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Hydrothermal treatment as a complementary tool to control the invasive Pampas grass (*Cortaderia selloana*)

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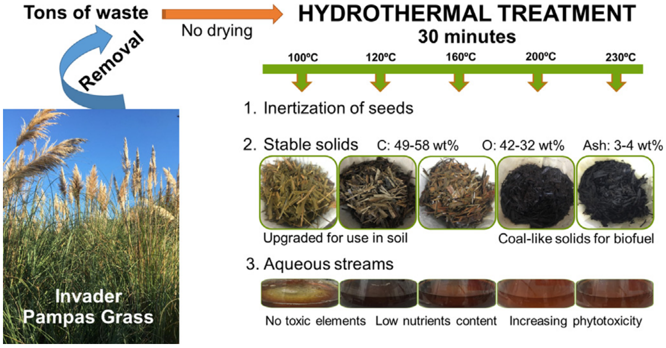
HIGHLIGHTS

- Hydrothermal treatment (HT) allows sustainable disposal of Pampas grass waste.
- Successful inertization of Pampas grass seeds by HT at 100 °C for only 30 min
- HT at 100–160 °C stabilizes and upgrades the Pampas grass waste for use in soil.
- HT at 200–230 °C converts the Pampas grass residues into coal-like solids.
- Agrochemical properties of liquid HT by-products are poor and worsen with temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

The rapid spread of invasive Pampas grass (PG) is having not only ecosystems impact, but also significant economic and social effects. The tonnes of bulky waste from the plant disposal require proper treatment to avoid seed dispersal, greenhouse gas emissions and landscape damage. In the pursuit of zero-waste management, hydrothermal treatment (HT) appears as a challenging alternative. The possibility of mobile HT systems offers an alternative to accomplish on-site both the PG waste management and the application of the resulting by-products within a circular framework. As a first step, this research shows that, without a prior drying step, the hydrothermal treatment at 100-230 °C under autogenous water vapor pressure for only 30 min allows safe seeds inertization, while a stable carbon-enriched solid and an aqueous stream are generated. Prolonging the process for 2 h has no profitable effects. As the reaction temperature increases, the PG residue is converted into a material with 49–58 wt% of carbon, 41–32 wt% of oxygen and 3–4 wt% of ash. The pH (~6.3), low electrical conductivity (1.21–0.86 dS/m), high carbon content, open porosity (5–8 m^2/g) and improved performance in seed germination and in the early growth test suggest the potential of HT-solids derived at 100–120 °C as amendment to sequester carbon in the soil and improve its physico-biological properties. The phytotoxicity detected in the peat/lignite-like solids obtained at 200–230 °C limits its application in soil, but calorific values of 22–24 MJ/kg indicate their suitability as CO_2-neutral fuel. The agrochemical analysis of the liquid by-products indicates poor value on their own, but their use supplemented with compost may be an option.

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1. Introduction

Cortaderia selloana, commonly known as Pampas grass, is a flowering plant native of southern South America (Connor, 1973; Herrera and Campos, 2006; Starr et al., 2003; Testoni and Villamil, 2014) that currently behaves as a very aggressive invasive species of natural and semi-natural habitats in several countries. Its invasiveness is becoming an ecological emergency in USA, China, New Zealand, Australia, Tasmania, Cook Islands, South Africa, Swaziland, etc. (Connor, 1971; DiTomaso, 2000; Gosling et al., 2000; Harradine, 1991; Houliston and Goeke, 2017; Knowles and Ecroyd, 1985; United States Department of Agriculture, 2014). In Europe, it has spread rapidly along the coastal corridor around the 'Atlantic arc' from France to Portugal and, more recently, some areas of Italy have also been affected (Stopcortaderia.org, 2021; United States Department of Agriculture, 2014).

Pampas grass is initially established in highly disturbed areas with degraded soils and its high capacity to adapt to diverse ecosystems and climates, low-demanding ecological needs, and great ability to survive in extreme conditions drove the displacement of surrounding autochthonous vegetation. Along its lifetime, each plant can produce over one million seeds easily dispersed by the wind, which increases its dangerousness exponentially (Ecroyd et al., 1984; Saura-Mas and Lloret, 2005; Stopcortaderia.org, 2021; Vourlitis and Kroon, 2013).

The magnitude of the problem must be assessed not only in environmental terms, such as loss of biodiversity and drastic alteration of ecosystems by the disappearance of native flora and fauna, but there are also collateral effects with great economic and social impact, e.g. damage to agricultural and livestock activities, landscape degradation and adverse effects on the population health through increased respiratory allergies during the flowering season (DiTomaso, 2000; Fernández Rojo et al., 2015; Genovesi and Shine, 2004; Harradine, 1991; Moore, 1994; Reichard and White, 2001; "Stopcortaderia.org"). The need to urgently face this expansion has prompted joint efforts, such as the recent "Transnational strategy to combat *Cortaderia selloana* in the Atlantic Arc" (Stopcortaderia.org, 2021), an interdisciplinary platform to exchange information, share experiences and coordinate actions in the medium-long term.

Pampas grass (PG) grows in dense tussocks up to 4 m high (Fig. A.1). The inflorescences are produced in a white panicle 20–50 cm long on a 2–3 m stem, being surrounded by long (1–2 m) and thin (1 cm) leaves with very sharp edges. The particular structure of the latter with significant silica deposits (Fig. A.2) makes the plants unpalatable to livestock and difficult to access and remove.

All methods used for the elimination of Pampas grass, mainly manual or mechanical grubbing and herbicide application, require the cutting of the aerial part of the plant. This generates tons of bulky biomass waste, which must be properly managed to avoid seed dispersal, greenhouse gas emissions and impact on the landscape.

Based on the success of hydrothermal carbonization (HTC) for the recovery of biomass residues from different agricultural, industrial and municipal sources (Guardia et al., 2018; Ischia et al., 2021; Libra et al., 2011; Pavlovič et al., 2013; Saha et al., 2021; Shen, 2020; Suárez et al., 2020), hydrothermal treatment of Pampas grass waste appears as an attractive alternative to uncontrolled disposal.

Hydrothermal carbonization takes place at mild temperatures (150–250 °C) under the autogenous vapor pressure, and a carbon-enriched solid (hydrochar) is obtained through an easy and fast process with low energy requirements and CO_2 emissions. (Ischia et al., 2021; Libra et al., 2011; Yang et al., 2019; Zhang et al., 2019, 2021).

As far as HTC is carried out in the presence of water, this technology is particularly suitable for transforming lignocellulosic feedstocks with high moisture. The mechanism starts with a hydrolysis stage that makes the main components of the biomass less stable and degrade at lower temperatures. Under HTC conditions, hemicelluloses usually decompose in the range of 180 °C and 200 °C, most lignins between 180 °C and 220 °C, and cellulose above ~220 °C (Funke and Ziegler, 2010). In comparison, standard (dry) pyrolysis requires significantly higher temperatures: 200–400 °C for hemicelluloses, 300–400 °C for cellulose and 180–600 °C for lignins.

Hydrothermal carbonization occurs through typical pyrolytic reactions (hydrolysis, dehydration, decarboxylation, aromatisation and recondensation), but mostly involving ions as opposed to the radical-based pathways of low-temperature dry pyrolysis (Funke and Ziegler, 2010; Ischia et al., 2021; Libra et al., 2011; Shen, 2020; Wang et al., 2018; Zhang et al., 2021). Under HTC conditions, the dielectric constant of water decreases and a high ion concentration is produced (Shen, 2020; Wu et al., 2021). Such a catalytic environment for a few hours favors the decomposition of biopolymers and the solubilization of organic compounds (Möller et al., 2011; Wu et al., 2021).

As a result of HTC, 50–80 wt% of the feedstock (dry basis) is generally converted into hydrochar, accompanied by an aqueous phase (20-35 wt %). Gas emissions are limited to around 5 wt% (Funke and Ziegler, 2010; Nizamuddin et al., 2017). A promising behavior of both the hydrochar and the water reaction for soil ameliorate has been reported (Antero et al., 2020; Hitzl et al., 2015; Hou et al., 2020; Kambo and Dutta, 2015; Mau et al., 2019; Wu et al., 2021).

In the search for valorization ways, a recent paper has presented the capability of the leaves and stems of Pampas grass as renewable source of eco-friendly biofuels (char, oil, and gas) by applying conventional and flash pyrolysis at 750–850 °C (Pérez et al., 2021).

Rather than focusing on the interest of an invasive plant as feedstock, our study assesses the potential of hydrothermal carbonization as a complement to control de PG expansion by a sustainable waste management that allows seed inertization and helps to restore the habitat. Recent advances in mobile HTC systems (Ingelia.com, 2021; Saha et al., 2021) offer promising prospects for integrated on-site management of Pampas grass residues, thus avoiding their transport for processing. This would reduce both the risk of seed dispersal and overall costs.

For this systematic study, Pampas grass waste was treated in the presence of water (1:4 weight) at temperatures from 100 °C to 230 °C under the respective autogenous water vapor saturation pressure (1–30 bar) for 30 min and 2 h. Although temperatures above 150 °C are required for achieving carbonization, the present investigation also addresses the interest of gentler treatments at 100 and 120 °C that can be carried out by more affordable facilities with less demanding energy and safety requirements.

Germination tests confirm the success of seed inertization, while agrochemical analyses of the solid and liquid by-products indicate that, depending on the treatment conditions, they have potential for use in amending the impoverished soils where the plant was present. This would contribute to habitat restoration at no additional cost. On the other hand, the solid by-product can also be used as biofuel to supply energy to the HT reactor.

2. Experimental

2.1. Raw material

Pampas grass specimens collected in different regions of the central area of Asturias (northern Spain) were cut into smaller pieces to facilitate their processing in the reactor. A homogeneous and representative mixture of the different components of the aerial part (leaves, stems and inflorescences) of Pampas grass (10 kg) was used as raw material (Fig. 1). Specific studies about seed inertization were complemented with inflorescences from specimens from areas around Coimbra (Portugal).

2.2. Hydrothermal treatment

As a standard procedure, a mixture of 200–220 g of fresh PG and water at a ratio of 1:4 by weight (taking into account 61–69 wt%

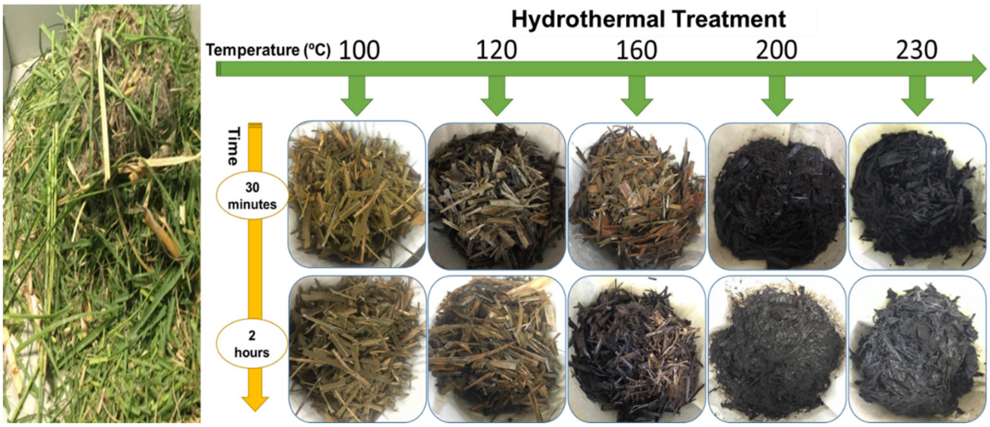

Fig. 1. Pampas grass waste and the solid products obtained by hydrothermal treatment under different conditions.

moisture of the biomass) was placed into a 3 L ILSHIN stainless steel jacketed pressure reactor and heated at temperatures of 100, 120, 160, 200 and 230 °C under the respective autogenous water vapor saturation pressure of 1, 2, 6, 16 and 30 bar. The samples were kept at the maximum temperature for 30 min and 2 h, stopping the reaction with the help of a cooling coil.

The resulting solid was separated from the aqueous phase by gravity filtration through a funnel with paper, and then 1.5 L of water was poured onto the material to remove the remains of the liquid by-product. The washing water was collected together with the reaction liquid. Finally, the solid was air-dried in an oven at 100 °C for 24 h.

The same protocol was applied to process exclusively inflorescences at 100 °C for 30 min and 2 h.

2.3. Germination tests of seeds

Considering that the seeds in hermaphrodite plants are few in number, less viable and more difficult to classify in terms of viable/non-viable based on their appearance, the study was carried out on seeds of female plants collected in October in several areas of Coimbra (Portugal).

After hydrothermal treatment at 100 °C for 30 min and 2 h, the seeds were removed by hand with the help of a magnifying glass, and those with the greatest possibilities to germinate (based on their size and appearance (Drewitz and DiTomaso, 2004)) were selected. The germination tests were accomplished at constant temperature of 25 °C, accompanied by a photoperiod of 14 h of light/10 h of darkness (Bacchetta et al., 2010). Six replicates of 25 seeds, deposited in autoclaved Petri dishes with moistened filter paper, were germinated for each of the processes considered, totalizing 150 seeds per treatment. Petri dishes were routinely monitored every 2 days (Monday-Wednesday-Friday), to remove the germinated and rotten seeds and to add distilled water, if necessary. The trials lasted for 1 month.

2.4. Characterization of the solid by-product

The morphology of the solid materials was examined by Scanning Electron Microscopy (SEM) using a Carl Zeiss DMS-942 microscope. The moisture and ash content were evaluated in a LECO TGA701 following ASTM7582-10 and a Heraeus muffle furnace was used to determine the volatile matter following UNE-019 (ISO562). The CHNS composition analysis was performed by dry combustion on a LECO TruSpec Micro microanalyzer, the oxygen content being determined by difference. The calorific value (HHV) was evaluated in an IKAWEEME C4000 automatic pump calorimeter. The BET equation applied to the adsorption isotherm of N_2 at 77 K (Micromeritics ASAP 2010) provided the specific surface area.

The hydrochar yield (Y), energy densification ratio (E_d), energy yield (E_y), and carbon recovery (C_{rec}) in the hydrochar and thermal stability index (TSI) (Calvelo Pereira et al., 2011) were evaluated as detailed in the Appendix.

2.5. Agrochemical analysis of solid and liquid by-products

The agrochemical properties were determined by using standard protocols for organic amendments (Faithfull, 2002; Thompson, 2001). In short, the pH and the electrical conductivity of the solids were estimated, respectively, in suspensions and extracts, both obtained in a biomass/water ratio of 1:10. In the case of the liquid phase, these parameters were determined in undiluted samples.

The dry matter content in the aqueous streams was derived from the mass loss after drying in an oven at 60 °C for three days and the dissolved organic C content was evaluated by catalytic combustion in a Shimadzu TOC-VCSH analyzer.

The total content of macronutrients, micronutrients and heavy metals (P, K, Ca, Mg, Na, Mn, Zn, Cu, Fe, Pb, Cd, Cr, Ni and As) were estimated in both by-products by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after digestion with nitric and perchloric acid. The total contents of N, NO_3-N and NH_4-N were obtained colorimetrically by the 2,6-dimethylphenol and indophenol blue methods (ISO7150-1, 1984; ISO7890-1, 1986).

As commonly used for the ecotoxicological evaluation of soil amendments (Cárdenas-Aguiar et al., 2019; Kebrom et al., 2019), potential phytotoxicity was examined using seed germination and early growth tests on garden cress (*Lepidium sativum* L.) and wheat (*Triticum aestivum* L.), following the method proposed by Zucconi et al. (Zucconi et al., 1981). In particular, water extracts of solids were prepared at a sample/water ratio of 1:10. Twenty seeds of the test crop were incubated in the dark at 28 °C on filter paper in Petri dishes with 5 mL of either water or water extract from solid (hydrochar) or reaction liquid. The percentage of germinated seeds (G) was calculated as (number of germinated seeds/total number of seeds) × 100, the root growth rate of the germinated seeds (L) were determined after 60 h as the average root length (sum of root length of germinated seeds/total number of seeds), and the germination index (GI) was estimated as $(G_{extrac}/G_{water}) \times (L_{extract}/L_{water}) \times 100$, where $G_{extract}$ and G_{water} were percentage of germinated seeds in water extract or water, respectively, and $L_{extract}$ and L_{water} were average length of germinated seeds in water extract or water, respectively (Zucconi et al., 1981).

The assessment of phytotoxicity was referred to a pattern found previously (Emino and Warman, 2004; Luo et al., 2018; Zucconi et al., 1981), whereby germination percentages $< 50\%$ and between 50%-80% may suggest high and moderate phytotoxicity, respectively, while values above 80% indicate the absence of phytotoxins.

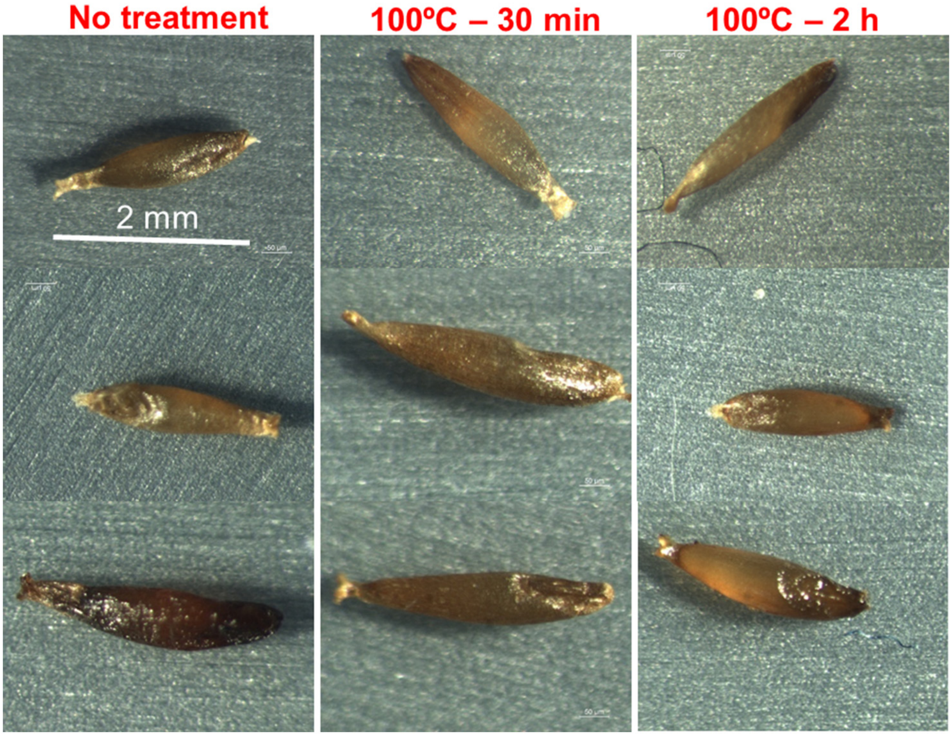

Fig. 2. Images of fresh and hydrothermally treated seeds of Pampas grass.

3. Results and discussion

3.1. Hydrothermal treatment and seeds viability

In the first stage, the hydrothermal treatment was approached with the sole objective of inertizing the Pampas grass seeds, so the HT was applied exclusively to the inflorescences. Female specimens were used on the basis of their higher seed production and germination rate, when compared with the male ones.

Seeds retain their morphology, although with an increase in size due to reaction water absorption, after HT at 100 °C for 30 min and 2 h (Fig. 2) and are successfully inertized. Tests with a photoperiod of 14 h light/10 h dark at 25 °C did not detect seed germination along the trial month, while the majority of fresh seeds usually germinated within the first week.

It should be noted that, in addition to the inertization of the seeds after only 30 min, this gentle HT treatment of this part of the plant has further advantages from a practical point of view. Although the inflorescences do not show any relevant morphological degradation (Fig. A.3a) and their mass loss is limited to about 15% by weight (dry basis), the resulting wet plumes occupy 40% less space than the original ones. They undergo some expansion on drying, but are easily packaged into very small pellets (Fig. A.3a). This facilitates handling, transport, storage and use as biofuel with a calorific value of 20.5 MJ/kg.

3.2. Morphological changes and process yield

The images in Fig. 1 reflect the impact of temperature and time of the hydrothermal process on the morphology of the PG residues. Although a color change towards brownish tones is observed, the biomass remains practically unchanged until the treatment at 160 °C for 2 h. In this case, some densification and blackening of the resulting solid is detected, suggesting an incipient carbonization. On the other hand, a clear transformation is observed when the operation runs at 200 °C for 30 min, which progressively becomes more pronounced up to 230 °C-2 h.

SEM observations of the major component of PG, the leaves, detail the evolution of biomass degradation (Fig. 3). As the severity of the

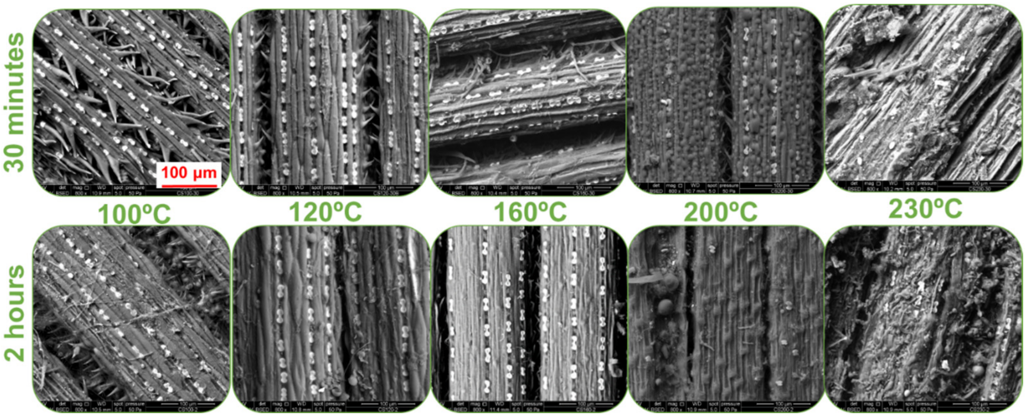

Fig. 3. Evolution of the structure of *Pampas grass* leaves with the hydrothermal treatment conditions (magnification 800×).

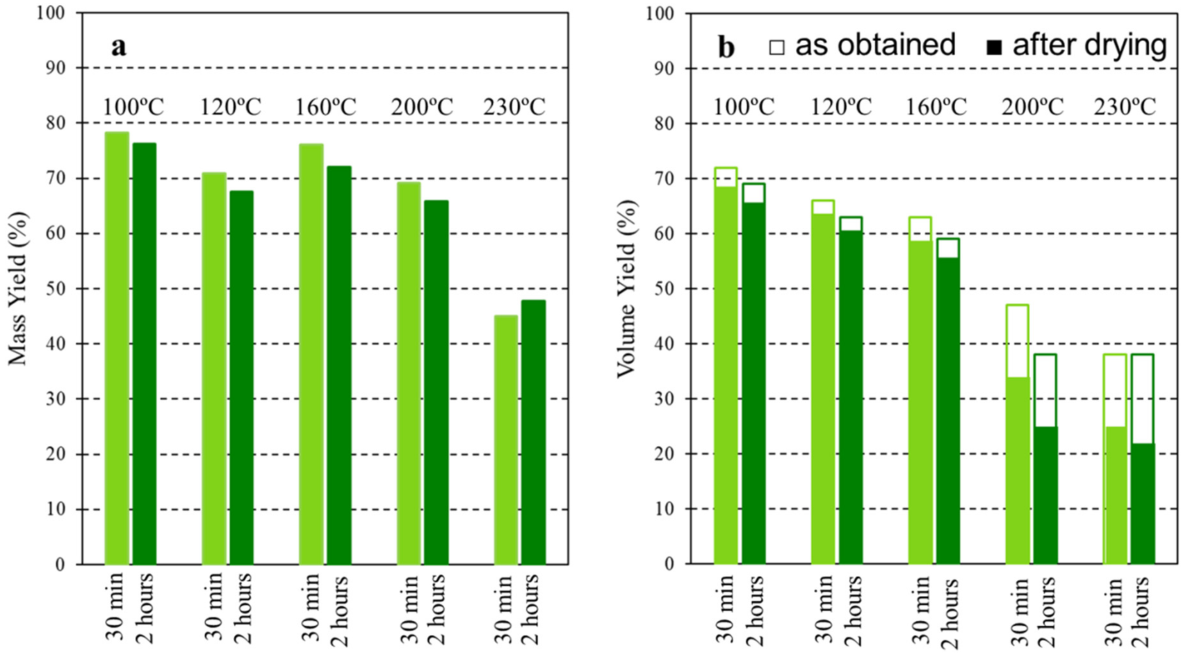

Fig. 4. Evolution of the weight (a) and volume (b) of the PG waste as a function of the hydrothermal treatment conditions.

operating conditions increases, the ordered skeleton, formed by a repetitive fibrillar unit of biopolymers and siliceous deposits, loses definition. Fig. A.4 illustrates the progressive reduction of the external inorganic spikes, being practically non-existent after HT at 160 °C for 2 h. The initial structure of the biomass is definitely degraded when the reaction takes place at 230 °C.

As summarized in Fig. 4a, the PG residue undergoes a weight loss between 20 and 30% with respect to the original material (dry basis) by treatment at 100-200 °C for 30 min. On the other hand, a reaction temperature of 230 °C causes a higher decomposition of the biopolymers and the initial mass is halved.

The transformation of PG by HT at 100–160 °C for only 30 min is accompanied by a simultaneous reduction of its volume by ~30–40% (referred to the fresh sample) (Fig. 4b-empty columns). Temperatures of 200 and 230 °C are much more efficient in this respect and the resulting solids take up 50–60% less space than the feedstock. In addition, the final drying has a much greater effect on the materials obtained at high temperature, and the corresponding solids eventually occupy ~30-20% of the volume of the raw biomass (Fig. 4b-full columns).

The comparison illustrated in Fig. 4 reveals that the reaction time has a limited impact on both the mass and the volume reduction and it is not worth extending the operation to 2 h.

3.3. Physico-chemical features of the solid by-product

Except for the reduction in the ash content by dissolving a fraction of the inorganic matter, hydrothermal treatment at temperatures between 100 and 160 °C and times of 30 min and 2 h has little effect on the chemical composition of the PG waste (Table 1).

The carbon balance reveals that, under these HT conditions, 70–80% of the carbon in the original residue is recovered in the resulting solid and the sequestration capacity decreases very slightly by prolonging the reaction for 2 h (Table A.1).

The calorific value remains around 19.5-20.9 MJ/kg (Table 1), which largely surpasses the minimum value of 14.5 MJ/kg set by the standard (ISO17225-6, 2014) for single feedstock pellets to be applied as solid biofuel of non-woody origin.

No statistically significant variations in the H, N and S content of PG are observed after HT, but they are relevant in the percentages of C and O. The decrease in O/C and H/C ratios clearly shows that the reaction above 160 °C simulates the natural carbonization process (van Krevelen, 1993) and hydrochars are successfully produced as a by-product (Fig. 5). This process is able to convert the PG residue into a peat-like solid with HHV of 21.8 MJ/kg in only 30 min at 200 °C, while a product closer to lignite that provides 23.9 MJ/kg is generated at 230 °C (Funke and Ziegler, 2010; Suárez-Ruiz et al., 2019). Fig. 5 also

Table 1
Chemical characteristics and calorific value (referred to dry basis) of the PG feedstock and the solids produced by hydrothermal treatment.

Treatment conditions		Ash (wt%)	Volatile matter (wt%)	Fixed carbon (wt%)	C (wt%)	O (wt%)	H (wt%)	N (wt%)	S (wt%)	HHV MJ/kg
Raw waste (PG)		4.2	80.5	15.3	47.4	41.1	6.2	0.9	0.2	19.3
100 °C	30 min	2.7	81.6	15.7	48.5	41.6	6.1	0.9	0.2	19.5
	2 h	3.3	79.3	17.4	48.4	41.3	5.9	1.0	0.1	19.5
120 °C	30 min	2.8	80.7	16.5	48.4	42.0	5.9	0.8	0.1	19.6
	2 h	3.2	78.9	17.9	48.4	41.3	6.1	0.9	0.1	19.6
160 °C	30 min	2.9	81.5	15.6	49.4	40.6	6.2	0.8	0.1	20.4
	2 h	3.2	79.3	17.5	51.2	38.3	6.1	1.1	0.1	20.9
200 °C	30 min	3.1	77.2	19.7	53.5	36.1	6.1	1.1	0.1	21.8
	2 h	3.6	73.8	22.6	54.9	34.3	6.0	1.1	0.1	22.7
230 °C	30 min	3.3	70.7	26.0	58.0	31.5	6.0	1.1	0.1	23.9
	2 h	4.0	58.8	37.2	65.8	22.9	5.7	1.4	0.2	27.4

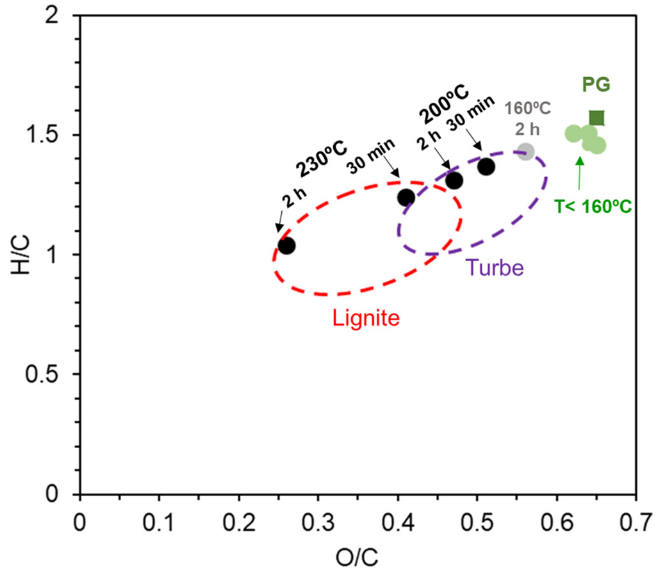

Fig. 5. Evolution of the O/C and H/C ratios of PG waste as a function of temperature and time of hydrothermal treatment. The limiting values for peat and lignite are indicated by the dashed lines (Suárez-Ruiz et al., 2019).

reflects that the loss of volatiles and reactions of condensation and aromatization are much more relevant when the 230 °C treatment takes place for 2 h. Under such conditions, the energy densification ratio (E_d) improves up to 1.4 (Table A.1) and the corresponding hydrochar reaches a calorific value of 27.4 MJ/kg (Table 1) at the boundary between lignite and high volatility bituminous coal (Suárez-Ruiz et al., 2019). It is worth noting that the presence of extractives acting as a natural binder facilitates the pelletization of hydrochars at room temperature (Fig. A.3b). This feature, together with the low concentration of inorganic impurities (Table 1), makes the PG-hydrochars obtained at 200–230 °C an advantageous source of bioenergy.

However, it should be noted that the solid yield (Y) at 230 °C for 30 min drops to 45 wt% and the retained carbon (C_{rec}) accounts for 55 wt% (Table A.1) due to more complex pyrolysis reactions. Secondary reactions between the intermediate compounds lead to further formation of solids after 2 h and, finally, 66 wt% of carbon is recovered. As a consequence of the reduced amount of solid obtained the energy yield (E_y) is limited to 54-67% against 80-69% reached by HT at lower temperatures (Table A.1).

3.4. Agrochemical characteristics of the solid by-products

All the solids derived from HT have a pH lower than that of the initial waste (pH = 7.1), tending to decrease with temperature from slightly acidic (6.0-6.6) for materials obtained at $T \leq 120$ °C to acidic (4.6-5.3) for those resulting at $T \geq 160$ °C (Table 2). The electrical conductivity of the feedstock (2.15 dS/m), as well as the macro- and micronutrient contents, also decrease to 0.63–1.21 dS/m, although no clear trend with the treatment conditions is found (Table 2).

With respect to the initial PG residue, the hydrothermal treatment improves seed germination, root growth, and germination index of wheat (Table 2). A similar trend is observed for cress, especially after processing at 100–120 °C. These positive results are likely associated with the lower electrical conductivity of the resulting products compared to the untreated PG. The better performance of the hydrochars obtained at 100–120 °C in cress seeds germination and early growth tests may be related to the relatively higher O/C ratio, indicating a higher abundance of surface oxygenated functionalities that may enhance cation exchange capacity for nutrient retention in soil and sorption of positively charged pollutants (heavy metals) (Uchimiya et al., 2011; Xue et al., 2012). Further, reaction above 160 °C may result in increased phytotoxicity due to the generation of organic compounds such as phenols, aldehydes and organic acids (Becker et al., 2013; Hao et al., 2018).

As a whole, the pH values and low electrical conductivity of the hydrochars, together with the absence of contaminants and the improved performance in seed germination and in the early growth test with respect to the untreated feedstock, suggest that these materials could be safely applied to soil without harmful effects on plants (Tables 2 and A.2). Their low nutrient content prevents HT-solids from acting as fertilizers on their own, but the above characteristics, together with their high organic C content and open porosity with S_{BET} = 5–8 m^2/g (Fig. A.5), suggest their potential as organic amendments to sequester C in the soil and improve its physical and biological properties. This would enhance the action of fertilizers by reducing the amount of compounds that are lost in surface runoff, facilitate the nutrients retention, and stimulate microbial activity (Fang et al., 2018; Sun et al., 2020).

The lower O/C and H/C ratios (Fig. 5) and the increased thermal stability index (TSI) (Table A.1) suggest that higher temperatures make the carbon fraction retained in the solid more stable (Bai et al., 2014), and therefore with a longer half-life in the soil. Hydrochars obtained at 200 °C and 230 °C markedly decrease seed germination, root growth, and germination index of wheat and cress, compared to those produced at lower temperatures, but it has been reported that most of the potentially phytotoxic substances generated at high temperatures are water soluble, and their negative effects on plants can be avoided by washing, diluting, co-composting, or applying the hydrochars to the soil several weeks before sowing (Bargmann et al., 2014; Busch et al., 2013; Fang et al., 2015; Melo et al., 2019).

3.5. Agrochemical characteristics of the liquid by-products

As the possibilities of using HT liquid by-product will condition the feasibility of this alternative process for the management of PG waste,

Table 2
Main agrochemical properties of the PG waste and solids obtained by hydrothermal treatment under different conditions.

Property	PG	100 °C		120 °C		160 °C		200 °C		230 °C	
		30 min	2 h	30 min	2 h	30 min	2 h	30 min	2 h	30 min	2 h
pH	7.1	6.1	6.4	6.6	6.0	5.3	4.7	4.6	5.0	4.8	5.0
Electrical conductivity (dS/m)	2.15	1.21	1.06	0.86	0.94	1.29	1.09	0.98	0.70	0.63	0.95
P (mg/kg)	850	562	831	690	630	627	494	453	652	870	1356
K (mg/kg)	8097	3330	3514	2727	2441	3150	2437	1822	1298	1127	2258
Mn (mg/kg)	30.3	13.9	15.6	17.5	13.6	12.3	17.2	11.2	16.0	12.0	18.1
Zn (mg/kg)	51.6	58.3	30.8	31.1	29.8	25.1	58.9	37.7	40.5	47.8	35.4
Cu (mg/kg)	6.8	4.4	3.7	3.4	3.2	3.3	5.9	4.2	5.9	4.7	7.1
Fe (mg/kg)	1372	426	244	409	196	194	809	498	573	365	497
Germination percentage[a,b]	0.0/74.1	82.5/83.3	89.5/75.9	82.5/75.9	77.2/87.0	3.5/83.3	19.3/63.0	12.3/79.6	73.7/74.1	8.8/75.9	24.6/81.5
Root growth rate[a,b]	0.0/43.9	26.3/65.4	25.7/47.6	26.3/46.6	17.1/62.1	0.4/50.3	3.1/37.5	1.4/42.4	21.7/29.2	1.0/58.8	4.3/64.3
Germination index[a,b]	0.0/32.6	21.8/55.3	23.1/37.6	21.8/35.9	13.2/54.4	0.0/41.9	0.9/24.4	0.3/34.6	17.0/21.5	0.1/44.8	1.4/52.8

[a] Respect to water.
[b] Garden cress/wheat.

Table 3
Main agrochemical properties of the liquid by-products obtained by hydrothermal treatment under different conditions.

Property	100 °C		120 °C		160 °C		200 °C		230 °C	
	30 min	2 h	30 min	2 h	30 min	2 h	30 min	2 h	30 min	2 h
Dry matter (g/L)	2.60	2.48	2.62	3.23	1.90	6.16	5.49	6.10	4.78	8.29
pH	4.2	6.7	6.6	6.6	5.3	3.9	3.6	3.8	3.9	3.9
Electrical conductivity (dS/m)	0.95	1.10	1.16	1.45	0.83	1.52	1.51	1.80	1.47	2.09
Dissolved organic carbon (g/L)	1.21	1.02	1.19	1.21	0.76	4.10	4.22	4.07	3.47	5.36
N total (mg/L)	152	466	583	293	961	346	264	314	1181	836
N-NO_3 (mg/L)	20.4	23.0	23.8	28.2	25.0	60.8	63.7	55.0	52.7	59.5
N-NH_4 (mg/L)	7.7	20.7	22.9	31.6	21.8	4.3	4.3	6.1	4.0	1.1
P (mg/L)	6.8	8.5	10.1	9.9	5.3	18.1	18.1	10.6	6.8	4.5
K (mg/L)	201	250	309	347	182	282	277	426	280	457
Mn (mg/L)	0.1	0.1	0.1	0.2	0.1	0.4	0.4	0.4	0.3	0.5
Zn ((mg/L)	2.2	0.2	0.1	1.7	1.1	0.3	0.4	0.4	0.4	0.6
Cu (mg/L)	0.2	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
Fe (mg/L)	0.5	0.4	0.3	0.3	0.5	1.1	0.7	1.1	0.7	1.4
Germination percentage[a,b]	86.0/74.1	86.0/90.7	91.2/94.4	57.9/101.9	77.2/98.1	0.0/5.6	0.0/0.0	0.0/0.0	0.0/1.9	0.0/0.0
Root growth rate[a,b]	18.6/29.2	38.9/75.5	28.5/61.7	8.5/76.5	11.8/62.0	0.0/0.8	0.0/0.0	0.0/0.0	0.0/0.3	0.0/0.0
Germination index[a,b]	16.0/21.5	34.9/68.7	26.0/59.3	5.7/78.5	9.2/62.0	0.0/0.1	0.0/0.0	0.0/0.0	0.0/0.0	0.0/0.0

[a] Respect to water.
[b] Garden cress/wheat.

a first screening of the agrochemical features of the resulting aqueous streams under the various experimental conditions (Fig. A.6) was also conducted.

The pH is slightly acidic for the liquids obtained at lower temperatures and decreases to ~4 when the reaction temperature is ≥160 °C and a carbonization process occurs (Table 3). The low electrical conductivity of the liquids tends to increase with temperature and time up to about 2 dS/m, which may be somewhat high for some crops sensitive to salinity (Bar-Yosef, 1999; Eynard et al., 2005).

The contents of the toxic elements examined are below detection limits in all liquid by-products, but their macro- and micronutrients contents are also too low to be considered as valuable liquid fertilizers (Tables 3 and A.3). Nonetheless, the fertilizer potential of these liquid by-products could be improved by recirculating them in the HT process (Leng et al., 2020; Mau et al., 2019). Another option to valorize these liquid by-products in soil and, at the same time, eliminate potential issues of phytotoxicity could be through their application supplemented with appropriate dosages of compost.

4. Conclusions

Hydrothermal treatment at temperatures from 100 to 230 °C for 30 min makes both the seed inertization and the integral valorisation of the aerial part (stems, leaves and inflorescences) of the invader Pampas grass feasible. The biomass waste is converted into a stable carbonaceous solid and an aqueous stream, whose characteristics are highly dependent on the reaction temperature. No relevant improvements are achieved by prolonging the process up to 2 h.

HT at 100 °C and 120 °C does not provoke relevant changes in the chemical composition of PG waste, but its phytotoxicity on wheat and cress seeds is considerably reduced. The agrochemical parameters suggest the potential of low temperature HT-solids to sequester carbon and improve physico-biological properties of the impoverished soil affected by this invader plant. On the other hand, HT at 200-230 °C involves a carbonization process that directly transforms Pampas grass residues into hydrochars with better prospects for utilization as CO_2-neutral fuel. Due to the low content of carbon and nutrients, the HT-aqueous streams should be supplemented with an adequate dose of compost for use in soil.

CRediT authorship contribution statement

Loreto Suárez: Conceptualization, Investigation, Methodology, Resources. **Tomás Emilio Díaz:** Funding acquisition, Investigation, Methodology, Supervision, Writing – review & editing. **Iria Benavente-Ferraces:** Investigation, Methodology, Writing – review & editing. **César Plaza:** Investigation, Methodology, Writing – review & editing. **Mónica Almeida:** Investigation, Methodology, Writing – review & editing. **Teresa A. Centeno:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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