Material and energy recovery from mushroom and lavandin stem wastes by hydrothermal carbonization

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Annually, millions of tons of organic waste are generated from agricultural activities, requiring proper management to prevent environmental risks (Khan et al., 2024). The EU agri-food sector is concentrated in the Mediterranean region, with Spain being one of the leading mushroom producers on the market and recently expanding into the lavandin essential oil (LEO) extraction industry. Both mushroom cultivation and LEO extraction industry generate significant amounts of waste, such as spent mushroom substrate (SMS) and lavandin stems, respectively. Inefficient disposal of SMS waste can lead to soil and water contamination due to leaching of residual elements (Kojić et al., 2021). On the other hand, lavandin waste, which are normally burned in vacant lots, can generate CO_2 emissions and increase soil alkalinity (Saha & Basak, 2020). Hydrothermal technologies promise the proper management of biomass waste with high moisture content by avoiding a pre-drying step. Unlike other thermal technologies such as pyrolysis and gasification, hydrothermal carbonization (HTC) operates under mild reaction conditions (180 – 250 ºC). HTC produces three products: carbonaceous material (hydrochar), an aqueous stream (process water, PW), and to a lesser extent, a gaseous fraction composed mainly of CO_2. Depending on the characteristics of the hydrochar, it can be used as a biofuel, soil improver, adsorbent and/or catalytic support. The process water can potentially be used for the recovery of nutrients to obtain solid fertilizers, for crops irrigation, or biologically treated by anaerobic digestion or dark fermentation.

The present work evaluates the potential of HTC for treating agricultural wastes and the suitability of hydrochar as a solid biofuel and/or soil improver. Spent button mushroom substrate (BM), spent oyster mushroom substrate (OM), and lavandin stems (LV) from LEO extraction industry were treated by HTC at several reaction temperatures. In addition, the PW was characterized to explore its potential for further applications.

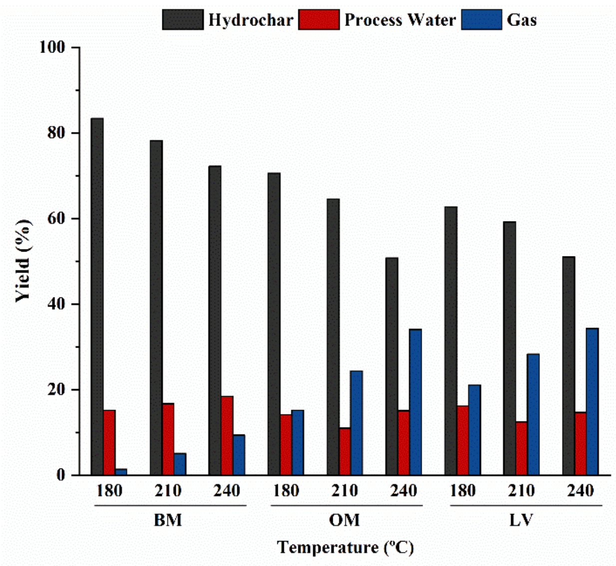

Figure 1. Product distribution on a dry basis of HTC treatment of BM, OM and LV.

Table 1. Proximate and ultimate analysis of feedstock and hydrochars.

	Proximate analysis (%)			Ultimate analysis (%)			
	FC	VM	Ash	C	H	N	S
BM	8.4	60.0	31.6	29.6	3.6	2.5	1.3
HC-BM180	5.0	52.6	42.5	32.3	3.6	2.3	2.4
HC-BM210	5.3	53.6	41.2	32.6	3.4	2.3	2.5
HC-BM240	11.0	48.2	40.8	33.8	3.2	2.5	2.6
OM	9.9	75.8	14.3	39.1	5.2	1.5	0.1
HC-OM180	8.1	75.0	16.9	42.6	5.0	1.3	0.1
HC-OM210	12.9	68.9	18.2	43.8	6.8	1.4	0.1
HC-OM240	5.9	67.4	26.7	47.4	4.1	1.9	0.2
LV	17.9	78.3	3.8	47.8	6.0	1.1	0.1
HC-LV180	16.4	79.0	4.6	54.0	6.0	1.2	0.1
HC-LV210	27.7	70.5	1.8	56.5	5.7	1.1	0.1
HC-LV240	33.5	62.1	4.4	63.4	5.8	1.4	0.1

BM, OM, and LV waste were provided from Agri-food and Forestry Regional Research and Development Centre (IRIAF) in Cuenca (Spain). The samples showed moisture contents of 74% for BM and OM, and 10% for LV. The carbon and ash contents of the samples were determined as follows: BM (29.6% C and 31.6% ash); OM (39.1% C and 14.3% ash); and LV (47.8% C and 3.8% ash). Feedstock samples were stored as received prior to the HTC experiments. HTC reactions were carried out in a 2 L Parr 4530 reactor (PARR Instrument company, USA). The reactor was loaded with a mixture of feedstock and water, with a solid content of 15% on a dry weight basis. HTC experiments were conducted at 180, 210, and 240 ºC for 1 h under autogenous pressure. Hydrochars were characterized by proximate analysis (volatile matter, VM; fixed carbon, FC; and ashes), elemental composition (C, H, N, and S), and mineral content and heavy metals composition by ICP-OES. In addition, the hydrochars were analyzed by CO_2 adsorption–desorption isotherms. The combustion behavior of the hydrochars were evaluated through kinetic and thermodynamic analysis: ignition (T_i) and burnout (T_b) temperatures, activation energy (E_A), CCI index, and other relevant parameters. The slagging and fouling propensity of the ashes were analyzed considering the acid-base ratios ($R_{b/a}$), slagging index (SI), fouling index (FI). These analyses provide insight into the thermal stability, reactivity, and suitability of hydrochars for biofuel applications. The potential of PW was assessed through the analysis of pH, conductivity, total organic carbon (TOC), total nitrogen (TN), total solids (TS), volatile solids (VS), and the concentration of NO_2-N, NO_3-N, NH_4-N, and PO_4-P species.

Figure 1 shows the distribution of the products from the HTC treatment of agricultural waste. In general, the hydrochar yield decreased as the temperature increased. The hydrochar yield was very high for BM (72% to 83%) due to the high ash content of the raw material. The hydrochar yields of OM (51% to 71%) and LV (51% to 73%) were significantly lower. The PW yield ranged from 11% to 18%, regardless of the temperature. The gaseous fraction increased with temperature and was more noticeable for OM and LV assays at the highest temperature. Table 1 shows the proximate and ultimate analysis of feedstock and hydrochars. The results of the proximate analysis showed that the CF increased with temperature, while the VM decreased. The ultimate analysis showed an increase in hydrochar C content as the temperature increased, while the N and S content did not appear to be affected by temperature. The HHV values increased significantly compared to feedstock, with LV hydrochars showing the highest values (21 – 25 MJ/kg). Textural analysis showed the development of microporous structures in hydrochars with relevant surface areas (140 – 250 m^2/g). Hydrochar characteristics were evaluated according to ISO/TS 17225-8:2023 (VM < 75%, N < 2.5%, S < 0.3%, ash < 12%, HHV > 17 MJ/kg) to identify the most suitable candidates for biofuel applications, revealing that certain OM and LV hydrochars fulfilled the ISO standards. The combustion analysis revealed that LV hydrochars showed better characteristics to be used as biofuel, with more stable reactivity, a rapid combustion process at relatively low temperatures (T_i: 257 ºC, T_b: 482 ºC), and a lower risk of slag formation and ash fouling. The mineral and heavy metal content of hydrochars allowed compliance with RD 1051/2022 (Spain) and EU 2019/1009 regulations for sustainable nutrition of agricultural soils and fertilizing products, highlighting their potential as soil improvers. The PW analysis showed acidic pH independent of reaction temperature. On the other hand, the conductivity did not depend on temperature, but on the composition of feedstock. The nitrogen species, TS, VM showed a decreasing trend with increasing temperature, while TOC did not depend on temperature ranging between 12 to 20 g/L.

The HTC treatment of the agricultural waste studied produced hydrochars with differentiated characteristics for their potential use as biofuel and/or soil improver. Combustion analysis revealed that LV hydrochars had higher combustion efficiency, stability and reactivity, making this material suitable for biofuel applications. In addition, the analysis of minerals and heavy metals showed the availability of hydrochars to be used as soil improvers. The potential use of process water for the recovery of nutrients and energy plays a fundamental role in the valorization of these wastes within a circular economy framework.

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