

Thesis Review. Sustainable biomass-derived hydrothermal carbons for energy applications

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Objectives and novelty

The need to reduce humankind reliance on fossil fuels by exploiting sustainably the planet renewable resources is a major driving force determining the focus of modern material research. For this reason great interest is nowadays focused on finding alternatives to fossil fuels derived products/materials. For the short term the most promising substitute is undoubtedly biomass, since it is the only renewable and sustainable alternative to fossil fuels as carbon source. As a consequence efforts, aimed at finding new synthetic approaches to convert biomass and its derivatives into carbon-based materials, are constantly increasing. In this regard, hydrothermal carbonisation (HTC) has shown to be an effective means of conversion of biomass-derived precursors into functional carbon materials. However the attempts to convert raw biomass, in particular lignocellulosic one, directly into such products have certainly been rarer. Unlocking the direct use of these raw materials as carbon precursors would definitely be beneficial in terms of HTC sustainability. For this reason, in this thesis the HTC of carbohydrate and protein-rich biomass was systematically investigated, in order to obtain more insights on the potentials of this thermochemical processing technique in relation to the production of functional carbon materials from crude biomass.

Results

First a detailed investigation on the HTC conversion mechanism of lignocellulosic biomass and its single components (i.e. cellulose, lignin) was developed based on a comparison with glucose HTC, which

was adopted as a reference model. In the glucose case it was demonstrated that varying the HTC temperature allowed tuning the chemical structure of the synthesised carbon materials from a highly cross-linked furan-based structure ($T = 180\text{ °C}$) to a carbon framework composed of polyaromatic arene-like domains. When cellulose or lignocellulosic biomass was used as carbon precursor, the furan rich structure could not be isolated at any of the investigated processing conditions. These evidences were indicative of a different HTC conversion mechanism for cellulose, involving reactions that are commonly observed during pyrolytic processes (Fig. 1).

The evolution of glucose-derived HTC carbon chemical structure upon pyrolysis was also investigated. These studies revealed that upon heat treatment (Investigated temperatures $350 - 900\text{ °C}$) the furan-based structure was progressively converted into highly curved aromatic pre-graphenic domains. This thermal degradation process was observed to produce an increasingly more hydrophobic surface and considerable microporosity within the HTC carbon structure.

In order to introduce porosity in the HTC carbons derived from lignocellulosic biomass, KOH chemical activation was investigated as an HTC post-synthesis functionalisation step. These studies demonstrated that HTC carbons are excellent precursors for the production of highly microporous activated carbons (ACs) and that the porosity development upon KOH chemical activation is dependent on the chemical structure of the HTC carbon, tuned by employing

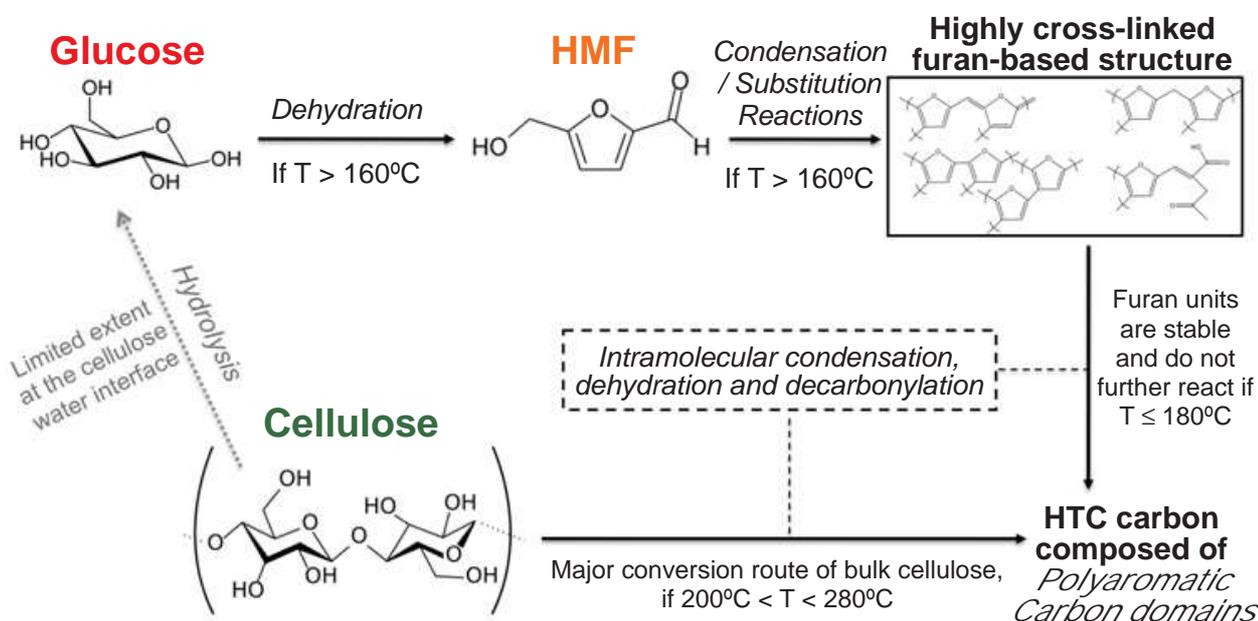


Figure 1. Proposed model for cellulose conversion during hydrothermal treatment under mild processing conditions ($180\text{ °C} < T < 280\text{ °C}$). [NB: Dotted lines represent minor reaction routes].

different HTC temperatures. Preliminary testing of the ACs for CO₂ capture or high pressure CH₄ storage yielded very promising results, since the measured uptakes of both adsorbates (i.e. CO₂ and CH₄) were comparable to top-performing and commercially available adsorbents, usually employed for these end-applications.

The combined use of HTC and KOH chemical activation was also employed to produce highly microporous N-doped ACs from microalgae. The hydrothermal treatment of the microalgae substrate was observed to cause the depletion of the protein and carbohydrate fractions and the near complete loss (i.e. 90%) of the microalgae N-content, as liquid hydrolysis/degradation products. The obtained carbonaceous product showed a predominantly aliphatic character indicating the presence of alkyl chains presumably derived from the lipid fractions. Addition of glucose to the initial reaction mixture was found out to be extremely beneficial, because it allowed the fixation of a higher N amount, in the algae derived HTC carbons (i.e. ≈ 60%), and the attainment of higher product yields (50%). Both positive effects were attributed to Maillard type cascade reactions taking place between the monosaccharides and the microalgae derived liquid hydrolysis/degradation products, which were in this way recovered from the liquid phase. KOH chemical activation of the microalgae/glucose mixture derived HTC carbons produced highly microporous N-doped carbons (Fig. 2).

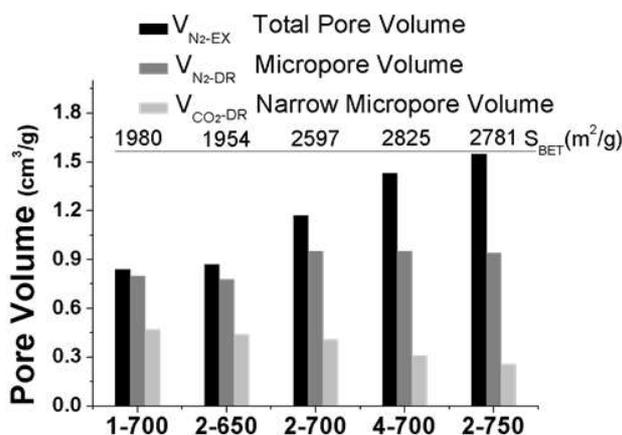


Figure 2. Porosity analysis summary. Calculated surface area (S) and pore volume (V) using different models (subscript) on either N₂ or CO₂ isotherms obtained for microalgae derived activated carbons. Name of the samples (A-B) – A corresponds to the Activation Ratio and B to the activation temperature (°C)

Conclusions

In this thesis the hydrothermal carbonization (HTC) of carbohydrate-rich (i.e. lignocellulosic biomass) and protein-rich (i.e. microalgae) raw biomass has been investigated as a synthetic route towards functional carbon materials. Post-treatment processing (i.e. pyrolysis and chemical activation) has also been studied in order to improve the synthesized material properties (eg. porosity, surface chemistry). Overall the presented work in this thesis represents major progresses towards the exploitation of raw biomass for the synthesis of sustainable and functional carbon materials. It highlights the high potential of the hydrothermal method as a means of conversion of waste or cheap biomass into value added products in complete agreement with the "Biorefinery Concept". Furthermore it represents an

important contribution to the overall HTC research field, since it proposes a new reaction mechanism for cellulose HTC conversion and it presents a detailed investigation of HTC carbon pyrolysis, which can be used as a further post-synthesis functionalization step. It also demonstrates the high suitability of HTC carbons as precursors for the synthesis of highly microporous ACs having several foreseeable applications (e.g. CO₂ capture, high pressure CH₄ storage and electrochemical double layer supercapacitors electrodes) and representing a carbon neutral/negative alternative to the fossil fuels derived high performing carbon materials.

Related publications

- ¹ M.M. Titirici, R. J. White, C. Falco, M. Sevilla, *Black Perspectives for a Green Future: Hydrothermal Carbons for Environment Protection and Energy Storage*, Energy and Environmental Science, 2012, 5, 6796-6822.
- ² C. Falco, M. Sevilla, R. Rothe, R. J. White, M.M. Titirici, *Renewable Microalgae-derived Nitrogen Doped Carbonaceous Materials*, ChemSusChem, DOI: 10.1002/cssc.201200022.
- ³ C. Falco, F. Perez Caballero, F. Babonneau, C. Gervais, G. Laurent, M.M. Titirici, N. Baccile, *Hydrothermal Carbon from Biomass: Structural Differences between Hydrothermal and Pyrolyzed Carbons via ¹³C Solid State NMR*, Langmuir, 2011, 27 (23), 14460-14471.
- ⁴ C. Falco, N. Baccile, M.M. Titirici, *Morphological and structural differences between glucose, cellulose and lignocellulosic biomass derived hydrothermal carbons*, Green Chemistry, 2011, 13 (11), 3273 - 3281.