

SustainChem2011

**International Conference on Materials and
Technologies for Green Chemistry**

jointly with

Workshop of COST Action CM0903 (UBIOCHEM-II)

September 5-9, 2011

Radisson Blu Hotel Olümpia,
Tallinn, Estonia

Abstract Book and Program

THE YIELDS OF THE BETULA PENDULA OUTER BARK BETULINE CONTAINING EXTRACTIVES

Janis Rizhikovs, Janis Zandersons, Baiba Spince, Aigars Pazhe

*Latvian State Institute of Wood Chemistry, 27 Dzerbenes Str., LV-1006 Riga, Latvia,
E-mail: j.rizikovs@edi.lv*

Birch (*Betula pendula*) in the Northern hemisphere is a very widespread tree species, which is widely used in the furniture, pulp and plywood production. 2.0% of birch veneer blocks' mass is composed from outer bark, and it is a readily accessible raw material and is already concentrated in one place, as it is pulpmill or plywood plants residues. In Latvia, there are great potentialities to produce betuline and suberine acid, because 252 000 m³ of veneers was exported in 2007, for the production of which 693 000 m³ or about 370 000 t of oven dry birch chumps were processed. The betuline content (35–40% from o.d.s.) and suberine content (45% from o.d.s.) in our common birch outer bark are the highest in the species.

Birch bark components – lupane type pentacyclic triterpenes – betuline and betulinic acid have a pronounced biological activity, which provide the applicability in folk-medicine (in the form of outer birch bark powder) and are promising in professional medicine as a remedy against the development of cancerous cells, for example, for treating melanomas, the positive results are obtained also in experiments in Latvia. These preparations have demonstrated very positive results against HIV virus infections, and many other fields [1]. Recently, also suberine and its application fields are intensively investigated, for example, as a resource for novel macromolecular materials [2]. However, although those compounds comprise 35-40% (triterpenes) un 45-50% (suberines) from outer birch bark' mass, they have not found the industrial applicability, although the basis for their production is more than sufficient: in a pulp mill with the annual capacity 400 000 t of pulp, it is possible to produce in parallel 8000 t of betuline. The potential of the plywood factory located in Riga is about 1000 t of betuline per year.

At the first stage of outer bark processing, after its separation from phloem and grinding triterpenes are extracted with organic solvents (alcohols, carbohydrates etc.), whose solubility only at their boiling temperature is suitable for extraction. Experimental activities are focused on the yield of the raw material (outer birch bark) extractives. The yields of the outer bark extractives depending on the outer bark dispersion degree and the solvent were tested in a Soxhlet extractor.

The betuline extractives yield from *Betula Pendula* was greatly influenced by the ethanol concentration in water. Results showed that higher betuline extracting yields (up to 40%) can be obtained using 85% ethanol than 75% or 95% ethanol, if the extraction time is 10h. Optimal outer birch bark fraction is 0.4 - 1.0 mm and fractional composition above or below this range would lead lower extracting yields.

References:

1. J. Freysdotir, M.B. Sigurpalsson, S. Omarsdottir et. al. Immunology Letters, 136 (2011), 90-96.
2. A. Gandini, C.P. Neto, A.J.D. Silvestre. Prog. Polym. Sci. 31 (2006), 878-892.

LIGNOCELLULOSIC BASED NANOPOROUS CARBON MATERIALS FOR SUPERCAPACITATORS

Aleksandrs Volperts¹, Galina Dobele¹, Vilhelmine Jurkjane¹, Teresa Centeno²

¹*Latvian State Institute of Wood Chemistry, Latvia*

²*Instituto Nacional del Carbon-CSIC, Oviedo, Spain*

e-mail: quizzus@marshal.lv

Lignocellulosic wastes are the lucrative source of raw materials for further processing of all biomass components and the development high value novel materials. Current needs for low-cost nanoporous carbons have led to growing research on the reassessing of lignocellulosic residues as precursors of activated carbons with uses in a large variety of fields.

At the present moment so-called supercapacitors or capacitors with electric double layer (EDLC) are being considered as the prospective devices since they exhibit high capacitance, fast recharge and discharge times, and high power range. Nanoporous active carbons (AC) with highly developed surface are widely used in EDLCs as polarized electrodes due to their lower costs, good working conditions range, and high potential comparing to other carbon nanomaterials, such as nanocarbon tubes and fullerenes.

The aim of this work is the thermocatalytic synthesis of carbon nanomaterials with highly developed specific surface consisting mainly of 1-10 nm sized micropores using woody lignocellulosics and sodium hydroxide as activating agent, as well as testing of their galvanostatic charge-discharge voltage cycles.

Our ACs were synthesized basing on wastes of mechanical and chemical processing of birch and gray alder, 0,16-0,2 mm fractions. Materials were prepared by a 2-stage thermal treatment method (400 and 700 °C) with subsequent washing of alkali excess and drying.

The benefit of two stage treatment is that such low-temperature carbonization of lignocellulosic materials at the first stage notably decreases the oxygen content available to react with the activating agent (NaOH) and, therefore, its consumption is significantly reduced.

In the course of second stage of pyrolysis carbonized lignocellulosics go through the intermediate stage where polyconjugated structures are being (PCS) formed. Due to the π -electron delocalization on the conjugation chains PCS are characterized by ionization potential values closure, easily polarized conjugation blocks, affinity to donor-acceptor interactions, and decrease of oxygen content. These factors lead to electric conductivity, paramagnetic properties, catalytic activity, and high reaction ability.

The pore volume distribution (BJH) and surface area (BET) for were calculated from nitrogen adsorption-desorption isotherms. ACs were tested in specially assembled experimental supercapacitors with organic ((C₂H₅)₄NBF₄/acetonitrile) and aprotic (H₂SO₄) electrolytes. The electrochemical measurements involved galvanostatic charging-discharging cycles at current densities between 1 and 100 mA/cm².

The analysis of the N₂ adsorption-desorption isotherms reports that porosity of ACs obtained consists mainly of micropores with volumes between 0.24 and 1.15 cm³/g, average widths above 1 nm and have specific surface areas more than 1500 m²/g which signals that extremely porous material has been developed. Galvanostatic experiments show specific capacitances as high as 300 F/g in the aprotic electrolyte and 200 F/g in the organic medium, surpassing the values found by typical activated carbons and their capacitive performance of our ACs at high current density competed well with that found for commercial carbons used in supercapacitors.