggesting that following initial depolymerization, many of the resulting fragments recombine to form the forerunner of the eventual porous carbon structure that is formed at higher HTT. The new structure, which could arise from the adduction of species emanating from the same or from a mixture of the original biopolymers will have a lower density than the parent biopolymer mass, which can explain the observed structural dilation and porosity development that occur in parallel with crosslinking and repolymerization².

Approach

In order to test the validity of the hypothesis that has been presented, the approach to this investigation was to make the assumption that the process of repolymerization involves the combination of fragments that have been produced by the depolymerization of the different biopolymers. This being the case, it should be possible to perturb the repolymerization process through the addition of appropriate chemicals that could also be incorporated into the new structure. Depending upon the composition and concentration of the added species, measurable changes would be expected in the pore structure and other properties of the activated carbons. Therefore, it could also be anticipated that this technique, if successful, could offer a route for the selective modification of the properties of wood-derived activated carbons.

Results

As projected, it was found that the additives could exert a significant influence on the pore structure of the activated carbons. The extent of the possible change is illustrated in Figures 1 and 2, which shows the nitrogen adsorption isotherms for activated carbons produced from a few of the white oak - additive combinations. The presence of micropores is evidenced by adsorption at relative pressures below 0.3, and adsorption in mesopores occurs at higher relative pressures.

It is apparent that very substantial modifications can be made to the pore structure, the nature of which is dependent upon the type of additive. Relative to the product from the parent wood, certain additives enhance the microporosity, and others increase the mesoporosity, Figure 1. For example, the additive flavianic acid hydrate (2,4-dinitronaphtholsulfonic acid) effects a drastic increase in mesoporosity and also increases the microporosity. On the other hand, the additive "high-boiling alkylpyridine" {a term for a commercial product that consists of a mixture of

pyridines with a boiling point range from 220°C (5%) to above 285°C-300°C (50%)} results in a carbon that is purely microporous, as shown by the fact that there is no additional adsorption above relative pressures of N₂ of 0.3, Figure 2. The other additives give pore size distributions between these two extremes.

The common features of the additives shown in Figure 1 are that nearly all of them increase the mesopore volume, most of them increase the micropore volume, and they all possess oxygen-containing functional groups (principally carboxylic acid groups). The last of these characteristics indicates that the presence of appropriate oxygen functionalities is a prerequisite for adduction with the oxygen groups in the biopolymer fragments, or for the attachment of phosphoric acid which leads to formation of phosphate and polyphosphate esters that possibly cause mesopore development.

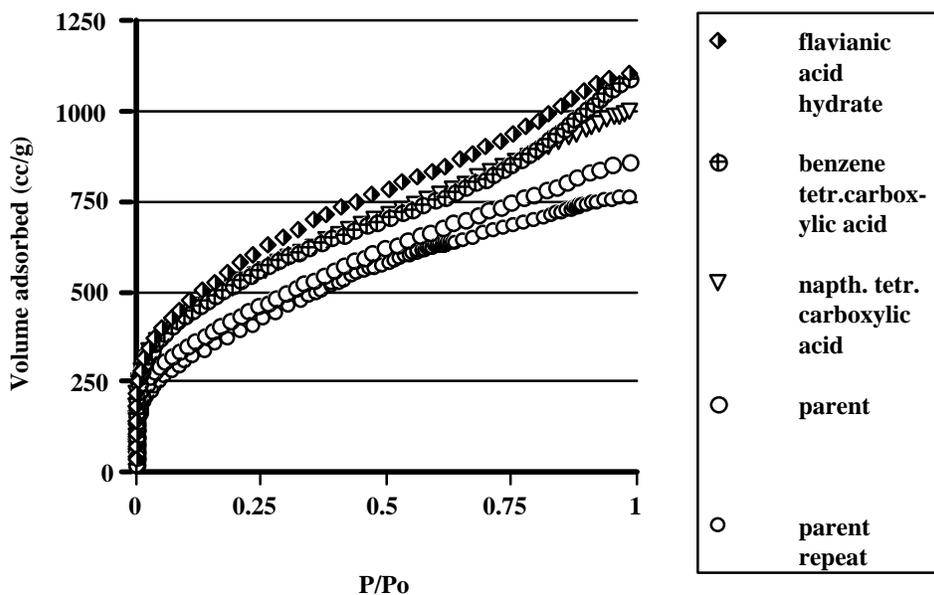


Figure 1: N₂ adsorption isotherms for carbons from white oak with different additives that increase pore volume (HTT: 450°C, additive:precursor = 0.2 g/g, H₃PO₄:precursor + additive = 1.45 g/g)

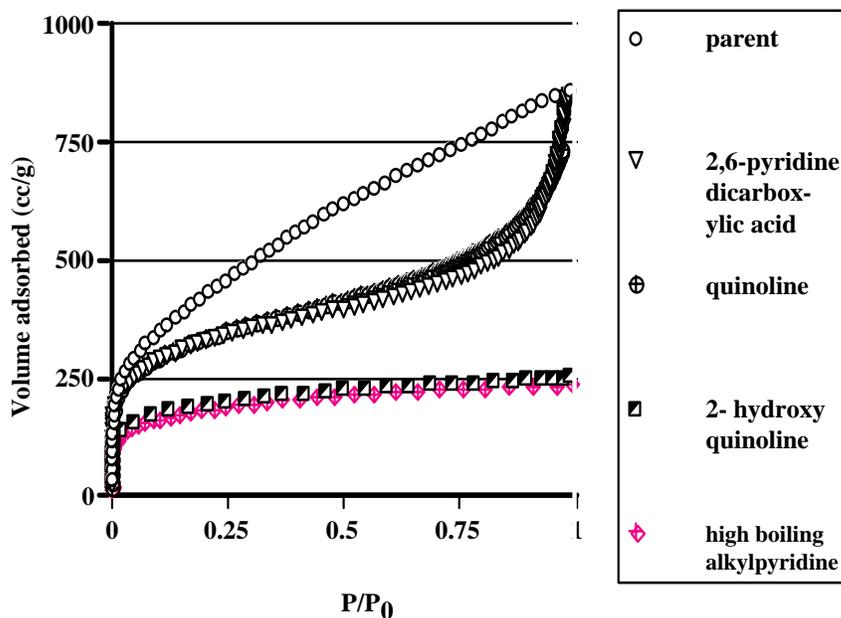


Figure 2: N₂ adsorption isotherms for carbons from white oak with different additives that decrease pore volume (HTT:450°C, additive: precursor = 0.2 g/g, H₃PO₄:precursor + additive = 1.45 g/g)

Synopsis

The intention of the research was to examine the importance of the depolymerization of biopolymers and the subsequent repolymerization of the fragments to the process of structural dilation and porosity development that occurs during phosphoric acid activation. The evidence for initial depolymerization, from other studies and from these results seemed quite clear. The further detail provided on the yield of water-insoluble product at low temperatures, strongly suggest that crosslinking and repolymerization reactions begin to dominate at temperatures above about 130°C. The present studies have also demonstrated that the introduction of additive compounds can perturb the course of repolymerization and porosity development. Depending upon the composition of the additives, porosity can be enhanced or inhibited³.

Principally, the presence of carboxylic acid groups in the additives increases the total pore volume of the activated carbon, and selectively increases mesoporosity. Where the central or core molecule is composed only of carbon and

hydrogen, the number of carboxylic acid groups has a much greater (positive) influence on porosity development than the structure of this core. The presence of groups such as NO₂ and SOOH may also be beneficial but the data obtained in the present work is too limited to be conclusive.

In contrast, the substitution of hydroxyl groups for carboxylic acid removes the preference for mesopore development, but can somewhat increase the micropore volume. Here, the structure is more lignin-like: lignin alone produces an activated carbon that is predominantly microporous.

Quite different results are obtained when the central structure of the additive contains heterocyclic nitrogen (or possibly sulfur). In this case, the development of porosity in both size ranges is strongly inhibited. It is possible that the interaction of nitrogen bases with H₃PO₄ modifies the action of the reagent, tending to produce a more highly crosslinked and microporous carbon. At the same time, the use of

additives containing heteroatoms can provide a means to introduce different functional groups into the activated carbon, and could provide a method to alter the selectivity of the carbon in adsorption or catalysis.

References

1) Jagtoyen, M. and Derbyshire, F.J., *Carbon*, Vol. 31, No.7, pp.1185- 1192, 1993.

2) Solum, M. S. , Pugmire, R. J., Jagtoyen, M. and Derbyshire, F. , *Carbon*, 33 (9), 1247 - 1254, 1995.

3) US Patent # 6,057,262: Derbyshire, F. J. and Jagtoyen, M. , May 2000.