

DURABILITY AND NARROW PORE SIZE DISTRIBUTION (PSD) OF CARBONS FABRICATED FROM *SALIX VIMINALIS* WOOD

Jerzy P. Łukaszewicz*, Krzysztof Zieliński

Nicholas Copernicus University, Faculty of Chemistry, ul. Gagarina 11, 87-100 Toruń, Poland

Microporous carbon molecular sieves of extremely narrow pore size distribution were obtained by carbonization of a novel raw material (*Salix viminalis*). The precursor is inexpensive and widely accessible. The pore capacity and specific surface area are upgradable by H₃PO₄ treatment without significant change of narrowed PSD. The dominating pore size indicates that these molecular sieves are a potential competitor to other nanoporous materials such as opened and purified carbon nanotubes.

Keywords: *Salix viminalis*, carbon molecular sieves, specific surface and pore structure, wooden charcoal, activated carbon

1. INTRODUCTION

Numerous raw materials are widely used to fabricate active carbon on industrial scale. Beside synthetic substrates including poly(vinylidene) and other resins or polymers (Gierak and Seredych, 2002) these also include such natural products as bamboo, coco nut shell, sucrose, hard wood (Macias-Garcia et al., 2003) and lignocellulosic biomass (Mohamed et al., 2010). Despite the fact that wood of different types is in general easily accessible, the utilization of oak-wood, beech-wood, and spruce-wood (Zhag et al., 2004) typical for moderate climate zone usually does not yield active carbons with properly tailored size of pores. Under the term “properly tailored” one understands the presence of pores of possibly uniform size and shape. Thus, simple carbonization of natural substances does not always lead to carbons possessing pores of narrow pore size distribution (PSD) which are also named carbon molecular sieve (CMS). The applicability of CMSs and similar carbons is potentially wide and includes gas separation (Mochida et al., 1995) and gas storage (Mendez et al., 2006). Literature describes sophisticated and multistage methods for fabrication of mesoporous CMSs (Lee et al., 2004). The methods offer steerable size of mesopores. However, the application of some harmful reagents (HF) as well as the complicity of fabrication reduces their application in wide (industrial) practices. Because of high production cost and some environmental aspects (application of hazardous reagents) such CMSs can be considered but as laboratory material. Carbon nanotubes after opening offer tubular pores of uniform inner diameter. Tubes can be regarded as a sort of microporous adsorbent in contrast to CMSs obtained by the template method. Despite the theoretical prediction, real samples of CNTs are not ideal CMSs (Li et al., 2004). Due to high content of carbon-based impurities and the fact that CNTs are closed, carbon nanotubes (even bought from chemical reagent suppliers) exhibit poorly developed pore structure and specific surface area. Such samples need to be purified and tubes must be opened. That can be performed by the application of strong oxidants in the liquid phase (Zhou et al., 2002) or in the gas phase (Bekyarova et al., 2003). However, the so far exploited methods of synthesis and purification of CNTs are expensive and relatively inefficient. 1 kg of opened and purified CNTs is worth much

*Corresponding author, e-mail: lukaszju@chem.uni.torun.pl

above the limits acceptable by industry and wide scale experiments. Micropores (according to IUPAC classification) in the above mentioned carbon materials have a similar size (ca. 1 nm and below) but the pores can be (in general) different in shape. Slit-like pores are expected in pyrolytic carbons obtained by heat-treatment of carbon-rich precursors (Albomoz et al., 1999) while tubular pores exist in CNTs as well as volumes between parallel CNTs. However, these differences in pore shape should not hinder the ability of some of microporous carbons to molecular sieving. A possibly narrow pore size distribution is commonly regarded as the key factor.

Regarding the statements on CMSs and current technologies to fabricate them, one may conclude that there is an obvious need for inexpensive microporous CMSs. The main task of the current study is to find a novel, inexpensive and widely accessible raw material that subjected to carbonization in oxygen free conditions yields directly a micropore carbon molecular sieve of a very narrow pore size distribution in the sub nanometer region. Additionally, the authors intend to prove that very narrowed PSD of such obtained carbons (discovered in some preliminary studies) is a stable structure which can resist even a severe activation procedure. Such stability could improve practical applicability of carbons owing to better parameters such as BET surface area and V_0 total micropore volume.

2. EXPERIMENTAL

Our attention has turned towards short rotation woody crops (SRWC) which are widely investigated and described in literature regarding environmental issues. Such plants are commonly seen as a renewable source of energy due to high “harvested mass-to-exploited area” ratio. Growing of SRWC is claimed to be inexpensive and environment friendly since the necessity of fertilizer and herbicide usage is limited (Ledin, 1996). Some reports on SRWC describe investigations of thermal treatment of harvested SRWCs and some rough estimation of surface properties of such obtained carbons (charcoals) are rarely made public. However, the so far announced results on porosity and surface area are rather side information since the reports were focused on other properties of such obtained carbonaceous solid. (Zanzi et al., 2001).

The authors decided to perform complex studies on the properties of carbons obtained via carbonization of selected SRWCs wood. Among SRWCs *Salix viminalis* seems to be an outstanding candidate for CMSs fabrication since it grows fast in mild climate zone and harvested wood is hard.

Carbonization followed a description given in the patent application (Łukaszewicz et al., 2006) and paper (Łukaszewicz and Wesołowski, 2008). In summary, carbonization is divided into two major stages. At first, one performs a low temperature heat-treatment up to 500-600 °C (1-2 hours in nitrogen flow). During this stage volatile products evolve intensively, including the release of water and tar. Then, the quartz carbonization vessel is cooled down to room temperature and cleaned from tar residue. The obtained low-temperature charcoal is put again into the vessel and heated up to the desired (final) carbonization temperature ranging from 700 to 900 °C. The second stage may be described as relatively clean since the amount of evolved volatile products is small. The obtained carbons need to be washed in deionized water for 24 hours (room temperature, continuous stirring, and 20-50 fold excess of water by volume). The obtained carbons were investigated as nitrogen adsorbing solid at the temperature of -196 °C. Nitrogen adsorption isotherms were determined by means of ASAP 2010 analyzer (Micromeritics, USA). The adsorption data were regressed using Horvath-Kavazoe model offered by the standard software of ASAP 2010. The model is based on the relation between micropore size and the adsorption potential energy of a gas molecule in a micropore of an assumed geometry (slit-like in our study). The potential energy in a micropore increases due to the overlap of potential fields created by opposite walls of a micropore. The model requires such parameters as polarizability, magnetic susceptibility, molecular surface density for gas adsorbate and solid adsorbent (in our study the data were provided by the ASAP 2010 software). The model has been improved over the years to give a

better description of adsorbate-adsorbate interactions in pores of different shape and it is still in common use for PSD determination.

In this way one determined pore size distribution function for the investigated samples. The pore size has to be understood as an “effective pore diameter”. It is a consequence of the applied method of data regression. Besides carbons obtained from mature *Salix viminalis* wood, the authors fabricated a series of carbons from the same sort of wood but impregnated with concentrated solutions of H_3PO_4 prior to carbonization. The aim of this procedure was to see whether the applied raw material is susceptible to one of typical activation procedures and whether the final carbon still possesses properties ascribed to CMSs.

3. RESULTS

The results published here are almost the first piece of information resulting from the research project being under extensive investigation. Figure 1 presents nitrogen adsorption isotherms recorded for the carbon obtained via carbonization of bare *Salix viminalis* wood. The figure also contains two N_2 adsorption isotherms recorded for wood impregnated with 50% phosphoric acid prior to carbonization. The difference between the latter N_2 adsorption isotherms results from the washing procedure. One of the curves, corresponding to high N_2 uptake, was recorded for the carbon (obtained for a H_3PO_4 -impregnated precursor) exposed to a more intensive washing procedure (boiling in de-ionized water for 24 hours). The second curve corresponds to carbon obtained via the acid impregnation but rinsing was not so intensive (6 hours of stirring in demineralized water at room temperature). It is clear that the washing procedure (satisfactory for carbons obtained from a virgin precursor) has to be extended to samples obtained in the pathway involving phosphoric acid. It is also visible that the proposed activation measure is effective causing high N_2 uptake. This phenomenon is in strong relation with the determined specific surface area (multi point BET) and the total pore volume (Table 1). These values are double for the carbons obtained via impregnation of bare wood.

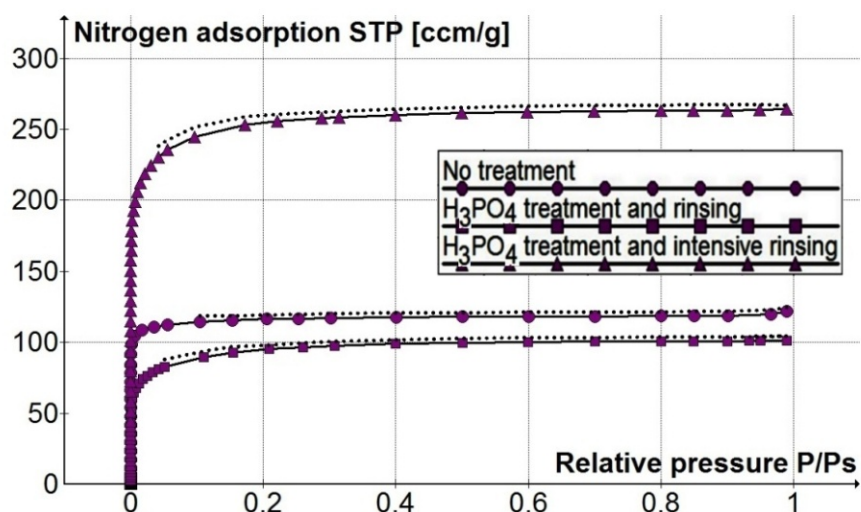


Fig. 1. Nitrogen adsorption isotherms recorded for CMSs obtained from bare and H_3PO_4 treated *Salix viminalis* wood. The dotted lines represent desorption isotherms

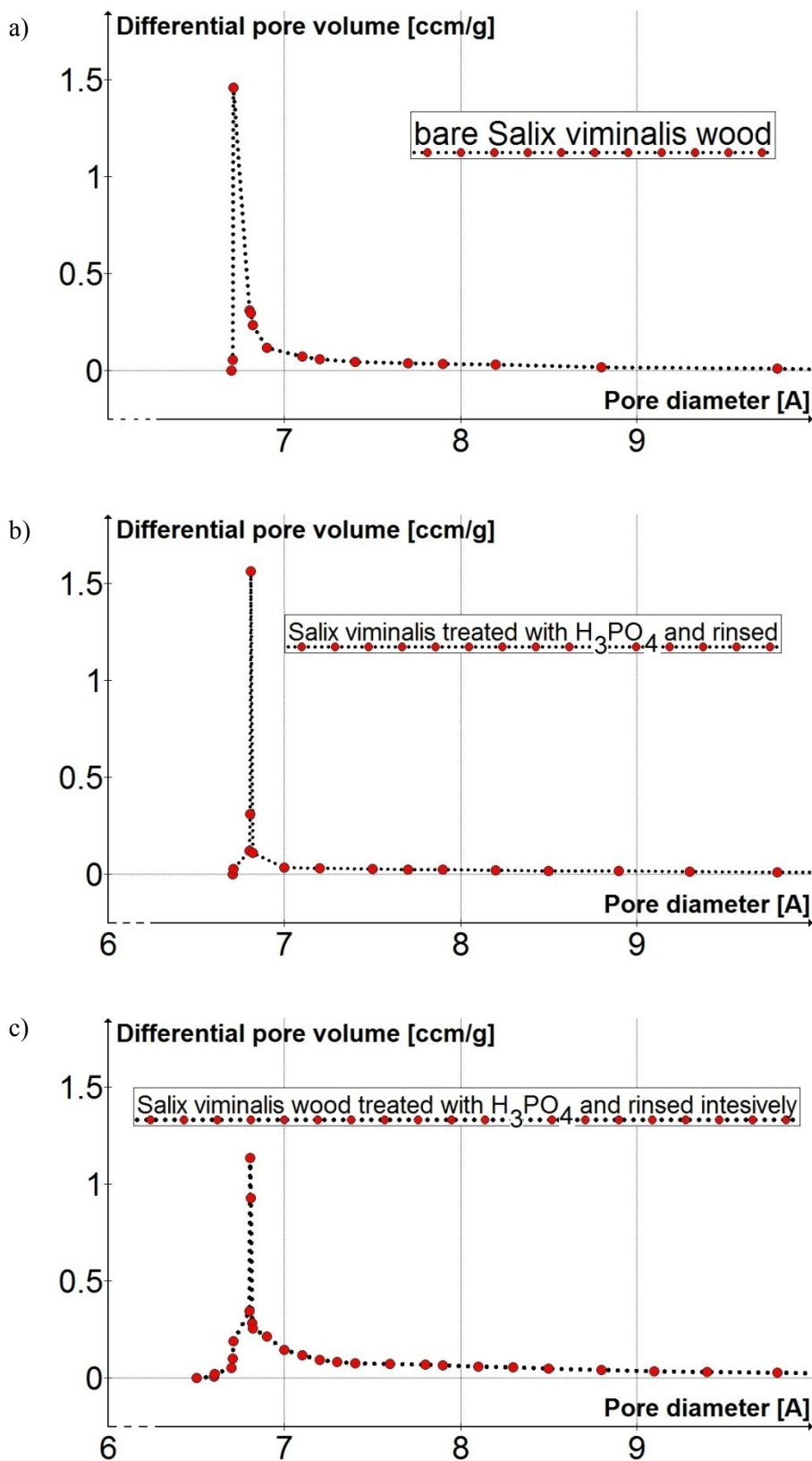


Fig. 2. Pore size distribution functions determined from nitrogen adsorption data. CMSs obtained from bare (a) and H_3PO_4 treated *Salix viminalis* wood (b – rinsed, c – intensively rinsed)

Table 1. Specific surface area and pore structure properties of CMSs obtained from bare and acid treated *Salix viminalis* wood

Raw material for CMS fabrication	BET Surface Area [m ² /g]	V_0 Total pore volume [cm ³ /g]	Maximum at PSD [nm]
Bare <i>Salix viminalis</i> wood	380.0	0.188	0.67
<i>Salix viminalis</i> wood impregnated with 50% H ₃ PO ₄	308.8	0.156	0.68
<i>Salix viminalis</i> wood impregnated with 50% H ₃ PO ₄ + intensive rinsing of obtained carbon	788.1	0.408	0.68

Figure 2 (a, b, c) presents pore size distribution determined for all the three carbons. As expected, regarding the shape of adsorption isotherms (I type), all the samples are strictly microporous. Moreover, the carbons may be regarded as perfect microporous carbon molecular sieves. In fact, the existing pores are of sub-nanometer size and are nearly exclusively contributing to the total pore volume. In comparison to other pyrolytic active carbons obtained by heat-treatment of wood (Pastor-Villegas et al., 2006), the PSD for *Salix viminalis* originated CMSs is extremely narrow. The proposed activation method, including extended rinsing, does not influence the size of pore corresponding to the maximum on PSD curves (ca. 7 angstrom).

Figure 3 presents a SEM micrograph of the surface of *Salix viminalis* originated CMSs (H₃PO₄-treated). High magnification (250 k) allows to observe a granular constitution of the carbon. The granular structure justifies in part the assumption of the existence of slit-like intergranular cavities that play the role of micropores responsible for N₂ adsorption in the relatively low pressure range (Herzog et al., 2006).

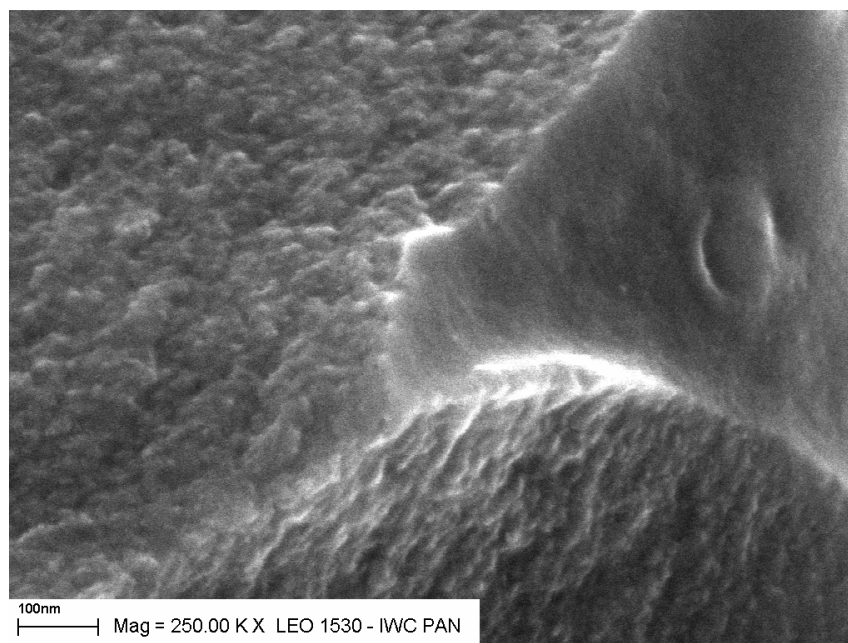


Fig. 3. SEM micrograph showing granular structure of obtained CMSs (phosphoric acid treated *Salix viminalis* wood)

Desorption isotherms have been determined and are depicted in Fig. 1 as the dotted lines without experimental points. No significant adsorption-desorption hysteresis was observed which can be treated

as an additional argument against the existence of mesopores in fabricated CMSs. The weight content of elemental carbon decreases upon H_3PO_4 treatment of *Salix viminalis* wood (Table 2).

Table 1. Elemental composition of CMSs obtained from bare and acid treated *Salix viminalis* wood

CMS Sample	N- content [%]	C-content [%]	H-content [%]	Residue [%]
Bare	1.2	88.2	1.7	8.9
Impregnated with 50% H_3PO_4	0.5	59.4	3.1	37.0

4. CONCLUSIONS

In summary, the wood of *Salix viminalis* (bare or treated with H_3PO_4) is a good candidate for fabrication of microporous CMSs exhibiting very narrow PSD. The fabrication of sub-nanometer CMSs is relatively easy and does not require hazardous chemicals. Severe H_3PO_4 -based activation leads to CMSs of improved surface area and micropore capacity provided carbonization is followed by an intensive rinsing. The fabrication of 1000 g amount of CMSs requires low financial investment. The dominating pore size is comparable to the pore size in opened single walled carbon nanotubes but one has to remember about other geometrical inconsistencies such as a different shape of pores: tubular in CNTs and slit-like in CMSs. The applicability of the obtained CMSs to gas separation or gas storage needs to be confirmed and is under intensive investigations.

SYMBOLS

PSD	Pore Size Distribution function
CMS	Carbon Molecular Sieve
CNT	Carbon Nanotube
BET Surface Area	specific surface area determined by BET method, m^2/g
V_0	total pore volume, cm^3/g

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