

# Natural carbon nanoprecursors for special utilization

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Available online 6 October 2006

## Abstract

The article presents the effect of activation grinding of biomass sample—*Phragmites australis* in planetary mill. The polydisperse input of biomass with the middle extent of grain  $19.88\ \mu\text{m}$  and surface area  $1.61\ \text{m}^2/\text{g}$  was prepared by grinding after 60 min at speed of 550 rpm. The weight and density distribution curves of volume yield versus granularity show maxima at  $1\ \mu\text{m}$ ,  $18\ \mu\text{m}$  and  $18\ \text{nm}$ , respectively. Analytically significant concentrations (0.006–0.041 mg/l) of PAHs (naphtalene, acenaphtene, phenanthrene, fluoranthene, pyrene, chrysene) in the sample of biomass were confirmed with HPLC-FLD (High Performance Liquid Chromatography) method in the experiments of microwave-assisted extraction of biomass.

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**Keywords:** Biomass—*Phragmites australis*; Natural cellulose; Mechanical activation; Microwave-assisted extraction; PAHs; HPLC

## 1. Introduction

Polymers offer a unique class of materials with the natural length of polymer chains and their morphologies in the bulk lying precisely at the nanometer-length scale. This together with the large number of possible configurations available to a macromolecular chain indicate considerable room for creating polymeric materials of new properties and functions even without any change in their chemical composition [1]. The preparation of new polymer based materials exhibiting electric and/or magnetic properties and being effective catalysts has been extensively investigated by many researchers in various countries.

In the past decades a chemical field dealing with the preparation of polymers containing nanoparticles of low molecular weight compounds including metals was widely studied. Intercalation of metal particles to polymer matrices is mainly performed in solutions and gels of synthetic polymers [2]. The experiments of the replacement of the synthetic cellulose by natural insoluble polymer cellulose are realized in this research [2,3]. All processes on cellulose begin at the heterogeneous conditions at the surface and cause variable changes in the cellulose chemical composition and/or in supramolecular structure of the cell wall and at high degree of modification, in the entire structure [4]. Within this research natural composite

materials have great value as well. Among them are energetic biomass, wood, straw, grass, stems, etc., they mainly consist of polysaccharides (cellulose and hemicellulose) and lignin [5].

The renewable lignocellulosic biomass is suitable for production of chemicals, for example lignin and hemicelluloses, for the polymeric industry and for papermaking from cellulose with new perspectives in polymer nanotechnologies [5]. The main straw biomass contains cellulose, hemicellulose, lignin and small amounts of *p*-hydroxycinnamic acids such as ferulic and *p*-coumaric acids, glycoproteins, pectins, wax and ash [6,7]. Important in the group of accessory (extractive) organic substances are the polycyclic aromatic hydrocarbons (PAHs). The article presents the occurrence of polyaromatic hydrocarbons in the microwave-assisted extraction of biomass.

## 2. Experimental

The research was carried out with the samples of *Phragmites australis* from the East Slovakia.

Chemical analysis of studied samples was: extractive organic compounds 5.18%, cellulose 37.10%, lignin 23.89%, the content of carbon 48%, hydrogen 6.2%, nitrogen 0.3%, analytical water 7.89% and humic acids 16.02%.

CHN analysis was realized using elementary analyser Carlo Erba Model 1106 equipped with the microprocessor and recorder. Helium (purity 99.998%) was used as the carrier gas, oxygen (99.999%) was used as the oxidizing agent and argon created an inert atmosphere during measurement. The chromatographic column was filled with the Porapak QS with the granularity 80–100 mesh. The standard material was used the cyclohexanone–dinitrophenylhydrazone (content of N = 20.14%, C = 51.79% and H = 5.07%). The remaining constituents of sample were estimated by other

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standard analytical methods. The studied sample was pretreated in mill and then the sample of a 0.5 mm granularity was activated by grinding in planetary mill Pulverisette 6 (Fritsch) in air at the following conditions: granularity of input 0.5 mm, mass of sample 20 g, grinding speed 550 rpm, time of grinding 5, 10, 20, 60 min.

The specific surface was measured by Micromeritics Gemini 2360 apparatus using BET method. The granulometric analysis was carried out using Sympatec Helos (Germany) in wet conditions.

The granulometric analysis of sub-microns particles in the range from 1 nm to 1  $\mu\text{m}$  in the area of nano-particles was carried out with dynamic laser radiation dispersion using ALV detection equipment (Germany) with ALV 5000 correlator. The equipment consisted of argon laser Spectra Physics Stabilite 2017-0.4 S (USA) working within the wave length of 514.5 nm at the out put of 400 mW. The data were analysed using CCNTIN method and ALV 800 transputer.

SEM microscopy was performed using microscope type TESLA BS 340 (Slovakia). For contrast observation we used the secondary electron image.

Microwave-assisted extraction of the biomass samples was realized in a Whirlpool at the power 500 W and frequency 2.45 GHz. The extraction was realized in the non-polar solvent of toluene at boiling point 110.6  $^{\circ}\text{C}$  for 10, 30 and 60 min. Boiling point of solvent in the microwave was measured using the contactless thermometer Raytek MX4.

Chromatographic analyses were performed using HPLC-FLD Hewlett-Packard type 1100 equipped with column Hypersil Green PAH (250  $\times$  2.1 mm, 5  $\mu\text{m}$  i.d.). Mobile phase was acetonitrile and water Milli-Q+. Identification of measured mass spectra was performed using software ChemStation Rev. 5.2.

### 3. Results and discussion

Natural carbon precursors (generally referred to as biomass) are alternatives for syntetic polymers in nanotechnologies. At the nanometer scale, the wave-like properties of electrons inside matter and atomic interactions are influenced by the size of the

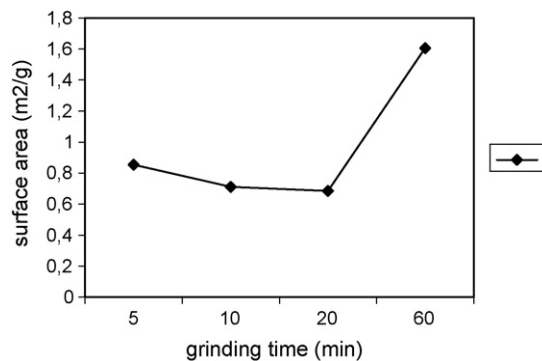


Fig. 1. Dependency of surface area of studied biomass sample vs. activation grinding time.

material. Due to the high surface-to-volume ratio associated with the nanometer-sized materials, a tremendous improvement is also achievable in the chemical properties through the reduction of size in the process of mechanical activation. Fig. 1 illustrates the dependency of surface area (SA) of the studied sample versus grinding time. The doubling of SA occurs after 1 h of grinding. In the first phase of grinding the major changes of surface area do not occur, but grain fragmentation is observed (see Fig. 2). Fig. 2a–d shows the micrographs of mechanically activated grains during various periods of grinding. Evaluated micrographs and granulometric characteristics (Fig. 3) confirmed, that the cellulose structure of biomass is a polydispersed linear homopolymer. This is in accordance with Heredia et al.

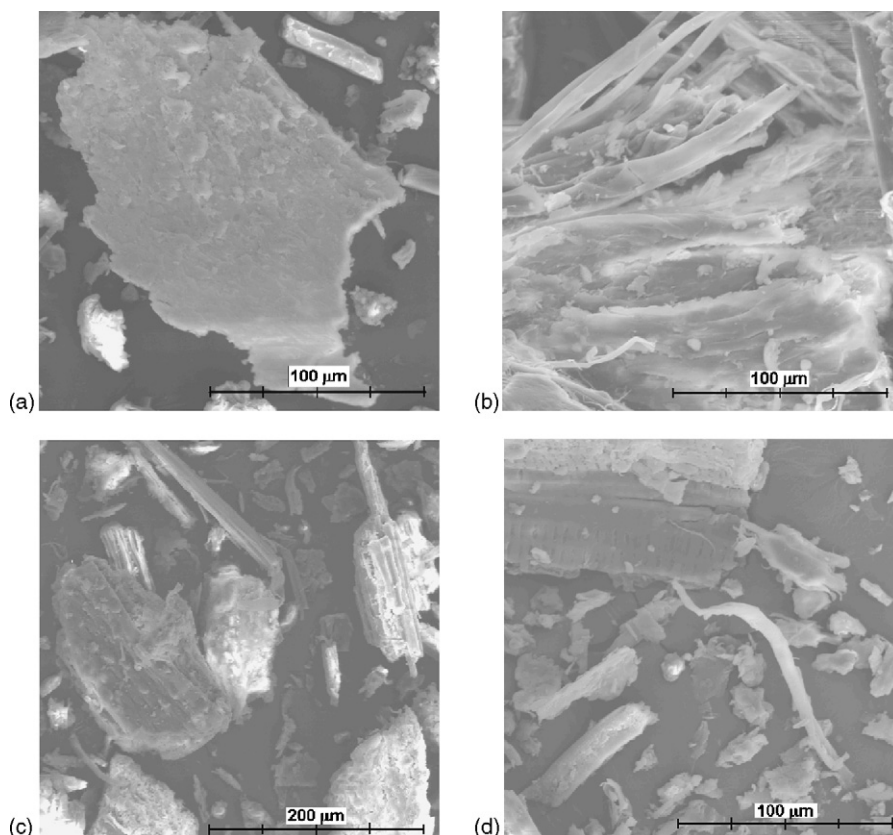


Fig. 2. Images of biomass samples—*Phragmites australis* from scanning electron microscope at different times: (a) 5 min; (b) 10 min; (c) 20 min; (d) 60 min.

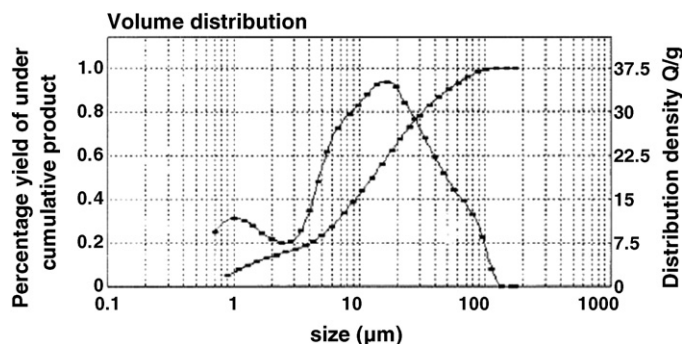


Fig. 3. Cumulative curve of undersize fraction and distribution curve of density vs. granularity of biomass sample—*P. australis*.

[8], that the microfibrils forming a *para*-crystalline structure stabilized by intra- and intermolecular hydrogen bonds are oriented in parallel or antiparallel manner [8]. Micrographs of mechanically activated biomass also indicate, that the structure contains linear parallel oriented macromolecules of cellulose, which according to [9] create in cell-walls the supramolecular aggregates with high ordered crystalline and disordered amorphous areas. X-ray diffraction studies suggest, the crystalline structure is surrounded by xylans, having a structure similar to the amorphous phase [8]. Theoretical and experimental knowledge assume the bonds among the cellulose and xylan are extreme resistant and are not destroyed after the effect of acid. The presented results indicate that the active grinding of biomass requires high energy mills. Optimal pretreatment of biomass sample required 60 min of grinding at the highest amplitude. Figs. 3 and 4 illustrate the granulometric characteristics of the sample (micro- and nanoparticles). Fig. 3 shows, that the distribution curve of density is polymodal with two maxima. First lower maximum is at the granularity  $1\ \mu\text{m}$  and the second maximum is at the granularity  $18\ \mu\text{m}$ . In accordance with above and according to Heredia et al. [8] our granulometric results confirm polydispersive character of the main cellulose compound of biomass. Cumulative curve of undersize fraction shows, that the content of ultra-fine grains with granularity  $1\ \mu\text{m}$  of the first maximum is around 10% and the content of ultra-fine grains with granularity  $18\ \mu\text{m}$  of the second maximum is around 57%. The middle average size

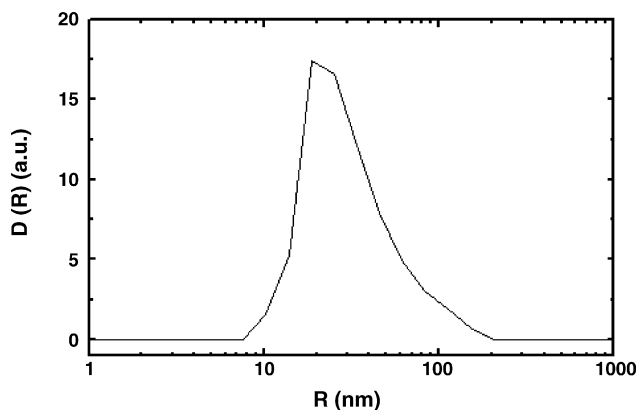


Fig. 4. Weight distribution of particles  $D(R)$  vs. grain size  $R$ .

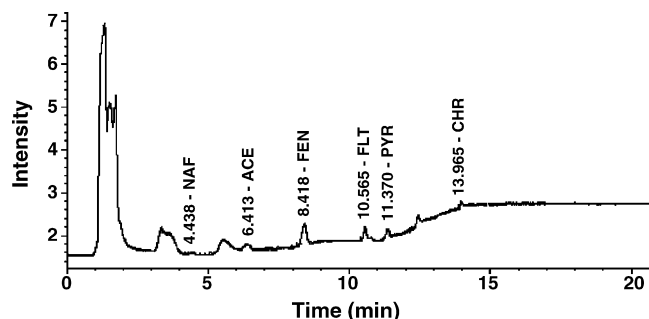


Fig. 5. Representative HPLC chromatogram of extract of mechanically activated sample after microwave-assisted extraction in methanol at 10 min (NAF: naphthalene, ACE: acenaphthene, FEN: phenanthrene, FLT: fluoranthene, PYR: pyrene, CHR: chrysene).

of grains of mechanically activated sample is  $19.88\ \mu\text{m}$  with surface area is  $1.61\ \text{m}^2/\text{g}$ . Fig. 4 illustrates the weight distribution of particles with radius  $R$  versus particles granularity. The weight distribution of particles of optimally mechanically activated sample of biomass is monomodal with maximum at 18 nm. From the continuance of the weight distribution of nanoparticles it is possible to state that the content is 7.5% for 18 nm grains in the mechanically activated sample of biomass.

Fig. 5 shows the representative HPLC (High Performance Liquid Chromatography) chromatograph of PAHs occurrence in the microwave extract of biomass in methanol at period of extraction 10 min. The figure shows, that six polycyclic aromatic compounds occur in the evaluated sample of biomass. Depending on the time of extraction, the concentration of PAHs is changed (Fig. 6). Comparison of first three curves (curve 1: naphthalene; curve 2: acenaphthene; curve 3: phenanthrene) shows the decrease of the concentrations of PAHs with the time extension to 30 min and thereafter the increase with time to 60 min (besides curve 2). PAHs concentrations at these conditions of extraction are lower than at optimal time 10 min (besides curve 1). Other 3 PAHs samples (curve 4: fluoranthene; curve 5: pyrene; curve 6: chrysene) show less significant changes of concentration with extraction time. Only the sample of chrysene (curve 6) shows the increase at 30 min of extraction and next sharp decrease with the time of extraction to 60 min. With time extension of extraction occurs the degradation of identified PAHs. This assumption was

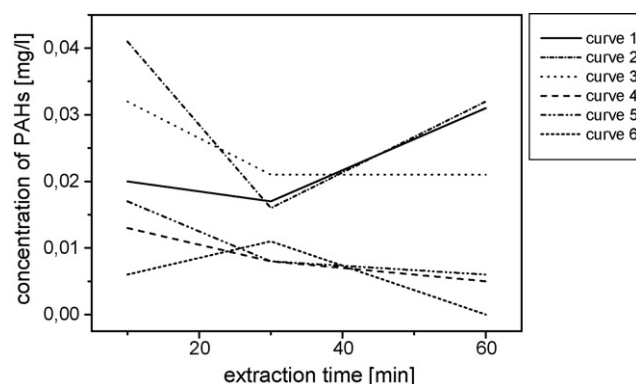


Fig. 6. Dependency of PAHs concentration in the sample of biomass vs. time of microwave-assisted extraction.

verified by method of standard PAHs addition to analysed sample of biomass in the process of microwave-assisted extraction. It was confirmed that degradation of analysed PAHs occurring at the extraction time 10 min occurs 74%, at 30 min 37% and at 60 min 47%. This knowledge has great value in the process of optimization of microwave-assisted extraction for extraction time minimization. According to the literature [9,10] the specific solvents for PAHs extraction exist to prevent the ecological valuation of biomass in nanotechnologies.

#### 4. Conclusions

Experimental results of PAHs occurrence in mechanically activated biomass confirmed six ecological significant organic compounds of PAHs type. It was confirmed, in the process of intense grinding in planetary mill for 60 min the ultra-fine poly-dispersive input of biomass with middle extent of grain  $19.88 \mu\text{m}$  and surface area  $1.61 \text{ m}^2/\text{g}$ . The weight and density distribution curves of volume yield versus granularity show the maxima at  $1 \mu\text{m}$ ,  $18 \mu\text{m}$  and  $18 \text{ nm}$ , respectively. It was also confirmed, that the analytically significant concentrations ( $0.006\text{--}0.041 \text{ mg/l}$ ) of PAHs in natural sample of biomass can be found with HPLC method in the experiments.

#### Acknowledgement

This work was supported by the Agency for Science and Technology of ME SR, Grant No. 51-036102.

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