# Lignocellulosic waste valorization by hydrothermal carbonization and anaerobic digestion

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Keywords: anaerobic digestion, circular economy, energy recovery, hydrothermal carbonization.
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## Introduction

The increasing generation of urban residues demands the development of an efficient management. Until now, several thermal treatments have been studied for the valorization of these residues such as pyrolysis, torrefaction or gasification. Hydrothermal carbonization (HTC) emerges as an interesting thermochemical process to treat wet biomass under mild temperatures (180–250 °C) and autogenous pressure. The main products of the HTC are a carbonaceous solid called hydrochar (HC), with suitable properties to be used as a biofuel, and a process water (PW), rich in soluble organic compounds and nutrients (Villamil et al., 2018). The present work investigates the synergistic integration of HTC and anaerobic digestion (AD) as a novel valorization route of urban pruning waste (UPW) within the framework of circular economy of biomass waste.

## Material and Methods

HTC runs were conducted in an electrically heated 4 L ZipperClave® pressure vessel. The UPW has a very low moisture content (≈ 5%), hence it was mixed (20:80 (w:w)) with deionized water (DW). 1.2 kg of the mix (UPW+DW) was hydrothermally carbonized at three different temperatures 180, 210 and 230 °C for 1 h. The HCs and PWs obtained were labelled as HC180, HC210, HC230, PW180, PW210 and PW230, respectively, related to the HTC temperature used. Elemental composition (C, N, S, and H) was determined by a CHNS analyzer. Proximal (ash, VM and FC) and thermogravimetric (TG and DTG) analysis were carried out by a TGA Discovery SDT 650. Higher heating values (HHV) were determined using the Schuster`s equation (Schuster et al., 2001). Elements were quantified by inductively coupled plasma atomic emission spectroscopy (ICP-OES) on an Elan 6000 Sciex instrument (Perkin Elmer).

, Anaerobic digestion assays of process water from HTC and raw UPW were carried out in 120 mL glass serum vials under mesophilic condition (35 ºC) with an inoculum-to-substrate ratio (ISR) of 2 on a VS basis. The inoculum used was a granular anaerobic sludge from an industrial digester processing brewery wastewater. APHA methods 2540B, 2540E, 5220D, 2320B and 4500E were used to determine total solids (TS), volatile solids (VS), soluble chemical oxygen demand (SCOD), total alkalinity (TA) and ammonia nitrogen (TAN) (APHA, 2005), while the volatile fatty acids (VFA) were determined by gas chromatography (GC) on a Varian 430-GC instrument (De la Rubia et al., 2018).

## Results and Discussion

Table 1 collects the proximate and elemental analysis of UPW and HC as well as their HHV and the fouling (FI), slagging (SI) and alkali (AI) indexes. The rise of temperature is related to an increase in the HC carbon content (6–21 %), and therefore in HHV from 19 to 23 MJ/kg. Nevertheless, the energy yield decreased with the temperature from 92 to 85% because of the transference of carbonaceous species to the PW. HCs shown low SI, FI and AI (0.16, < 3.1 and < 0.1 kg/GJ, respectively) related to low content in alkaline metals. These elements could reduce heat transfer and process inefficiencies in the boilers. The obtained HCs fulfil the quality standards for solid fuels produced from thermally treated biomass (HHV > 17 MJ/kg, volatile matter content < 75 %, and sulphur and nitrogen content < 0.5 % and < 3 %, respectively) (ISO/TS 17225-8, 2016).

Table 1. Characterization of urban pruning waste and hydrochars

| | Mass yield (%) | Volatile matter (%) | Fixed carbon (%) | Ash (%) | C (%) | H (%) | N (%) | S (%) | O* (%) | HHV (MJ/kg) | Energy yield (%) | SI | FI | AI (kg/GJ) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| UPW | - | 76.5 | 18.4 | 5.1 | 46.9 | 6.1 | 0.9 | 0.4 | 40.6 | 19.7 | - | 0.53 | 7.47 | 0.3 |
| HC180 | 87.6 | 67.1 | 29.6 | 3.3 | 49.8 | 5.3 | 1.3 | 0.2 | 40.1 | 20.7 | 92.0 | 0.16 | 3.08 | 0.09 |
| HC210 | 74.3 | 67.6 | 28.6 | 3.7 | 53.5 | 5.4 | 1 | 0.1 | 36.3 | 22.3 | 74.3 | 0.15 | 2.56 | 0.07 |
| HC230 | 68.3 | 60.9 | 34.1 | 5.0 | 57.1 | 5.3 | 1.1 | 0.1 | 31.4 | 24.5 | 84.9 | 0.16 | 2.08 | 0.07 |

O* Calculated from the mass balance: O=100-C-H-N-S-ash; Percent by weitgh

Fig. 1 shows the TG and DTG analysis for the UPW and HCs. HC180 presented the best characteristics for combustion such as lower ignition temperature (242 ºC), higher mass loss rate (95%), lower energy

activation (62.3 kJ $mol^{-1}$) and comprehensive combustibility index ($8.0 \cdot 10^{-7}$ $min^{-2}$ $ºC^{-3}$) compared to the other hydrochars.

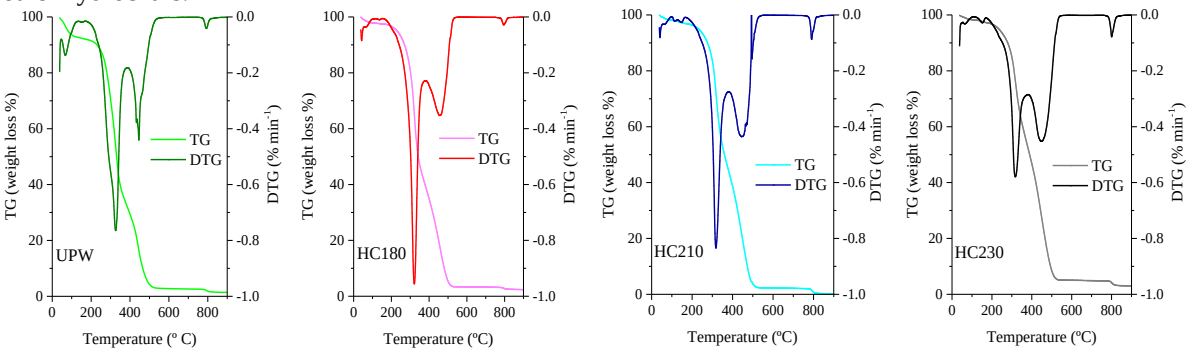


**Fig 1.** TG and DTG profiles of UPW and HCs.

Methane yields of the UPW and PW obtained from HTC are shown in Fig. 2. The highest methane yield (≈ 326 mL $CH_4$ STP/g $COD_{added}$), combined with a 65% of COD removal, were obtained with the PW generated at 180 ºC. The methane production significantly decreased for the PW obtained at higher temperature (253 - 269 mL $CH_4$ STP/g $COD_{added}$), because of the formation of recalcitrant compounds during HTC process. The lowest methane yield was obtained for the raw UPW (75 ± 3 mL $CH_4$ STP/g $COD_{added}$), due to the low biodegradability of lignocellulosic biomass mainly composed by cellulose, hemicellulose and lignin. PW180 was fitted with first order kinetic model for its early methane production and no latency periods and modified Gompertz as there is a latency or suitability stage for the PW210 and PW230 (≈ 7 days).

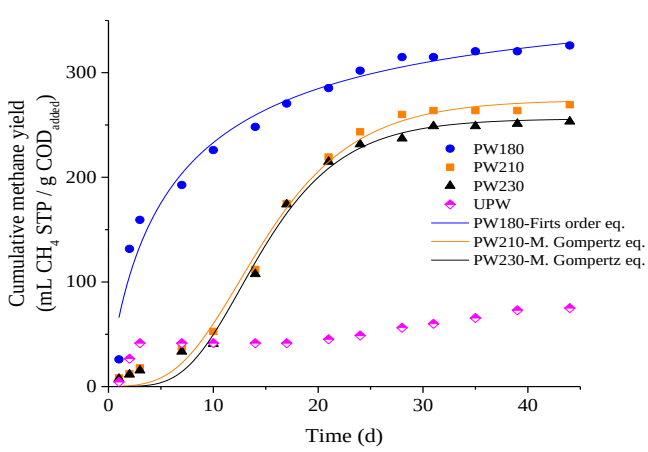


**Fig 2.** Cumulative methane along the anaerobic digestion of UPW and PW. Symbols represent experimental values and solid lines represent calculated values fitted

HTC at 180 ºC led to an energy recovery around 94 % of the total energy content on UPW taking into account both hydrochar and methane from anaerobic digestion of process water, while an increase of the HTC temperature affected negatively the energy recovery. Therefore, a combined HTC–AD treatment provides a seemingly effective method for valorizing urban pruning waste, opening new ways for renewable energy production and promotes the development of a circular economy.

**Acknowledgements**

Authors greatly appreciate funding from Spain's MICINN (PID2019-108445RB-I00) and Madrid Regional Government (Project S2018/EMT-4344). R.P. Ipiales acknowledges financial support from Community of Madrid (IND2019/AMB-17092) and ZoitechLab Company.

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