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HYDROTHERMAL CARBONIZATION OF BIOMASS WASTES: SUSTAINABILITY AND GEOCHEMISTRY

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Introduction

To reduce the stream of solid waste going to landfills, innovative means for beneficial use are essential. The diversity and volume of organic wastes pose singular problems and opportunities for recovery and circularity. Common processes for organics include conversion to biofuels and carbonization to biochar, typically done by torrefaction (dry pyrolysis). Research on biochar explores its potential as pollutant adsorbent, agricultural or polluted soil amendment, biofuel (directly or as feedstock), and for carbon sequestration (Ighalo et al., 2022; Cavali et al., 2023). Recently, other processes at lower temperatures such as hydrothermal carbonization (HTC) offer new possibilities (Seshadri et al., 2016; Madsen et al., 2017). The properties of both biochar and hydrochar are strongly dependent on the biomass feedstock type (e.g., wood vs. algae) and on the carbonization process employed. In a "real world" pilot study, the public company for solid waste management in Asturias, Spain (COGERSA SAU) experimented with HTC of organic waste streams, including treated wood waste (mainly bulky waste, furniture, etc.), winery bagasse, and the organic fraction from separate collection of municipal solid waste (OFMSW). An advantage of HTC is that the feedstock can be processed wet, as received. Water was added to achieve a uniform 1:4 solid to water mass ratio and the mixtures were processed in a 2 m^3 reactor vessel (195 °C, 1.3 MPa, 3 h) fed by the superheated steam available at the COGERSA plant (waste-to-energy of clinical waste by rotary kiln). Then, excess water was expelled mechanically (30 MPa) and the solids were dried in air at 100 °C. The resulting hydrochars were characterized by methods organic geochemists traditionally use in fossil fuel studies: proximate and ultimate analyses, porosimetry, thermogravimetric analysis, thermodesorption-gas chromatography-mass spectrometry (TD-GC-MS, heating in He at 350 °C for 20 s), and pyrolysis of the thermodesorption residue (Py-GC-MS, 610 °C, 20 s). For comparison, a commercial torrefied biochar (Vermichar S.L.) produced from *Quercus ilex* wood was also analyzed by the above methods.

Results

Yields of hydrochar varied from 65% (OFMSW) to 83% (wood) of the initial feedstock mass (dry, ash-free). Molar H/C and O/C ratios decreased by mean values of 10 and 24%, respectively, relative to the raw feedstocks. HTC increased the high heating values slightly, to a mean of 21 MJ kg^{-1}, in the range of sub-bituminous coal. Thermogravimetry overall shows a slight shift towards decomposition at higher temperatures, as well as peak narrowing after HTC. OFMSW TD-GC-MS yielded predominantly C_{16} and C_{18} saturated and unsaturated fatty acids and their methyl and ethyl esters (Fig. 1A). Subsequent Py-GC-MS results were similar, but with greatly reduced yield. In contrast, the Py-GC-MS yield for the wood was greater than that of the preceding thermodesorption, with abundant lignin (methoxyphenol) and polysaccharide markers, and minor, but notable, monoaromatic tricyclic terpenoids and methoxyphenol dimers (Fig. 1B). The TD-GC-MS of the biochar yielded little, while subsequent Py-GC-MS presented a predominance of simple monoaromatic hydrocarbons and phenols, along with phenanthrenes, retene in particular (Fig. 1C). Minor naphthalenes and monoaromatic tricyclic terpenoids are also noted.

Conclusions

Analytical techniques usually applied in advanced characterization of fossil fuels, such as Py-GC-MS, were shown to be useful in unraveling molecular hydrochar and biochar composition. This opens new possibilities for the study of these products in detail, including diverse applications such as tracking of the evolution of different feedstock materials after carbonization, the possible uses as biofuels (specially for the liquid fraction obtained in the HTC process), or even the identification of potential pollutants. In this preliminary study of several hydrochars and a commercial biochar, interesting general and specific features were revealed: the molecular composition of hydrochar was strongly influenced by feedstock type, the OFMSW hydrochar revealed potential for biodiesel production, and biochar presented marked differences from "woody" biomass hydrochars.

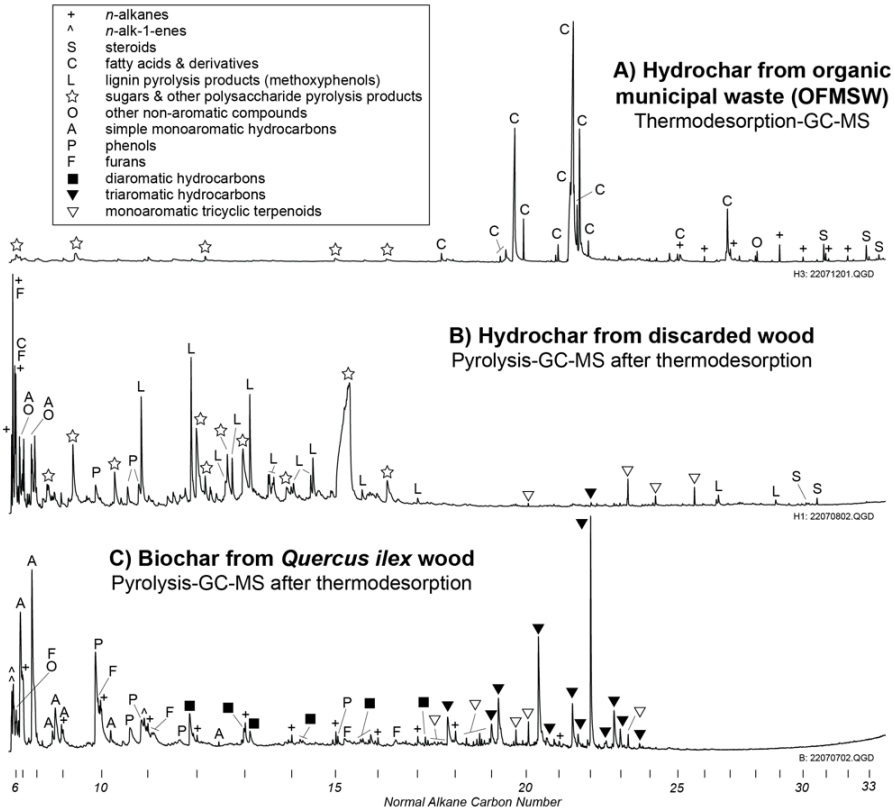

Figure 1. *Representative results from the TD-GC-MS and Py-GC-MS analysis of hydrochars. Results for a torrefied biochar are shown for comparison.*

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