



Kinetics of the hydrothermal treatment of tannin for producing carbonaceous microspheres



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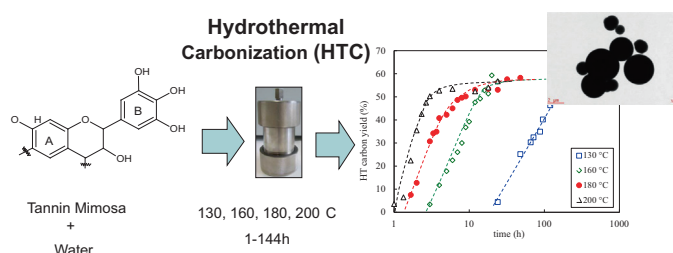
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HIGHLIGHTS

- Kinetics of hydrothermal carbonization (HTC) of tannin were determined.
- A first order reaction controls carbonaceous microspheres production by HTC.
- Activation energy equal to 91 kJ/mol was evidenced.
- Microspheres had a diameter lower than 5 μm and a surface area lower than 10 $\text{m}^2 \text{g}^{-1}$.
- Microspheres had constant composition, whatever the experimental conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Aqueous solutions of condensed tannins were submitted to hydrothermal carbonization (HTC) in a stainless steel autoclave, and the kinetics of hydrothermal carbon formation was investigated by changing several parameters: amount of tannin (0.5; 1.0; 1.5; 2.0 g in 16 mL of water), HTC temperature (130, 160, 180 and 200 °C) and reaction times (from 1 to 720 h). The morphology and the structure of the tannin-based hydrothermal carbons were studied by TEM, krypton adsorption at -196 °C and helium pycnometry. These materials presented agglomerated spherical particles, having surface areas ranging from 0.6 to 10.0 $\text{m}^2 \text{g}^{-1}$. The chemical composition of the hydrothermal carbons was found to be constant and independent of reaction time. HTC kinetics of tannin were determined and shown to correspond to first-order reaction. Temperature-dependent measurements led to an activation energy of 91 kJ mol^{-1} for hydrothermal conversion of tannin into carbonaceous microspheres separable by centrifugation.

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1. Introduction

Hydrothermal carbonization (HTC) has been recently rediscovered as an effective way of converting biomass into carbonaceous materials (Hu et al., 2010). HTC involves the

treatment of an organic precursor at moderate temperatures and moderate self-generated pressures in an aqueous solution. Biomass, or any other organic precursor, is introduced in an autoclave partly filled with water, which is next placed into an oven heated at the desired temperature for some hours. After cooling, a carbonaceous product is obtained, which can be easily filtered off from the solution. A number of works have described the HTC of several biosourced precursors such as glucose (Baccile et al., 2009),

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mixtures of glucose and ovalbumin (Baccile et al., 2010), sucrose (Zhang et al., 2012), chitosan and glucosamine (Zhao et al., 2010a), beet root chips (Riling et al., 2010), starch and rice grains (Cui et al., 2006) or maize silage (Mumme et al., 2011). When carbohydrates were submitted to HTC, the resultant materials were in the form of spherical particles, with diameters ranging from 700 nm to 5 μm , as a consequence of nucleation and growth processes after crosslinking and/or dehydration reactions taking place at temperatures lower than 300 °C (Titirici et al., 2012). Most of the aforementioned precursors were treated in HTC conditions at 180 °C and at reaction times ranging from 4 to 24 h. In some studies, the experiments were carried out between 120 and 280 °C (Falco et al., 2011) but, to the deepest knowledge of the authors, no detailed kinetics study of the HTC process have been performed so far.

Flavonoid tannin is considered as an “eco-friendly” base of resin when compared to homologous phenolic materials of petrochemical origin. Condensed tannin extracted from wattle barks is mainly composed of prorobinetinidin, which is based on two phenolic rings, called resorcinol (A) and pyrogallol (B) rings. Such phenolic and aromatic structure explains its reactivity as a base of resin and its high carbon yield (Tondi et al., 2009a,b). In wattle bark extract, flavonoid units are linked with each others and form oligomers whose molecular weights typically range from 500 to 3000 Da. On average, such oligomers are composed of two to eleven flavonoid units. Tannin extraction from wattle barks, but also from other biomass such as quebracho trunks, pecan nuts, gambier leaves, etc., is an easy and ecological process. The resultant material is non-toxic, renewable and cheap, around 1.5 € per kg.

Tannin is also an excellent precursor of carbonaceous materials, and different porous carbons have indeed been already synthesised from tannins: vitreous cellular carbon foams (Li et al., 2012; Tondi et al., 2009a,b; Zhao et al., 2010b), carbon cryogels and aerogels (Amaral-Labat et al., 2012; Szczurek et al., 2011a,b), ordered mesoporous carbons (Schlienger et al., 2012), carbon polyHIPEs and other forms of cellular carbons (Szczurek et al., 2013). HTC of tannin has been recently suggested in order to produce nitrogen-doped carbon materials, having nitrogen contents as high as 11.8 wt.% after HTC (Braghiroli et al., 2012). Moreover, tannin submitted to HTC and carbonized at 900 °C produced carbon microspheres, essentially microporous and with a surface of 640 m² g⁻¹ without further activation. Therefore, tannin submitted to HTC appears to be a promising source to produce new carbon material and is worth being investigated further.

In this manuscript, HTC of wattle tannin has been methodically studied in order to determine formation kinetics and properties of the carbonaceous materials appearing in the autoclave. Three variables were investigated separately: temperature, from 130 to 200 °C; tannin amount, from 0.5 to 2 g in 16 mL of water; and reaction time, from 1 to 144 h, the pH being nearly constant around 4.5. The resultant hydrothermal carbons were thoroughly characterized: morphology, surface area, HTC yield, and bulk and surface chemical composition.

2. Materials and methods

2.1. Materials synthesis

2.1.1. Tannin

Wattle tannin was used in the form of as-received commercial wattle bark extract (*Acacia mearnsii*, de Wild) supplied by the company SilvaChimica (Italy) under the name Tupafin, and extracted industrially in Tanzania. The industrial process consists in leaching wattle barks with a 1% sodium bisulphite aqueous solution at

70 °C. The effluents are then concentrated and spray-dried, leading to a light-brown powder, which generally contains 80–82% of actual phenolic flavonoid materials, 4–6% of water, 1% of amino and imino acids, the remainder being monomeric and oligomeric carbohydrates, in general broken pieces of hemicelluloses.

2.1.2. HTC of tannins

In a typical experiment, 0.5 g of tannin were dissolved in 16 g of water and introduced in an open glass vial in order to prevent autoclave contamination. The vial was then placed in a Teflon[®]-lined stainless steel autoclave for HTC. The inner volume of the autoclave was 50 cm³, so that the volume of liquid placed inside was exactly 1/3 of its capacity, taking the volume of the glass vial into account. The autoclave was directly installed in a ventilated oven pre-heated at different temperatures: 130, 160, 180 or 200 °C. After different reaction times depending on the temperature, ranging from 1 to 144 h, the autoclave was left to cool down at room temperature. The obtained solids were then separated from the remaining aqueous solution by centrifugation (6800 rpm for 20 min) and placed inside a vacuum oven at 80 °C for drying before characterisation.

2.2. Materials characterisation

2.2.1. Chemical composition

HTC samples, separated by centrifugation, were characterized by elemental analysis (EA) in a ThermoFlash 1112 apparatus for determining carbon, hydrogen, nitrogen and sulphur contents. Oxygen content was obtained by difference.

X-ray photoelectron spectroscopy (XPS) spectra were recorded with an ESCAPlus OMICROM system equipped with a hemispherical electron energy analyser. The spectrometer was operated at 10 kV and 15 mA, using a non-monochromatized Mg K α X-ray source ($h\nu = 1253.6$ eV) under vacuum ($<5 \times 10^{-9}$ Torr). Analyzer pass energy of 50 and 20 eV was used for survey scans and detailed scans, respectively. The C1s peak at 284.5 eV was used for binding energy correction. A survey scan (1 sweep/200 ms dwell) was acquired between 1100 and 0 eV. Current region sweeps for N1s, O1s and C1s were obtained. The CASA data processing software allowed smoothing, Shirley-type background subtraction, peak fitting and quantification.

2.2.2. Density and surface analysis

Skeletal density, ρ_s (g cm⁻³), was measured by helium pycnometry (Accupyc II 1340, Micromeritics, USA) for all samples after HTC. Samples were dried overnight at 80 °C under vacuum, placed into a calibrated volume chamber of 1 cm³, and the induced change of helium pressure was accurately measured. Each determination included 10 helium flushes prior to analysis, in order to clean the volume chamber, and 50 analytical runs.

Specific surface area was determined by krypton adsorption at –196 °C using a Micromeritics ASAP 2020 automatic apparatus. Samples were degassed for 48 h under vacuum at 80 °C prior to any adsorption experiment. Kr adsorption isotherms were treated for obtaining surface area (S_{BET}) from the BET calculation method.

2.2.3. Morphology and particle size

Samples were observed by transmission electron microscopy (TEM) using a FEI Philips CM200 apparatus. For that purpose, they were first ground and dispersed in chloroform by sonication. Then, a drop of the suspension was laid down on a TEM grid and dried before observation.

The equivalent average diameters, d (μm), of hydrothermal carbon particles, assumed to be non-porous (see below), were estimated according to:

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