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Physical characteristics of carbon materials derived from pyrolysed vascular plants

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Abstract

The purpose of this study was to develop new monolithic porous carbon materials from vascular plants using highly controlled pyrolysis. Perennial plants belonging to the grass family Poaceae such as bamboo (*Bambusa vulgaris*) and to the family Agavaceae such as yucca (*Yucca flaccida*) characterized by a homogeneous profile and homogenous vessel distribution were selected for the study. They were heat-treated at temperatures 550 and 950 °C in a nitrogen atmosphere to produce a crack-free monolithic porous carbon materials for which physical characteristics such as density, porosity, yield and dimensional changes were determined. The EPR spectroscopy, ultrasonic technique and optical microscopy were applied for further characterization.

All samples studied demonstrated a reduction in apparent density and dimensions due to carbonisation. It was found that similarly as in the case of hardwoods, the higher the carbonisation temperature, the greater the dimensional shrinkage. The greatest changes were observed in "transverse" to plant fibres directions, i.e., for radial and tangential. It was found that the dimensional changes under heat-treatment exhibited transverse isotropy. Carbonised plants were characterised by elastic moduli almost independent of apparent density in contrast to elasticity of precursors. Elastic moduli of samples carbonised to 950 °C were higher than those heat-treated to 550 °C. Results showed that materials carbonised at higher temperature were more stiff—more ordered in structure. Microscopic observations showed that during heat-treatment of yucca and bamboo, their tissue structure remained unaltered. There was the increase in order of aromatic layers in the walls of fibres expressed by the increase of optical reflectance values through the carbonisation process. It was found that heating plants to 950 °C quenched paramagnetic centres in carbonised samples. This effect resulted from an increase of multi-ring aromatic units in the samples. The observed lack of saturation of the EPR spectra evidenced that during slow pyrolysis defects were not created.

Carbonised woody stems of perennials studied were found as very porous, but stiff materials, which can be excellent precursors (as skeleton) for new eco-materials, e.g., for wood-ceramics.

Keywords: Vascular plants; Biotemplating; Carbonisation; Acoustical properties; EPR parameters; Optical reflectance

1. Introduction

Biomass feedstocks including wood or agricultural residues and byproducts (e.g., wood chips, sawdust, tree prunings, corn stover, bagasse and rice husks) or dedicated energy crops (e.g., fast-growing trees, shrubs and grasses) usually applied as biomass fuels are of significant interest, because they form the world's third largest primary energy resource after coal and oil [1,2]. However, some of these plants can also be precursors for the materials of various applications, especially for removal of colours, odours, organic and inorganic pollutants from industrial process to waste effluents.

The microstructures of natural-grown plants are characterized by a unidirectional, open porous system on the micrometer level which provides a transportation path for water in the living plant and yields anisotropic structural and mechanical properties [3]. The microstructural features of naturally grown plants are an attractive template for the design of novel porous ceramics. By using various monolithic wood specimens (tulip poplar, red oak white

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oak, lignum vitae, sugar maple, basswood, white pine, redwood and balsa) and highly controlled slow pyrolysis, Byrne and Nagle [4,5] have demonstrated for the first time a carbonisation process to convert wood materials into crack-free, porous, monolithic charcoals, so-called "carbonised woods" which were readily shaped by conventional methods. In spite of pure solid woods, wood-based materials were also intensively studied during the last years. Basic properties of woods or wood-based materials carbonised in neutral atmosphere are still being investigated [6–14]. Slow-carbonised cellulosic materials (wood blocks or wood-based fiberboards) were found as materials of electrical resistivity varied by several orders of magnitude for the range of heat-treatment temperature (HTT) between 600 and 1400 °C [6–8]. Volumetric shrinkage at HTT over 600 °C suggested that turbostratic crystallites were drawn closer together as the low-density disordered carbon was converted into high-density graphene sheets [9,14]. At approximately 900 °C, the large graphene sheets and the large turbostratic crystallites significantly impinged on each other. This increasing impingement of conductive phases with increasing carbonisation temperature may cause nonmetal-metal transition [9].

Klose and Schinkel [11] developed a mathematical model based on the population balance and mass balance to investigate the change in pore size distribution during the pyrolysis of woods.

Another method of carbonisation was proposed by Kurosaki et al. [12]. They prepared carbonised wood by flash heating at 800 °C for 1 h that, in contrast to conventional slow heating (4 °C/min to 800 °C for 1 h), exhibited pores that were surrounded by aggregates of carbon structures. The carbon structures were built up of clearly visible graphene layers that were often curved and overlap each other in a disordered manner.

Preparation of monolithic or granular microporous activated carbon adsorbents from precursors such as wood or agricultural waste materials (e.g., coconut shells) needs physical or chemical activation [15–18]. Cited above papers have focused on the effect of the preparation parameters (kind of the activation agent, temperature, time of agent action, etc.) on the physical properties of the activated carbons (surface area, pore size distribution, homogeneity within the monolith) as well as, on adsorption yield and adsorption kinetics. In the case of monolithic wood precursors chemical activation appeared to be a better method than physical activation to prepare activated carbon, but the choice of an appropriate wood is of paramount importance to obtain homogenous porosity and high surface area.

In the first papers [4,5,19], Byrne and Nagle have already suggested that net-shape polymer, ceramic and carbon composites can be produced using wood as a precursor. The controlled thermal decomposition of wood allows the formation of a monolithic carbon template without the presence of macro-cracks. Ozao et al. [20], as well as Hirose et al. [21] developed a new eco-material, wood-ceramic—a new porous carbon material obtained by carbonisation of wood or woody material impregnated with phenolic resin or liquefied wood. Another group of porous composites with carbonised monolithic softwood or wood-based templates produced using an infiltration technique of reactive Si-vapor (SiC-ceramics) or zirconium-oxychloride (YSZ ceramics) were proposed by Fey et al. [22] and Rambo et al. [3]. Recently, a new type of porous ceramic with wood-like microstructures was prepared by mimicking silicified wood by Mizutani et al. [23]. Titania, alumina and zirconia ceramic woods were produced by the sol–gel method using various natural hardwoods and softwoods as templates. Their microstructure was found the same structure as that of the raw wood with the pore sizes corresponding to those of the original wood. All these highly porous ceramics, especially the YSZ ceramics, are expected to be suitable for specific applications including sensors, filters, catalysts carrier, thermal isolation in high-temperature processes or electrolyte material for the solid oxide fuel cell.

All studies mentioned above involved monolithic specimens, generally cut from hardwoods, rarely from softwoods. It would be interesting to prepare carbon materials from plants of a different structure than that of hardwoods or softwoods. We decided to prepare and study carbonised monoliths from woody stems of plants such as bamboo and yucca. These plants belong to the category of perennial plants. They exhibit no branches or seasonal rings and are characterized by a homogenous profile and vessel distribution. The homogeneity of these plants can be important because of possible applications. Yucca and bamboo differ in terms of the stem cross-section. Yucca stem is characterized by quasi-cylinder shape, while bamboo stem is a collar with outside diameter varying within a wide range. High-speed growth of selected plants (especially of bamboo) is very advantageous in comparison with the growth of trees usually used for hardwood or softwood.

We chose two limit temperatures of heat-treatment, i.e., 550 and 950 °C. A choice of these temperatures was not accidental. As it was reported in early works of Byrne and Nagle [4,5] the physical parameters were sharply changed in the temperature range of about 500−1000 °C. For the HTT over this range the magnitudes of parameters studied were almost constant.

The aim of the investigation presented in this paper was to produce under slow, highly controlled pyrolysis monolithic carbon materials from stems of perennials such as yucca and bamboo, and characterise their physical structure.

2. Experimental section

2.1. Precursors

Perennial plants with woody stems such as bamboo (*Bambusa vulgaris*) and yucca (*Yucca flaccida*) were selected for the study.