

In-situ capture of degradation HTC products. Influence on hydrochar properties.

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Last decade has witnessed an exponential interest of hydrothermal carbonization (HTC) technologies as a solution to sustainably process biomass wastes, including high water biomass materials. While the number of scientists working in it has increased exponentially (34 references in Scopus in 2010 and 3844 in 2023), the companies applying this concept to industrial scale to upgrade diverse types of wastes have also emerged in different countries (Nicolae et al., 2020). To gain economic competitiveness when the focus is the hydrochar, HC, good quality and high solid yield (SY) are required, and, regarding this last aspect, it has been demonstrated that final HC mass is composed of two contributions: primary and secondary HCs, where the first is associated to the residue left after biomass structure is degraded and the second, as the carbon material formed as a result of liquid phase degradation product combination.

Previous pieces of research have reported that the secondary HC has a greater HHV than that of the HC resulting from the decomposition of biomass (primary HC). Kambo et al., (2018) attributed to this effect the rise on the HHV of HCs they found when water was recirculated from previous HTC processes. The degraded compounds from the biomass polymers present in the HTC process water might deposit in the porous structure of hydrochar, which may further augment the overall energy density of solid. The liquid phase is rich in organic acids, such as acetic (AA), formic (FA), levulinic (LA) or glycolic acid (GA), 5-Hydroxymethyl-furfural (5-HMF), and total organic carbon (TOC) compounds (Kambo et al., 2018).

This would in turn suggest that if we could isolate this secondary contribution and add it to another system with lower energetic value, we could increase it. This effect was investigated in this work, in which we added an Activated Carbon (AC) to the HTC reaction media. According to Polanyi adsorption potential theory, the molecules at the liquid phase might, in principle, have a higher affinity by the ACs, because its pore volume is larger and the adsorption forces are greater than those of the primary HC. On the one hand, the apparent surface of the AC is about 200 times bigger; on the other hand, the type of porosity is also different.

The ACs selected in this work, presented differences on their pore size distribution (one a big volume of micropores and presented a type-I isotherm, while the other one was microporous but had a contribution of mesoporosity (type IV isotherm)). Dissimilarly, the primary HC had poor porosity that in addition is mainly meso-macroporous.

The preferable adsorption on the HTC liquid products on the AC, instead than in the primary HC can be easily followed if we compare identical runs made with and without adsorbents. In Figure 1, the evolution of SY versus time has been plotted. The effects are clear: lower HC final mass if an adsorbent is inserted on the autoclave. In coherence, the AC mass increased its mass a (and modified its chemical surface functional groups) as a consequence of enhanced adsorption.

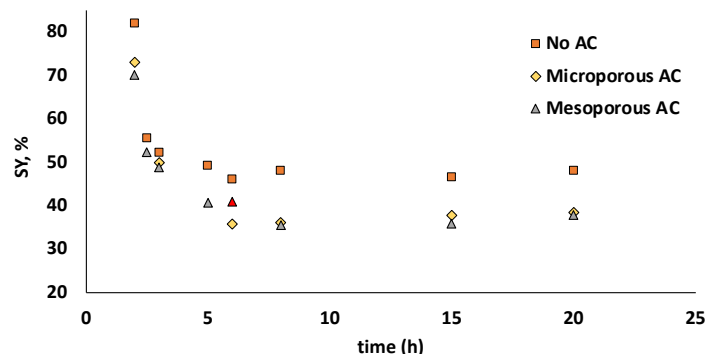


Figure 1. SY evolution with time for HTC depending on the addition of ACs of different pore size distributions

The rise in HHV of the AC was consistent with the drop of this parameter in the case of the primary HC, that losses a fraction of material as a result of the migration of these liquid phase compounds (because of the presence of adsorbent), that would otherwise contribute to increase the HHV.

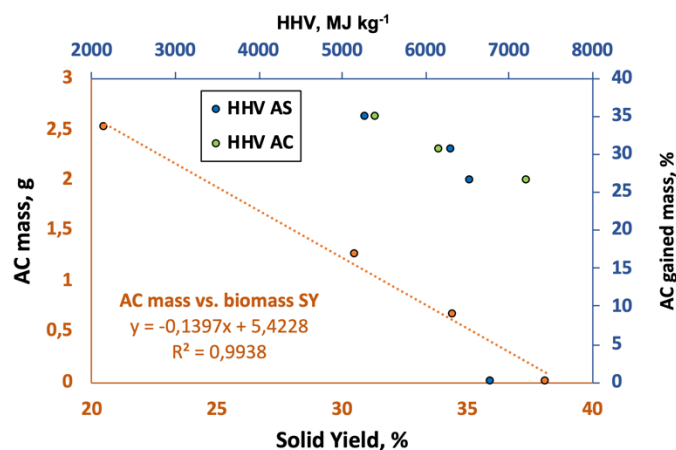


Figure 2. Relation of AC mass with biomass solid yield (orange spot) and relation between AC gained mass (%) with HHV of HC (blue) and AC (green)

SEM imaging can be very graphical and showed how these materials have deposited on the AC; as an example, the morphologies of the mesoporous AC used, both before and after the HTC process, have been plotted in Figure 3 (a and b). The emergence of microspheres on the adsorbent surface after HTC evidence the precipitation of the condensed macromolecules.

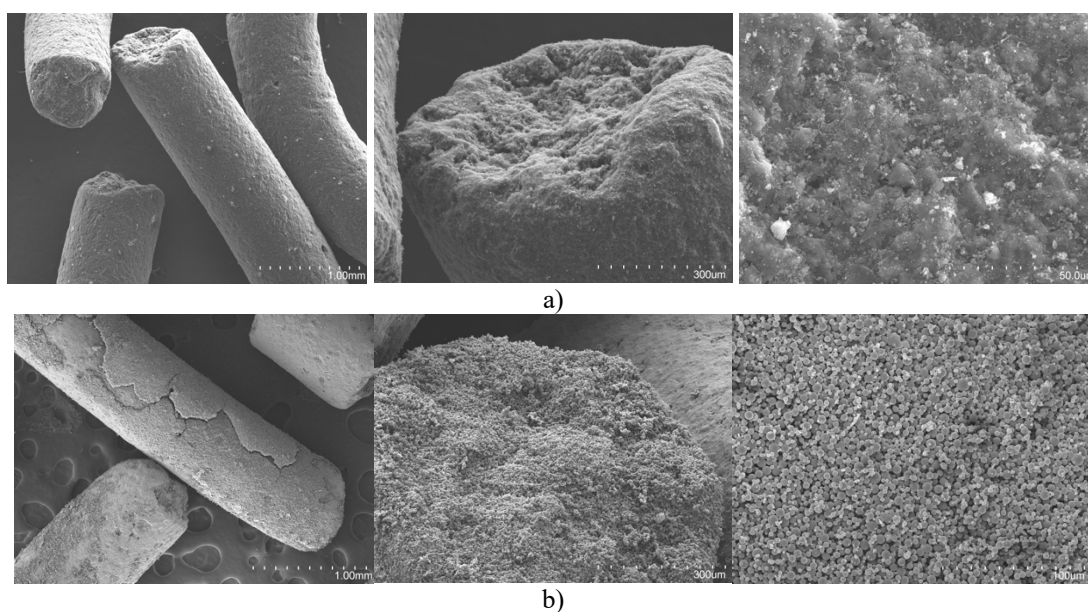


Figure 3. SEM micrographs of the AC ACPEL before (a) and after (b) its use in walnut shell HTC. Experimental conditions: 230 °C, 20h

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