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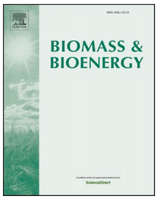

Hydrothermal carbonization of agro-industrial pomaces: Evaluating operational factors for realistic applications

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ABSTRACT

This study aims to develop a strategy for valorizing apple pomace (AP) and grape pomace (GP) through hydrothermal carbonization (HTC). We studied the production of hydrochar, with a focus on recycling the liquor and exploring its anaerobic digestion (AD), in line with circular economy principles. Initially, we performed HTC on AP and GP, with and without a drying pre-treatment, using two different batch reactors (50 mL and 2 L) at 180, 200, and 220 °C. The effects of reactor size, feedstock, and its possible pre-treatment, as well as reaction temperature, on product properties and carbon distribution were assessed. In the subsequent phase, HTC experiments were conducted with process water (PW) recirculation to favor hydrochar production. We selected a target HTC temperature of 200 °C. After five recirculation cycles, hydrochar yield increased for both AP and GP compared to HTC at 200 °C with fresh tap water. Although hydrochar composition remained largely unchanged, PW exhibited progressively higher total organic carbon (TOC) levels, indicating that recirculation concentrates soluble organics in the liquid phase. These organics could react and polymerize into secondary char, thereby increasing hydrochar yield. As an alternative option to valorize PW, we performed its AD, evaluating the effect of PW recycling on AD. The process was not inhibited by the stronger acidity and the increased concentration of organic compounds in recycled PW: all tested PWs showed biogas production in line with typical organic residues.

1. Introduction

Energy and material recovery from waste materials is an encouraging opportunity towards sustainability. Indeed, following the principles of circular economy, valorizing residual products as new resources could help reduce environmental impact while creating added value. In this sense, agro-waste materials represent optimal starting feedstocks, being easily available, relatively cheap, and generically rich in carbon [1]. These wastes include a large variety of residues, resulting from crop cultivation, agro-industrial processing, livestock activities and food production [2]. Even though they could be converted into different products (growing media [3], biofuels [4], adsorbent materials [5–7] and many more), their generally high moisture content may represent an obstacle to their exploitation. These feedstocks are typically treated using biological processes, which rely on microorganisms and require long residence times. Conversely, traditional thermal treatments, such as pyrolysis or gasification, are only viable if the materials undergo a cost-intensive drying pre-treatment. Another possible alternative, among the different conversion technologies, could be hydrothermal carbonization (HTC).

Also known as "wet pyrolysis'' or "wet torrefaction", HTC is a thermochemical process able to transform organic feedstocks into a carbon-rich solid product [8]. During HTC, the biomass is submerged in water, which acts as both reaction medium and catalyst, taking advantage of its ability to remain liquid at high temperatures (180–250 °C) and appropriate pressures (10–50 bar) [9]. HTC leads to the formation of three main products. The most important in terms of yield is the hydrochar, a solid phase that retains most of the carbon of the initial feedstock [10]. Hydrochar represents the principal outcome of HTC, and it could be valorized in several ways, such as the already mentioned soil amendments, biofuels or adsorbent materials, as summarized in detail by recent review articles [11–13]. Another HTC product is a gas phase,

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which is the smallest in terms of yield (5% or less). It is mainly composed of CO_2 with some traces of CH_4 and CO [10]. HTC also produces a liquid phase, called HTC liquor or HTC process water (PW). It is rich in dissolved organic compounds, such as formic acid and acetic acid, thus possessing a pronounced acidic nature [10]. While the gas spontaneously separates from the other two phases, the liquid and the solid must be divided by an appropriate treatment, such as filtration or centrifugation. After this step, the resulting PW must be appropriately managed due to its high organic load. Recycling back the PW to new HTC runs is described in literature as a possible strategy to reduce the environmental impact of the HTC processes [14–17]. This approach not only significantly reduces the need for additional clean water to the HTC reactor and saves energy if this PW is provided warm, but research also demonstrated that some of the soluble organics in the PW promote the formation of additional hydrochar. This is labelled “secondary char” and results from chemical species dissolved in the liquid phase, which react and polymerize, forming a new solid phase. Secondary char differs from the hydrochar deriving from solid-solid reactions that produce the so-called “primary char” [16]. If PW recirculation is not possible, partially or completely, another strategy could be the anaerobic digestion (AD) of PW, with the additional benefit of producing biogas [18]. More in general, HTC appears as an interesting intermediate in a biorefinery scheme, providing a more flexible route to material and energy recovery.

In this work, two bio-wastes were selected as initial feedstocks for HTC processes, considering their widespread availability. The first is apple pomace (AP), a residue generated during the processing of apples into products such as juice, cider or vinegar. Annual global apple production exceeds 90 million tons [19], with approximately a quarter destined for industrial processing, with the consequent production of large quantities of waste [20]. In particular, for every kilogram of apple juice, 0.12 kg of AP is generated (data provided by *Melinda*, one of the largest producers and processors of apples in Italy and Europe), consisting mainly of apple peel and pulp, with a minor percentage of seeds and stems. The second feedstock is grape pomace (GP), often called grape marc, the principal by-product of winery. Annual world grape production is nearly 80 million tons, of which over 30 million tons are processed to become wine, musts and juices [21], generating substantial volumes of organic residues, the most important of which is GP (around 10 million tons per year [22]). GP is a more heterogeneous material, composed mostly of grape skin, seeds and stems. It has been studied under HTC conditions in several works (see Table 1), providing a relatively well-documented understanding of its behavior. In contrast, AP has received less attention in this context, with fewer studies reported (Table 1). Beyond the novelty of exploring AP as an HTC precursor, comparing AP and GP is also interesting due to their different composition, especially in terms of sugar content, respectively 39.1 % and 29.2 % [23].

This work aims to develop a strategy to transform AP and GP into hydrochar, which could then be upgraded, with a focus on recycling the liquor and exploring its anaerobic digestion (AD), in line with circular economy principles. Since AP is a relatively new feedstock in the HTC field, we aimed to deepen the understanding of its behavior by investigating how product distribution is influenced not only by reaction temperature, but also by drying pre-treatment and reactor size. These aspects are generally less studied, with only a few works available in the literature [24]. In addition, PW recycling still presents several uncertainties, especially when HTC is applied to feedstocks retaining their original moisture content. Furthermore, to our knowledge, this is the first work addressing the effect (if any) of PW recirculation on its behavior in AD.

Table 1
Overview of similar HTC studies in literature showing feedstock, main research goals and process conditions.

Reference	Feedstock	Main research goal	HTC conditions	
			Temperature	Residence time
[45]	Wheat straw, grape pomace and wood chips	Optimization of HTC process parameters	70–230 °C	1 and 2 h
[46]	Grape pomace, corn cobs and *Miscanthus giganteus*	Mg-based pyro-hydrochars for methylene blue adsorption	220 °C	1 h
[47]	Grape marc	Biorefinery approach for the recovery of material and energy	220 °C	1 h
[3]	Digestate, spent coffee grounds and grape marc	Hydrochars as peat substitutes for growing media	220 and 240 °C	1 h
[48]	Grape marc	Ignition properties of hydrochars and slurries	180, 200 and 260 °C	30 min
[49]	Vine pruning and grape pomace	Co-HTC for solid biofuel and phenols production	180–260 °C	1–7 h
[5]	Grape pomace and walnut shells	Production of carbonaceous matrix	180 and 200 °C	1 and 2 h
[50]	Grape marc and sugarcane bagasse	HTC as pretreatment for combustion and gasification of biomass	180, 220 and 260 °C	1 h
[51]	Grape pomace (skin, seeds, 50-50 % mixture)	Synergistic effect of grape marc seeds and skins during HTC for solid biofuel	180, 220 and 250 °C	0.5–8 h
[40]	Grape pomace, orange pomace and poultry litter	Liquor recirculation in HTC	225 °C	10, 15 and 30 min
[4]	Grape marc	Effect of HTC parameters on fuel properties	180, 220 and 260 °C	30 min
[52]	Grape marc	HTC for energetic valorization	180, 220 and 250 °C	1, 3 and 8 h
[53]	Apple pomace	Effect of HTC temperature on secondary char production and its impact on fast pyrolysis	175, 200 and 250 °C	2 h
[54]	Apple pomace	Clay-assisted HTC and pyrolysis	160, 180, and 200 °C	1 h
[55]	Apple pomace	Levulinic acid production	200 °C	2 h
[7]	Apple pomace	Mg removal using CO_2 activated hydrochar	230 °C	5 h
[39]	Apple bagasse	HTC for fuel and soil improvement applications	180 and 230 °C	2 and 4 h
[6]	Apple bagasse	Production of porous carbons	200 °C	12 h
[23]	Apple residues and grape pomace	HTC of various fruit wastes	190, 225 and 260 °C	15 min

2. Materials & methods

2.1. *Feedstock characteristics*

The GP used in this study consisted of a mix of Chardonnay and Pinot Grigio grapes, with an average moisture content of 63.3 ± 0.8%. The AP had an average moisture content of 72.9 ± 1.3%. Both feedstocks were supplied by companies located in the Trentino region (North–East of Italy). Before use, the materials were stored in a freezer at −24 °C to preserve their properties and prevent fermentation.

2.2. *Experimental campaign*

The experimental campaign, schematized in Fig. 1, comprises three different phases. Initially, we conducted foundational studies on both AP and GP. We used two different HTC reactors (50 mL and 2 L of internal volume) to test the effect of different reaction temperatures on the feedstocks. Changes in the properties of the products (yields, hydrochar dewaterability and composition) were registered, and the optimal temperature was selected. In the second phase, we performed HTC tests recycling the PW to enhance the production of hydrochar. To further valorize the liquid product, biogas production through AD was then performed on PW obtained by HTC tests without PW recirculation and after five PW recycling cycles.

2.2.1. *Foundational studies*

The aim of this portion of the study was to identify the temperature that provided the optimal balance between hydrochar yield and dewaterability, highlighting the effects on the two different feedstocks. We tested AP and GP at 180, 200, and 220 °C. These values were chosen with industrial applications in mind, as higher temperatures would require more energy for heating and lead to more challenging pressures to manage, increasing both Opex and Capex. Additionally, tap water was used to perform all the experiments, and the biomass was generically used as received, to maintain consistency with realistic industrial practices. Through the capillary suction time (CST) analysis (see section 3.3), we evaluated the dewaterability of the hydrochars. A product with high moisture content is indeed a big obstacle from an economic and logistic point of view. Applying a mechanical dewatering process would reduce its volume and consequently facilitate its storage and transportation, while minimizing the risk of fermentation [25,26]. The more hydrophobic the product is, the more efficient the dewatering step will be. CST analysis allows obtaining some preliminary insights into product behavior, as previously demonstrated in HTC studies on other feedstocks [27].

To better understand the behavior of AP under HTC conditions, still not well investigated, we conducted preliminary trials using a lab-scale reactor (batch, 50 mL). HTC was performed on both dried and raw (i.e., with its original moisture content) AP, enabling the evaluation of the effects of biomass drying pre-treatments.

Once these studies had been completed, raw AP and GP were submitted to HTC at 180, 200 and 220 °C using a bench-scale reactor (batch, 2 L). A distinctive feature of this reactor is the presence of four thermocouples (T1-T4) that measure temperatures at different heights, allowing the possibility of drawing vertical temperature profiles. Tests performed with raw AP using the two HTC reactors allowed us to evaluate the impact of using different reactor sizes, with the larger having a volume equal to 40 times the smaller.

Throughout all experiments, the biomass-to-water mass ratio and residence time were kept constant at 0.1 and 1 h respectively, with the biomass mass considered on a dry basis. The reactors were filled up to approximately 70% of their inner volume to avoid the risk of overpressure due to water expansion.

We performed all experiments in triplicate. Solid and gas yields were directly calculated, while the liquid yield, below referred to also as PW yield, was obtained by difference (details in Supplementary material).

ANOVA statistical analysis was performed to get specific insights regarding the effect of temperature, reactor size and biomass pre-

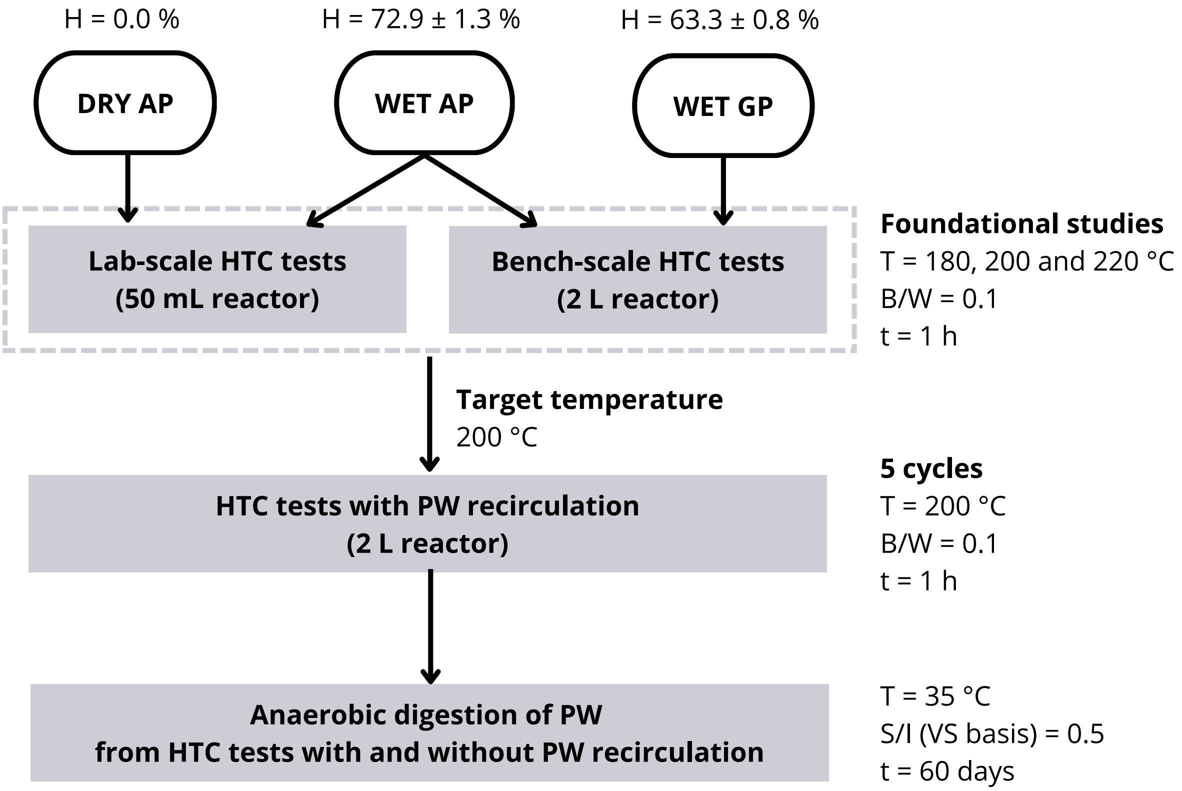

Fig. 1. Schematic representation of the phases of the experimental campaign. H = moisture content, T = temperature, B/W = biomass to water ratio, t = residence time, S/I = substrate to inoculum ratio, VS = volatile solids.

treatment on hydrochar and gas production during HTC. To perform the statistical analysis, Microsoft Excel Data Analysis tools were used: “ANOVA: single factor”, to evaluate only the impact of temperature among the different biomass/setup configurations, and “ANOVA: Two–factor with replications”, to investigate the joint effect on AP of temperature and drying pretreatment and temperature and reactor size. In all cases, a significance level (α) of 0.05 was considered.

2.2.2. *Bench-scale HTC tests with PW recirculation*

In this second part of the experimental campaign, we decided to recycle PW as a reaction medium in consecutive, subsequent HTC runs. In literature, this is described as a possible way to avoid disposing of PW and, at the same time, enhance the formation of secondary char. We selected 200 °C as the target temperature, considering the best compromise between hydrochar dewaterability and yield (see Section 4.2.2).

Since the PW obtained from each test (after separation through filtration of the HTC slurry) was not enough to reach a biomass-to-liquid ratio of 0.1 in the following one, some clean tap water had to be added. To standardize the procedure, be consistent, and maximize the amount of PW recirculated, the two fluids were always mixed with a fixed proportion: 65% of PW and 35% of tap water. The 2 L reactor was used to perform all the tests, and the rest of the procedure remained unchanged. A total of five recycling cycles were performed on both AP and GP. Solid, gas and liquid yields were measured for all the recycling cycles with the same method adopted in section 2.2.1. We conducted all the experiments in duplicate.

2.2.3. *Anaerobic digestion of the HTC process water*

Selected PWs obtained from the HTC of AP and GP were also subjected to anaerobic digestion (AD) to evaluate the viability of this process for their treatment. We tested both the PWs obtained after a single 200 °C test and those obtained after five recycling cycles (as described in the previous sub-section). The goal was to determine whether recycling the PWs could lead to the formation of toxic compounds, creating a liquid waste that is more difficult to treat via AD.

We evaluated the behavior of the liquors in AD through biochemical methane potential (BMP) tests, performed in accordance with international and national normative (UNI EN ISO 11734:2004 and UNI/TS 11703/2018, respectively). In brief, each sample was placed together with the inoculum in a 130 mL bottle, with a substrate-to-inoculum volatile solids (VS) ratio of 0.5. The bottles were placed in a thermostatic bath. By piercing the silicone seal at the top of the bottle, we were able to measure regularly the production of biogas and biomethane.

The BMP tests were performed in mesophilic conditions (35 ± 2 °C) using an inoculum that was collected from a full-scale AD plant located in Lana (South Tyrol, Italy). The plant employs mesophilic AD to treat the organic fraction of municipal solid waste (OFMSW). Prior to its use, the inoculum was incubated for three weeks to minimize endogenous biogas production. The inoculum properties after the incubation phase, determined through standard techniques, were as follows: total solids (TS, %) = 4.1 ± 0.1; volatile solids (VS, % of TS) = 59.4 ± 4.2; total volatile solids (TVS, %) = 2.4 ± 0.1; total Kjeldahl nitrogen (TKN, g/L) = 5.2 ± 0.1; pH = 9.2. All samples were tested in triplicate, including the blank and the control. The blank consisted of the post-incubation inoculum with no substrate addition, while the control was the OFMSW usually processed in the plant. After 60 days, the bottles were opened and their content analyzed in terms of solids, pH and volatile fatty acids to alkalinity ratio (VFA/alk) following standard methodologies.

2.3. *Analytical characterization*

Raw materials and derived hydrochars were further analyzed using elemental analysis. C, H and N mass fractions were determined through a LECO 628 Elemental Analyzer, in accordance with ASTM D-5375. The ash content was determined by incineration at 550 °C, following the EN 14775 procedure. The oxygen content was obtained by difference. To assess hydrochar dewaterability, the capillarity suction time (CST) was measured with a Model 304B CST equipment by Triton Electronics Ltd. In this case, the capillary suction pressure created by standard filter paper is used to draw PW from the wet hydrochar obtained after separation through filtration of the HTC slurry. The CST is determined by measuring the time it takes for the waterfront to move between two electrodes of the equipment, positioned at a fixed distance. The liquid phase was characterized in terms of total organic carbon concentration (TOC). TOC was measured with a FORMACS HT-iTOC analyzer (Skalar Analytical B.V., Netherlands), according to the ASTM D7573 standard. The pH value of the PWs was also measured (ProfLine pH 3310, by WTW). TOC analysis, together with the measurement of the different mass yields and the elemental analysis of the hydrochar, allowed the calculation of the carbon balances. The formulas used in the carbon balance calculations are reported in Supplementary material.

3. Results and discussion

3.1. *Sample identification*

The different experiments are identified by a code with the form BPTTTS_C, which accounts for the various characteristics of the trials: BP is the pomace type (AP or GP), TTT refers to the process temperature (180, 200, or 220 °C), S indicates the pre-treatment (D = pre-dried, W = wet, i.e. raw), and C is the reactor size (S = 50 mL, B = 2 L). For the sake of brevity, since all tests with PW recirculation were conducted using wet biomass in the larger reactor at the same temperature, the code was simplified to BP_RN, considering only the type of pomace (AP or GP) and the number of recycling steps (RN, where N ranges from 1 to 5).

3.2. *Temperature trends*

Fig. 2 shows the temperature profiles registered by the four thermocouples (T1 – T4) in the 2 L reactor for AP200W_B and GP200W_B. The thermocouples are numbered from the one located at the top of the reactor (T1) to the one at the bottom (T4). T3 was used as the reference for calculating the residence time. The heating phase, i.e. the time necessary to reach the set point temperature, lasted approximately 25–35 min (t_i). The temperature was then maintained constant for 1 h, which corresponds to the reaction time. After that, the cooling phase began (t_f), requiring an additional 30 min.

According to Lucian et al. [28], in batch reactors, the heating phase should not be overlooked, since carbonization reactions already start between 180 and 220 °C. T2, T3, and T4 are submerged in the biomass–water mixture and show an initial delay in temperature increase. Despite the supply of external heat, their readings remain almost constant for the first few minutes of the experiment, followed by a more rapid rise until the target temperature is reached. In the case of AP200W_B, this effect is more pronounced. Notably, in this case, T3 – located in the middle of the mixture – exhibits an even greater initial delay than T4, which is positioned at the bottom of the reactor, taking longer to reach 200 °C with respect to GP200W_B. However, as heating progresses, T3 eventually overtakes T4 before both thermocouples reach the set point. In contrast, T1, which is situated in the upper part of the reactor and registers the gas phase temperature, consistently shows lower values than those recorded by the other thermocouples throughout the entire HTC test.

Based on previous findings by Marchelli and Fiori [29], in a numerical study on the internal mixing of a non-stirred HTC reactor, these effects could be attributed to the high viscosity of the initial biomass-water mixture. This characteristic, especially evident in the case of AP, impedes the flow of the fluid, allowing heat transfer to occur only through conduction, which is slower and less efficient, thus causing the delay in temperature increase. In essence, the natural convection

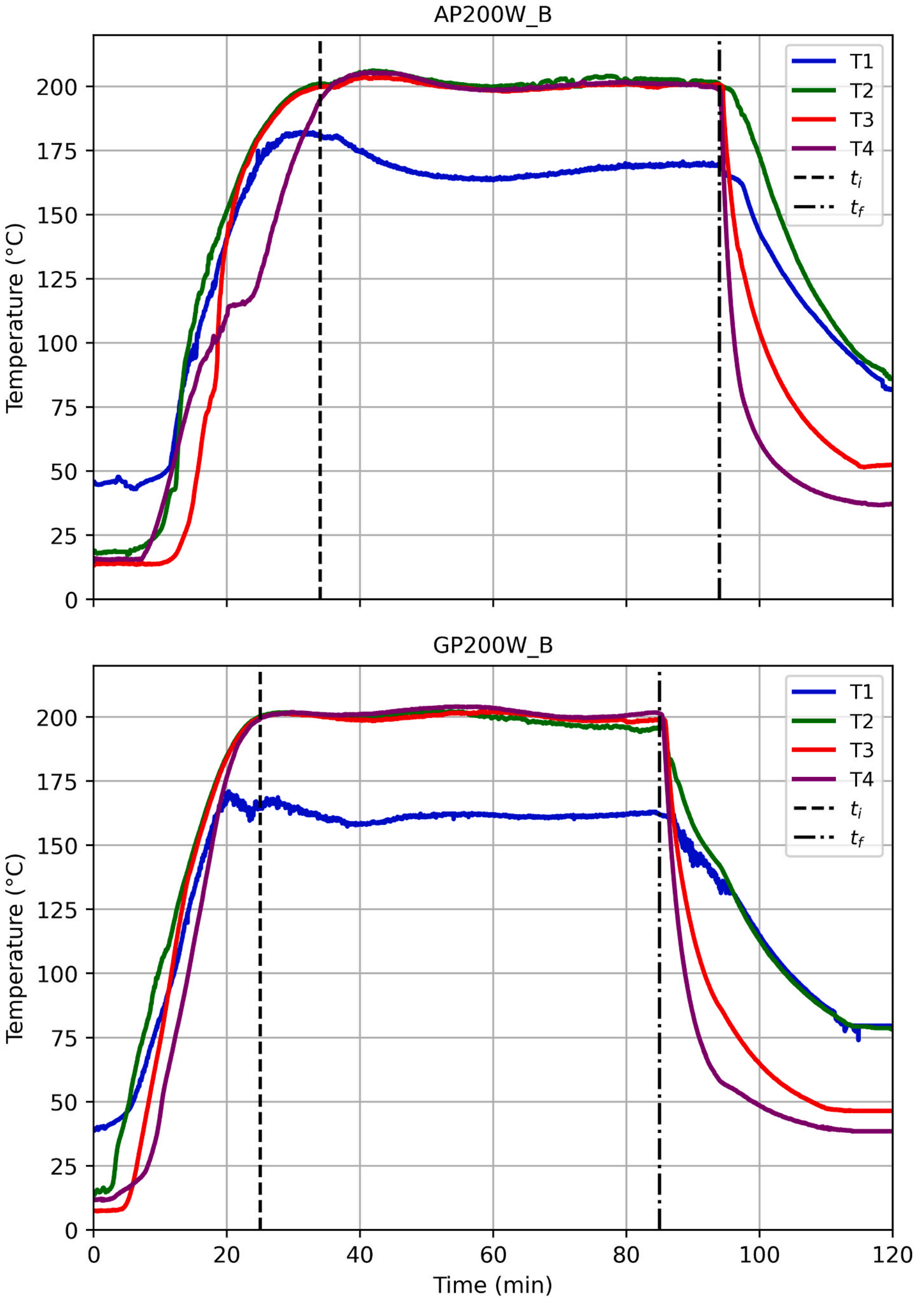

Fig. 2. Trends of temperature registered by the four thermocouples during an experimental run at 200 °C for AP and GP.

induced by temperature gradients within the mixture in the reactor is severely limited if not completely prevented. Additionally, the top remains cooler than the rest of the vessel, as reactor heating takes place on its lateral surfaces and the top is not in direct contact with the solid-liquid mixture, which is a better medium for heat transfer than the gas [29]. This explains why T1 registers lower temperatures throughout the run.

3.3. Foundational studies

3.3.1. Yields

Fig. 3 (a) shows the results in terms of hydrochar, PW and gas distribution obtained for AP and GP at the different HTC conditions tested during the preliminary phase. Interesting observations could be made by analyzing the hydrochar production. In general, the highest values are reached by GP (purple) at all temperatures, although the non-negligible standard deviations – ascribed to the heterogeneity of the feedstock – make it difficult to identify a clear trend (p-value = 0.513). By contrast, AP enables interesting comparisons among the different HTC conditions. In the 50 mL reactor, this feedstock was processed either dry (green) or wet (blue). Even though a slightly increasing solid yield trend for dry AP and a more pronounced decreasing trend for wet AP can be observed, ANOVA indicates that temperature alone does not appear to clearly affect the hydrochar production (p-value = 0.395). Conversely, its combined action with the drying pre-treatment yields a p-value of 0.007, indicating a statistically significant interaction. Additionally, wet AP was tested at different temperatures in the 2 L reactor (red), where an almost constant solid yield can be seen. Again, when these results are compared with those obtained for wet AP in the 50 mL reactor, no statistically significant effect of temperature alone can be observed, while a p-value of 0.031 was calculated when considering the combined effect of temperature and reactor size.

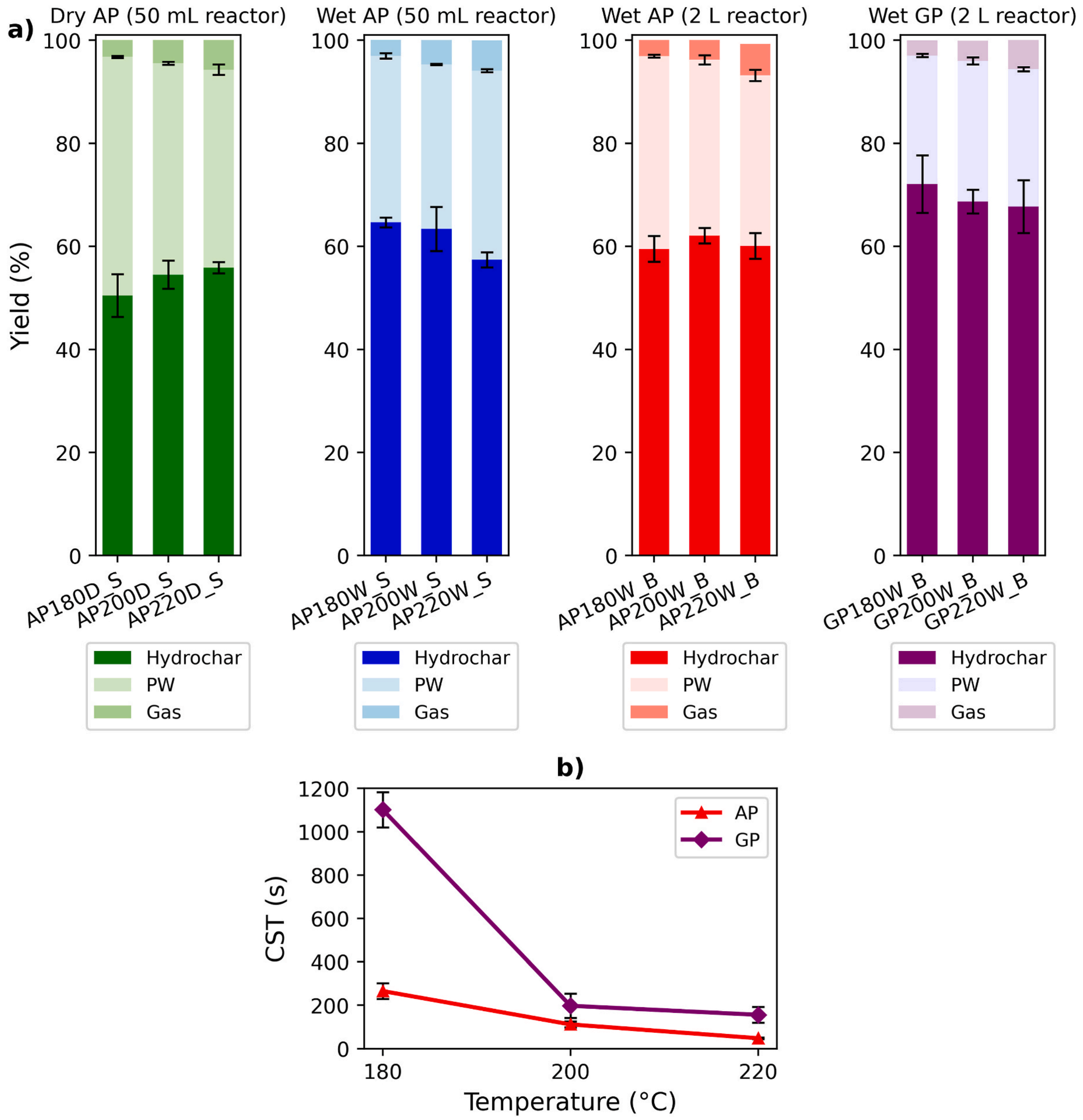

Fig. 3. a) Hydrochar, PW and gas yields (average of three repetitions ± standard deviation) for AP and GP. PW yield calculated by difference. b) Changes in the CST values with different temperatures (average of three repetitions ± standard deviation) for AP and GP.

Gas yields show a similar increasing trend with temperature in all cases, with no noticeable differences between AP (dry or wet) and GP. These trends are supported by p-values consistently below the significance level ($\alpha = 0.05$). In addition, ANOVA results did not reveal any significant influence of drying pre-treatment or reactor size on the gas production.

In the literature, several examples [30,31] can be found indicating that the increase in the severity of process conditions (such as higher temperature and longer residence times) enhances biomass conversion, resulting in lower solid and higher gas yields. Hydrolysis, decarboxylation and dehydration are just some of the reactions that progressively break down cellulose, hemicellulose and lignin as the temperature increases [8]. These biomass constituents are transformed into CO_2, which ends up in the gas phase, and soluble organics in the liquor. When the process water is rich in dissolved reactive compounds, the secondary char formation reaction may be favored, resulting in a subsequent increase in the solid yield [28].

Zhang et al. [23] suggest that the hydrochar yield also depends on the sugar content of the starting biomass, which could reach almost 40% in the case of AP and 30% for GP. During the HTC process, those sugars are released into the PW, mainly as glucose, but also as other monomers such as fructose and xylose, and sucrose. Ischia et al. [32] have demonstrated that HTC is already effective on glucose at 180 °C, leading to a significant formation of dissolved compounds in the liquid phase – such as 5-hydroxymethylfurfural (5-HMF), formic, levulinic or acetic acid – which, through polymerization, condensation and aromatization reactions, promotes the formation of secondary char, often observed in the form of spheres on the surface of the hydrochar. According to Zhang et al. [23], this phenomenon can increase or stabilize the solid yield at higher temperatures, especially where the initial sugar content is particularly high. An intensive gas production may also balance the hydrochar formation, potentially explaining the flat trends observed in some solid yield curves [32]. In addition, Inkoua et al. [33] report that the secondary char resulting from the polymerization of sugar-derived intermediates in the PW can also alter the structural properties of the material, making it more resistant towards cracking or gasification during a potential subsequent activation process.

The ANOVA analysis in this study also suggests that temperature and pre-treatment, as well as temperature and reactor size, may act synergistically, influencing hydrochar production. This finding aligns with previous research by Volpe et al. [24], who investigated the effects of HTC on pineapple, orange and tangerine peel waste, with or without drying pre-treatment, using 50 mL (not stirred) and 500 mL (stirred) batch reactors at different operating temperatures (180, 220 and 250 °C). In that study, HTC of the dried biomass in the smaller reactor resulted in an almost constant solid yield and a moderate increase in gas production with rising temperatures. In contrast, wet biomass showed a decreasing solid yield trend in the smaller reactor and a nearly constant one in the larger reactor, with increased gas production in both cases. In that case, the results suggest that the initial higher release of organics into PW from dried biomass may alter the degree of condensation and polymerization, affecting secondary char formation.

Altogether, these findings indicate that results obtained from HTC of dried samples may not be fully representative of sugar-rich agro-waste in real industrial-scale applications, since a pre-drying step is unlikely to be employed in practice.

3.3.2. *Improvement of dewaterability*

Materials with high moisture content, such as sewage sludges, are challenging to handle due to the additional difficulties encountered during their disposal or storage phases. Greater volumes, increased risk of fermentation and decomposition are just some of the possible problems. To solve these issues, dewatering and drying processes are often adopted, but their energy demand is often prohibitive. An improvement of the material's dewaterability may facilitate these operations.

After HTC treatments, the solid and the liquid phases are found in a mixture, often referred to as *slurry*. Since hydrochar is usually the desired product, it must be separated from the liquor. This operation is faster and more advantageous the higher the hydrochar's ability to separate from the PW.

In this study, dewaterability has been evaluated through the CST test. As it is shown in Fig. 3 (b), a great reduction in the CST value is visible for AP and especially GP between the HTC tests at 180 and 200 °C. This indicates that, after the hydrothermal treatment, the interstitial water held between the biomass particles by capillary forces is converted to free water, easier to remove [34].

This result creates a useful threshold for following HTC optimization experiments, guiding the choice of the target temperature to 200 °C.

3.4. *Hydrochar production by recycling PW*

Fig. 4 shows HTC product yields after several trials with PW recycling. For better comprehension, it is worth specifying that the values of AP200W_B and GP200W_B coincide with those reported in Fig. 3. Both AP and GP exhibited a general increase in hydrochar production with repeated PW recycling, in agreement with previous findings reported in the literature [14,15,17,35]. In the case of GP, this effect is more significant, starting with a solid yield of 68.7% for GP200W_B and reaching 81.5% for GP_R5, corresponding to an absolute increase of 12.8%. On the contrary, AP solid yield increased from 62.1% for AP200W_B to 68.9% for AP_R5, thus resulting in a difference of 6.8%. Besides that, neither feedstock experienced a constant growth in hydrochar production. The yield increases were more pronounced during the initial recirculation steps but could even become negative in the later stages. Gas production, instead, remains quite constant throughout all the recirculation steps, with no significant trends to highlight.

This phenomenon is a consequence of the increased reactivity of the liquid medium, a key variable in the carbonization mechanism during PW recirculation [16]. Indeed, the different chemical composition between tap water used in AP200W_B and GP200W_B and recirculated PW used to perform the R1-R5 experiments may influence the reaction pathways followed by biomass constituents during HTC. As already

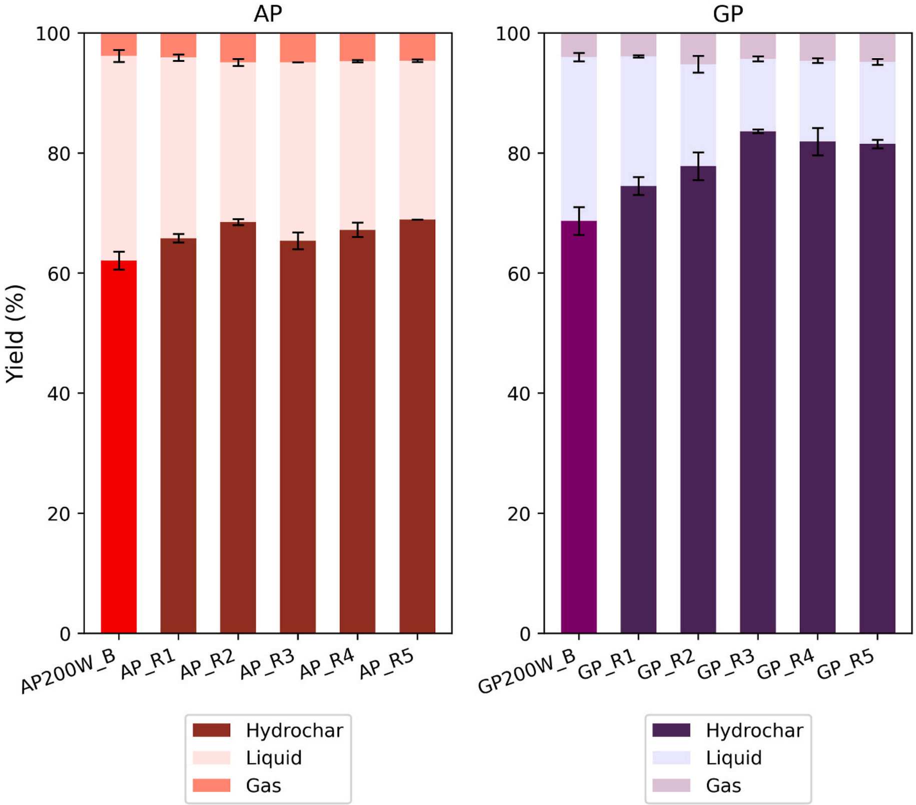

Fig. 4. Hydrochar, PW and gas yields (average of two repetitions ± standard deviation) for HTC tests with recirculation of PW for AP and GP. PW yield calculated by difference.

mentioned, HTC PW has been demonstrated to contain a wide range of soluble intermediates, including organic acids (formic, acetic and levulinic acids), glucose, fructose, 5-HMF, and furfural [36]. Even after a single recirculation step, these substances [37] can enhance not only the dehydration and degradation reactions of biomass, but also the condensation and polymerization of intermediates, leading to the formation of secondary char, in the form of carbon spheres deposited on the surface of the material, consequently increasing the solid yield [37]. In particular, the formation of such carbon spheres has been explained through different nucleation mechanisms, including the LaMer model, according to which the formation of spheres occurs when the concentration of aromatic clusters reaches the critical supersaturation point and subsequently spheres grow by molecular attachment [32]. Moreover, these secondary char particles themselves can act as potential polymerization cores [14], further promoting back-polymerization reactions.

As the number of recirculation steps increases, PW continues to be enriched in organic acids [15], until the concentration gradually stabilizes, eventually reaching a plateau, which results in milder variations in hydrochar yield [14,15,17]. At certain concentrations, these soluble intermediates may even inhibit the hydrolysis of raw materials [37], causing slight decreases in solid yield, as observed for AP_R3 (−3.2% compared to AP_R2) and GP_R4 (−1.7% compared to GP_R3).

3.5. Analytical characterization

3.5.1. Hydrochars composition

The changes in hydrochar composition were evaluated through elemental analysis. Looking at the results presented in Table 2, it is evident that HTC increases the carbon content (C%) in the solid phase. Temperature appears to influence carbon densification more than the recirculation of PW. For example, GP_RAW has a carbon content of 47.2%, which increases to 54.5% after HTC at 180 °C (GP180W_B), 57.8% at 200 °C (GP200W_B), and 60.1% at 220 °C (GP220W_B). Comparably, AP exhibits an increasing trend with temperature, whether in the smaller or the larger reactor. Starting from 49.9% in its original state (AP_RAW), the carbon content reaches 65.7% in AP220D_S, 66.3% in AP220W_S and 63.9% in AP220W_B, after HTC at 220 °C. Conversely, the recirculation of the liquor results in only minor fluctuations in C%. Concerning GP, values range between 56.8% (GP_R2) and 58.4% (GP_R5), while for AP, they vary between 60.1% (AP_R1) and 63.2% (AP_R4), without substantial variations across the recycling steps.

A similar trend is observed for oxygen content (O%), but in the opposite sense: higher temperatures lead to a greater oxygen loss, while liquor recirculation does not cause significant differences among the different recycling steps. HTC leads to a lower O% in the hydrochar compared to the original feedstock because of deoxygenation reactions [38]. Hydrogen (H%) and nitrogen (N%), conversely, remain relatively constant under all HTC conditions.

Finally, HTC also affects the ash percentage: although not following a clear trend, it consistently decreases after the treatment when compared to the raw materials. In the case of GP, slight increases in ash content are observed across the different recycling steps where the liquor was reused, even though the values remain below the raw material one. However, for AP, no clear trend can be established, as its ash fraction is so low that it makes precise quantification challenging.

It has already been proven in the literature [39] that more severe process conditions (higher process temperatures and longer residence times) typically result in greater oxygen loss and an increasing carbon content in the solid phase. The ash fraction reduction after HTC should be attributed to the aqueous phase leaching effect [16]. However, PW recycling may increase the concentration of inorganics in the liquid phase, resulting in a lower leaching efficiency from the starting biomass. Additionally, those dissolved inorganics in PW could be reabsorbed or precipitated on the hydrochar surface, increasing the ash content, as in the case of GP [16].

Table 2
Analytical characterization of the hydrochars by elemental analysis (mean of duplicates ± standard deviation, wt% dry basis) and atomic ratios. *Oxygen content obtained by difference. Standard deviations <0.1% and relevant to oxygen are not reported.

Sample ID		Elemental analysis				Ash	Atomic ratio	
		C	H	N	O*		H/C	O/C
AP	**AP_RAW**	49.9	8.2	0.9	39.4	1.6 ± 0.1	1.6	0.4
	AP180D_S	58.9 ± 0.5	7.6 ± 0.3	0.6	32.4	0.5 ± 0.1	1.5	0.4
	AP200D_S	64.1 ± 1.0	7.9 ± 0.6	0.7	27.3	<0.1	1.5	0.4
	AP220D_S	65.7 ± 0.5	7.5 ± 0.1	1.0	25.8	<0.1	1.5	0.3
	AP180W_S	58.5	7.9 ± 0.2	0.7	31.3	1.6 ± 0.2	1.4	0.3
	AP200W_S	62.6 ± 0.6	7.2 ± 0.1	0.8	29.1	0.5	1.4	0.3
	AP220W_S	66.3 ± 0.4	8.1 ± 0.1	0.6	25.0	0.9 ± 0.3	1.5	0.4
	AP180W_B	56.6 ± 0.6	7.6 ± 0.3	1.3	33.8	0.7	1.6	0.3
	AP200W_B	62.2 ± 0.6	8.2 ± 0.3	1.2 ± 0.1	28.4	0.1	1.6	0.3
	AP220W_B	63.9 ± 0.2	8.0 ± 0.1	1.2	26.6	0.2 ± 0.2	1.5	0.3
	AP_R1	62.4 ± 0.2	8.4	1.0	27.4	0.7 ± 0.3	1.5	0.4
	AP_R2	60.1 ± 0.8	7.8 ± 0.2	1.3	30.2	0.5 ± 0.1	1.5	0.3
	AP_R3	62.7	8.1	1.2	27.2	1.0 ± 0.5	1.5	0.3
	AP_R4	63.2 ± 0.3	8.2 ± 0.1	1.1	27.0	0.5	1.4	0.4
	AP_R5	61.4 ± 0.2	7.3 ± 0.5	1.3	29.7	0.2	1.4	0.4
GP	**GP_RAW**	47.2 ± 0.1	6.8 ± 0.3	2.0 ± 0.1	35.2	8.8 ± 0.3	1.7	0.6
	GP180W_B	54.5 ± 0.3	7.1	2.3	32.8	3.3 ± 0.1	1.5	0.5
	GP200W_B	57.8 ± 0.1	7.1 ± 0.1	1.9	29.7	3.6	1.5	0.4
	GP220W_B	60.1 ± 0.2	7.2 ± 0.1	1.6	27.7	3.3 ± 0.6	1.4	0.3
	GP_R1	57.3 ± 0.1	7.2	2.1	29.6	3.8 ± 0.2	1.5	0.4
	GP_R2	56.8 ± 0.1	6.9	2.1	29.9	4.3 ± 0.2	1.5	0.4
	GP_R3	57.3 ± 0.1	7.0	2.0	29.5	4.2	1.4	0.4
	GP_R4	57.1	7.0	1.9	29.4	4.5	1.5	0.4
	GP_R5	58.4 ± 0.2	6.6 ± 0.1	2.4 ± 0.1	28.6	4.0 ± 0.2	1.3	0.4

Existing research presents different results regarding the effect of process water recirculation on the composition of hydrochar. The different outcomes could be attributed to the variations in the initial feedstocks' compositions or to the conditions (temperature, residence time, biomass to water ratio, percentage of liquor recycled, …) adopted in the HTC process.

For instance, Catalkopru et al. [40] investigated the effects of HTC with PW recirculation (225 °C, 10–30 min) on grape pomace, orange pomace and poultry litter, observing that H/C and O/C ratios are not substantially affected by recirculation of HTC liquor, which aligns with our results. Conversely, Ipiales et al. [15] used garden and park waste as initial feedstock for HTC with PW recirculation (180 °C, 1 h), reporting that the recycling of process water promotes the biomass deoxygenation, dehydration and decarboxylation.

As a whole, these characterizations confirm that AP and GP behave as other common biomasses in HTC, yielding a hydrochar with enhanced composition and dewaterability. Identifying the most adequate further treatment and application of this hydrochar (agricultural amendment, pollutant adsorbent, fuel, electrochemical material) requires more advanced analytical techniques. Since the aim of this study is to optimize the HTC process, regardless of the hydrochar final application, this aspect will be dealt with in a future work.

3.5.2. Liquor characterization

The characteristics of the liquors, in terms of pH and TOC, are presented in Fig. 5. Both parameters were also measured for water put in contact with the dry and wet raw materials. These samples were placed in tap water at room temperature for 1 h, using the same B/W ratio used for HTC tests. After filtration, the obtained liquid was analyzed with the same procedure adopted for PWs.

All the samples exhibit an acidic pH, particularly after the HTC treatment. A slight increase with temperature is observed in the tests conducted in the larger reactor. In particular, the PW samples from AP220W_B and GP220W_B show a less acidic pH. For GP, after the first recirculation step, a slight rise in pH can be seen, which then remains nearly constant throughout the subsequent recycling steps.

Meanwhile, TOC values present several differences among the different treatments. Looking at raw material samples, wet AP and GP obtained higher TOC values than their respective dry counterparts. Moreover, AP_RAW (wet) reached a value of 9.6 g/L, which almost doubles that of GP_RAW (wet). Temperature also affects TOC concentrations. Indeed, higher temperatures result in lower TOC values because of the promotion of carbon densification and recondensation in the hydrochar [41], limiting the amount of carbon present in the liquid. The effect is marginally more evident for AP, with no big differences in the trend between the dry and the wet samples. In addition, the TOC of the liquors generally increases with recirculation, with a smaller growth as we proceed with recycle steps. The recirculation indeed rises the concentration of soluble organics in the liquid phase. The slower growth after several recycling steps may be due to the reaching of a sort of steady state condition, considering the reactive character of the HTC liquid phase rich in chemicals. Roughly speaking, as many organic compounds enter the liquid phase (through hydrolysis reactions and dissolution of the feedstock) as exit it (through reactions that lead to the formation of secondary char). Similar results can be found in the literature [17,40].

3.5.3. Carbon balances

Considering the data presented in the previous paragraphs, it was possible to evaluate the carbon balances of the process (see also Supplementary material). The results are presented in Fig. 6. The greatest carbon fraction is always the solid one, followed by the liquid and lastly the gas, coherently with the relative yields. A modest increase in the carbon content of the liquid fraction after PW recirculation is evident compared to the tests performed using only tap water.

It is important to point out that all the balances are associated with a

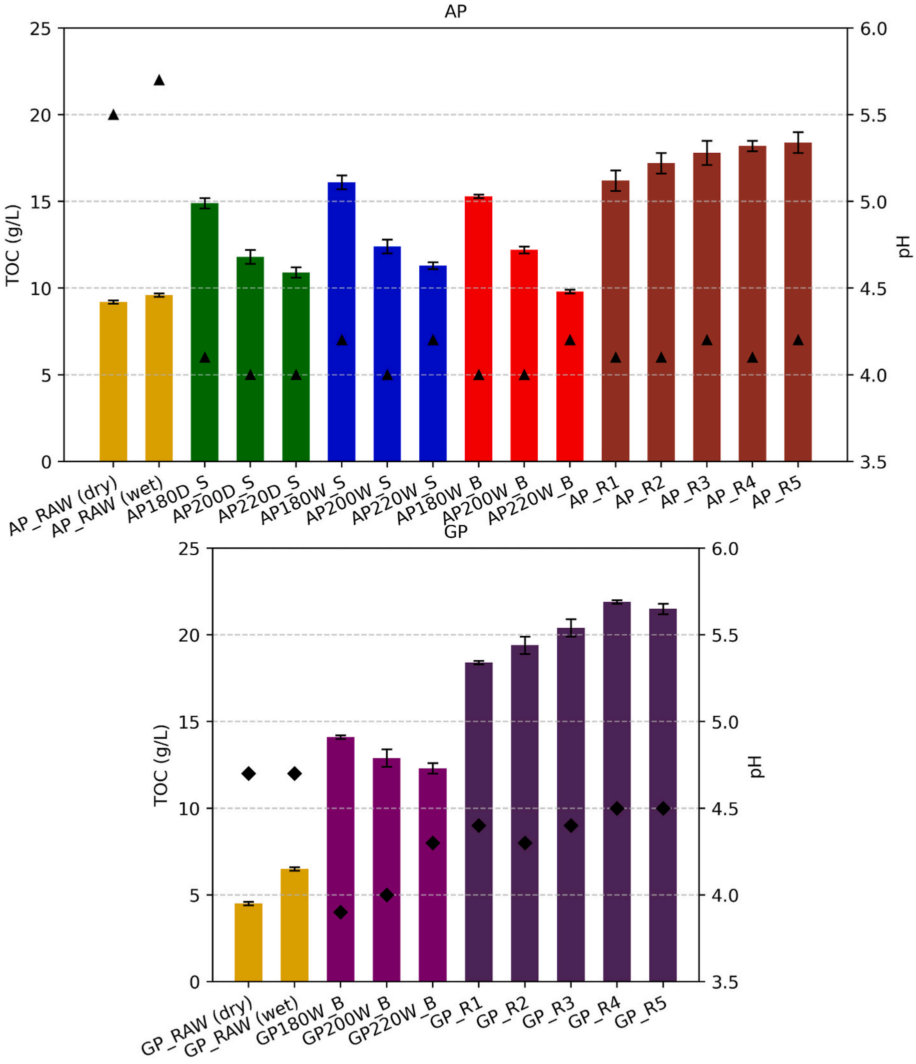

Fig. 5. TOC (bar chart, average of three repetitions ± standard deviation) and pH (scatter plot) values for AP and GP liquors.

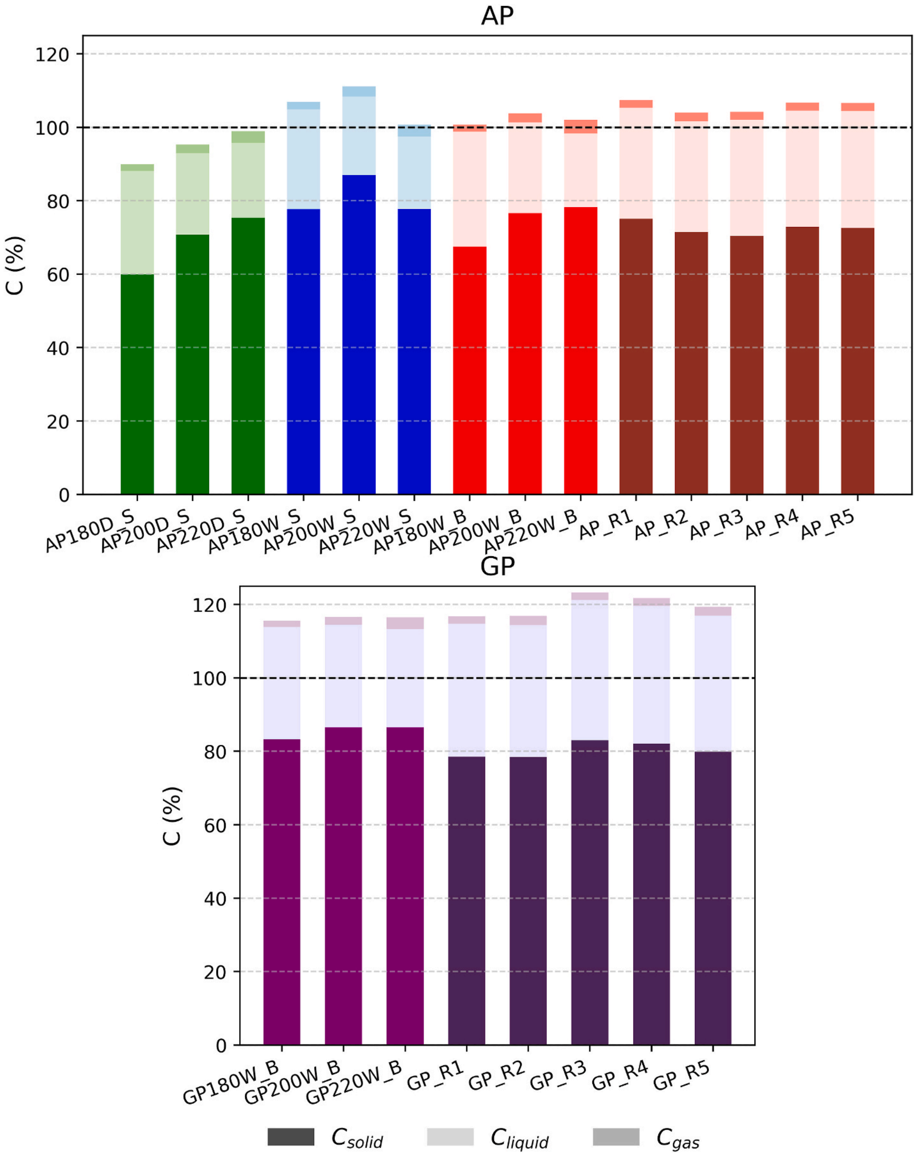

Fig. 6. Carbon balances for AP and GP materials - Carbon mass percentage (C, wt%), with respect to the carbon initially present in AP and GP.

total percentage error (TOT_{error}) between 10 and 20% (see Fig. 6). Among the several possible explanations for this inaccuracy, the overestimation of the liquid volume seems to be the one with the biggest impact. Hydrochar and gas mass fractions are directly measured. The PW, instead, is separated from the solid fraction through filtration of the HTC slurry (followed by drying of the wet solid), and its mass is always evaluated by difference, leading to a less accurate value. Due to the adopted experimental procedure (which mimics industrial applications without any water washing of the solid phase recovered after filtration), the heavier molecules present in the liquid phase that wets the solid after filtration are already “counted” in the solid phase, hence the overestimation of the PW mentioned above. Other causes of inaccuracies could be some approximations in the calculation of carbon percentage in the solid phase and the heterogeneity of the materials.

3.6. *Anaerobic digestion*

The HTC process produces a gas and a slurry phase, which consists of hydrochar particles and the carbon-rich liquor, here referred to as PW. The gas is mostly CO_2 and can be discarded or captured [42]. The solid is the desired product, leaving the liquid as the main by-product to be managed. As shown in the previous sub-sections, recirculating it to the reactor is a valid strategy. It simultaneously reduces the need for fresh water and increases the hydrochar yield. If full or partial recirculation of the liquor is not possible, other possibilities exist. Among these, extracting chemicals or synthesizing more advanced products are potentially interesting, but less established. Anaerobic digestion (AD) thus remains the most proven option.

The effectiveness of AD depends on the starting feedstock and the HTC operating conditions. If HTC is used as a pre-treatment, conditions can be chosen *ad hoc* to maximize biogas production rates and yields [43]. Conversely, if the process is tailored for optimal hydrochar yield and properties, AD may become more difficult and should be evaluated. The question is even more open if the liquor undergoes recirculation [44]. Recirculation is indeed known to increase the liquor acidity and concentration of organic compounds, possibly making it more toxic to microorganisms. To evaluate this effect, we tested the liquors obtained from the HTC of GP and AP at 200 °C. We tested both the liquor obtained after a single HTC run and the liquor obtained after five recirculation cycles. As far as we are aware, no similar comparison has been reported in the literature.

Fig. 7 reports the results of the BMP tests, expressed in terms of the

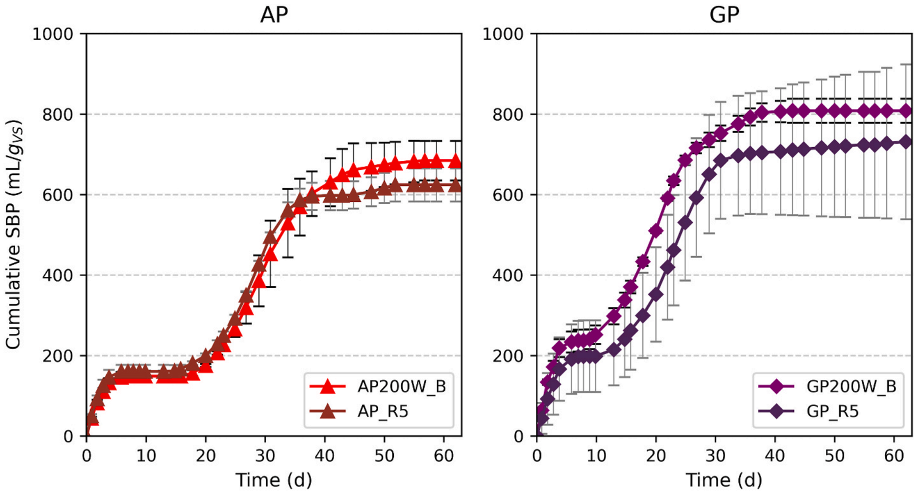

Fig. 7. Cumulative SBP from the HTC liquor obtained from AP and GP.

cumulative specific biogas production (SBP). The trends are rather similar for the two feedstocks, so the following comments apply generally. The biogas production is significant, reaching yields of 600–800 mL per gram of VS in the liquor. These values are comparable to or even higher than those obtained for the OFMSW processed in the full-scale digester from which the inoculum was collected (see Table 3). This suggests that these liquors could be co-treated in AD plants processing food waste with no negative impacts on the process. Justifying these results is challenging without detailed chemical analyses. However, the homogeneity and high concentrations of sugars and organic acids of the liquors likely play a role. OFMSW is much more heterogeneous and may contain toxic or recalcitrant compounds. The higher biogas production of the GP liquor is also difficult to explain without knowing its composition.

All the tested substrates follow a similar production pattern. The first production peak occurs within 5 days, followed by a 7–10 day lag phase. A second production peak then lasts for another 15–20 days. Although BMP tests are not always representative of the behavior of real plants, these time frames align with the typical residence times of industrial anaerobic digesters. They could also get gradually shortened if the bacterial community becomes more accustomed to the HTC liquors. Notably, there seems to be no significant difference in the biogas production from the liquors with or without recirculation. Despite the lower pH and higher concentration of dissolved compounds, the recirculation does not seem to cause any further increase in the toxicity of the liquor. As a result, its treatability through AD remains unaffected.

Table 3 summarizes the BMP test results, including biogas and biomethane production, the total volatile solids (TVS) content before and after digestion, and the final VFA/alk ratio and pH. The table also includes the results from the blank test (inoculum alone) and the control test (the OFMSW usually treated in the plant). The results are very positive and, for all parameters, in line with the control. Biogas yields are comparable to or higher than those of the control, with the volume fraction of methane around 50%. TVS reduction is between 32.4 and 37.1%, just slightly lower than the control (but the initial TVS of OFMSW is much higher). The final two reported parameters also confirm the efficacy of the treatment: the VFA/alk ratio is between 0.13 and 0.20, indicating that the organic acids have been efficiently removed, while the pH is always markedly basic. This indicates that the strong acidity of the HTC liquors is not detrimental to the process in the tested conditions. In real plant settings, liquor feeding rate would be even lower, further reducing any potential risks.

4. Conclusions

Agro-industrial pomaces, AP and GP, have been valorized through HTC to produce hydrochar, with a focus on recycling the PW and exploring its AD, in line with circular economy principles.

The high sugar content of AP and GP promotes secondary char formation during HTC, affecting hydrochar yield and properties. This behavior is influenced by drying pretreatment, indicating that small-scale tests on dried biomass may not reflect realistic industrial conditions and performances. Secondary char formation can also be promoted by the recirculation of the PW to the reactor, which increases the solid yield after five recycling steps. This trend correlates with the rise in TOC during recycling, confirming the role of soluble organics and organic acids in driving condensation and polymerization reactions. No negative effects on PW AD were observed, even after five recirculation steps, leading to high biogas yields (600–800 mL/g_{VS}), with around 50% CH_4 production and stable process parameters.

CRediT authorship contribution statement

Alice Zanoni: Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Filippo Marchelli:** Writing – review & editing, Validation, Supervision, Methodology,

Table 3
Biogas production and properties of the substrates before and after the BMP tests.

	Final SBP (mL/g_{SV})	Final CH_4 volume fraction (%)	TVS (%)				VFA/alk post BMP	pH post BMP
			Post HTC	With inoculum[a]	Post BMP	Reduction		
Inoculum	15 ± 10	33 ± 16	2.4 ± 0.1		1.98 ± 0.02	17.9%	0.11	9.22
AP200W_B	685 ± 49	49 ± 1	2.32 ± 0.07	2.38	1.61 ± 0.02	32.4%	0.20	9.53
AP_R5	624 ± 41	46 ± 1	2.69 ± 0.12	2.50	1.69 ± 0.01	32.4%	0.13	9.53
GP200W_B	808 ± 27	47 ± 2	1.52 ± 0.04	2.02	1.27 ± 0.01	37.1%	0.16	9.62
GP_R5	730 ± 190	57 ± 5	2.33 ± 0.07	2.38	1.61 ± 0.02	32.4%	0.17	9.67
OFMSW	601 ± 41	52 ± 3	14.53 ± 0.19	3.34	2.06 ± 0.02	38.4%	0.12	8.96

[a] Calculated.

Investigation, Data curation, Conceptualization. **Beatriz Ledesma:** Writing – review & editing. **Silvia Román:** Writing – review & editing, Conceptualization. **Luca Fiori:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biombioe.2026.109056.

Data availability

Data will be made available on request.

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