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Review

Research Needs and Pathways to Advance Hydrothermal Carbonization Technology

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Abstract: Hydrothermal carbonization (HTC) is a proven cost-effective and energy-efficient method for waste management and value-added product recovery. There are, however, several issues that require further improvement or research. Identifying the strengths and weaknesses of HTC in comparison to traditional pyrolysis is crucial for scientists to choose between them or use both (complementary) to achieve specific product properties. Additionally, sharing information on diverse modeling approaches and scales is crucial to enhance the robustness and universality of HTC process models. In addition, the study on the applicability of hydrochars on target applications such as soil amendment is crucial to give back nutrients to soils and face the dependence on finite specific feedstocks in this field. Also, proper management of the process by-products, especially process water, must be addressed to improve the carbon and hydric footprint of the process. Reviewing the suitability of HTC to treat specific challenging wastes, whose strength is not related to their calorific value but to their nutrient composition (i.e., manures), is also an appealing topic for HTC research. This paper aims to tackle the above-mentioned issues through an updated review and discussion of research gaps that require further investigation.

Keywords: hydrothermal; process water; HC applied to soil; HTC modelling; strategic feedstock; manure; lignocellulosic biomass

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1. Introduction

Since the first works reviving hydrothermal carbonization (HTC) as a low cost efficient process to densify the C content of residual biomass were published during the first years of the 21st century [1], a wide body of literature has been devoted to contribute to the knowledge on this technology.

HTC is a thermochemical process that can sustainably convert organic waste into added-value products, under self-generated pressure provided because of the tightness of

the system, at mild temperatures (180–350 °C). Wet or colloidal biomasses are ideal for HTC, since feedstock water behaves as a reactant (also a product) for the process; here lies one great advantage of this treatment, which allows a broadening of the input material options.

Water under subcritical conditions exhibits solvating properties, and in this way, it can hydrolyze the aliphatic cleavages of cellulose molecules, the first step in a complex interplay of processes (depolymerization, condensation, and recombination of products) that are catalyzed by the high amount of H+ ions produced and that have been described in detail for lignocellulosic biomass [2]. The reaction pathways are diverse and can be altered by the following operating conditions: temperature, time, biomass to water load (w/w) [3], system thermodynamic condition (vapor, compressed liquid or mixture) [4], and presence of acids or bases or other catalysts [5,6].

The distribution of phases (gas, liquid, and solid phases) and their properties are also defined by reaction conditions. In general, the solid product, known as hydrochar (HC), has a moderate C content, greater than that of the original feedstock, and can serve as fuel, or cover environmental applications such as soil remediation, adsorption, and catalysis.

Regarding process water (PW), the interest in extracting top chemical compounds from the process water has increasingly driven attention to this phase in recent years. There is a growing market for substances like furfural, 5-Hydroxymethyl furfural, Levulinic Acid, Humic Acids, or nutrients (like Phosphorus), all of them extractable products from HTC PW [6,7]. However, PW also contains some potentially toxic compounds such as furanic aromatics and phenols [8].

Even though the potential of HTC is undeniable, several challenging issues have not been fully addressed. These issues go from the use of strategic feedstocks, limitations of the factors, specific applications of the products, proper management of PW, and efficient methods for extracting valuable products, to the development of accurate models describing the correlation between the process or product properties, or knowledge on the fundamentals of the process including reactions, features of primary and secondary HCs, etc.

This work originates from the activities carried out during the workshop "Innovative Hydrothermal Systems to Valorize Agricultural Residuals: Roadmap Towards Implementation—Achievements and Barriers". This event, which was sponsored by the OCDE, took place in Seoul (South Korea) in May, 2023. The authors have identified the key points of this paper as the main challenging factors in the research field of HTC. These points are based on the survey conducted during the workshop, focusing on current knowledge gaps that need to be addressed and challenges that must be overcome before advancing towards the commercialization of the technology. More detailed information is provided in Figure S1, found in the Supplementary Materials. Subsequently, the key factors were elaborated further through bibliographic research on scientific databases.

In particular, this review covers the following aspects:

Section 2: HTC and pyrolysis have so many common features, with both methods involving treating a material to improve its C proportion and/or extract high-value chemicals in a liquid phase. Therefore, this chapter has been devoted to describing the similarities and differences between the two processes, their strengths and weaknesses, and the challenges they face today.

Section 3: The main modeling tools on HTC are described, and what needs to be done to advance the various techniques is highlighted.

Section 4: There is increasing interest in the use of hydrochars applied as soil amendment. This chapter reviews the literature studying the effectiveness of HCs as fertilizers, focusing on the properties that make them potentially phytotoxic, and pointing out significant issues regarding their ageing or emissions, as compared to biochar.

Section 5: A summary of the current understanding concerning process water management and valorization is made, emphasizing the main accomplishments and challenges faced to date.

Section 6: An update regarding the knowledge on the use of feedstocks that are especially interesting for HTC, such as plant biomass and manures.

2. HTC vs. Pyrolysis: Hydrochars vs. Pyrochars

One factor hampering the massive spreading of HTC technology can be its apparent competition with traditional pyrolysis. A bibliographic search of both processes using the keywords "pyrolysis" and "hydrothermal carbonization" on the Web of Science in the time period 2013–2023 gives, respectively, a total of 6839 and 736 citations (25 September 2023, only research and review papers considered). The combined use of both concepts gives a total of 466 references; of them, only a few really compare both processes regarding a given feedstock or make an analysis about the convenience of using one of them separately or using them together, complementarily (Figure 1).

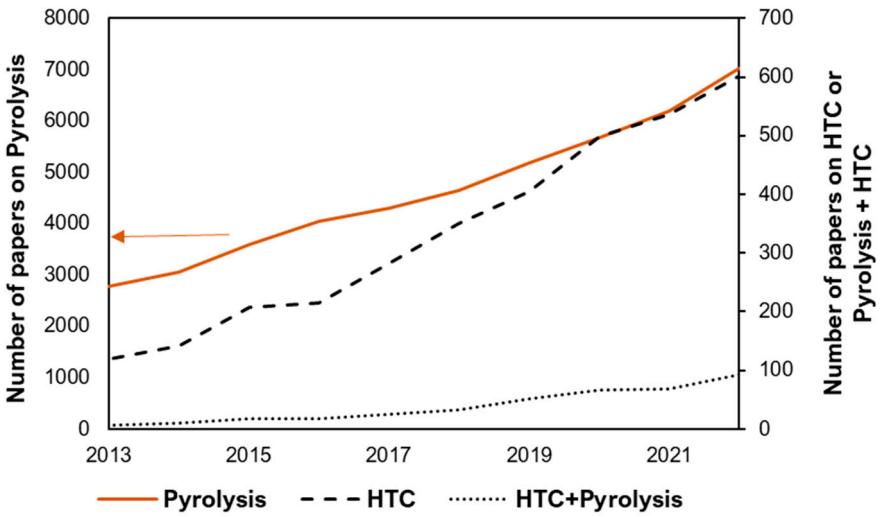

Figure 1. Number of yearly published articles on HTC, pyrolysis, or both according to the Scopus database as of 18 August 2023. Orange curve reads on the left vertical axis. Discontinuous curves read on the right one.

Products obtained from pyrolysis and HTC are formed under different reaction mechanisms, although there are many similarities between the two processes, which share the characteristic of being techniques that yield a char as a solid product [9–11]. Understanding the reactions associated with each of them is essential in order to choose the appropriate one depending on the feedstock characteristics, the power and source requirements, and the product-targeted properties for specific applications.

Pyrolysis is a widely used approach to produce a char (frequently named pyrochar to distinguish it from chars obtained by other methods), which allows the thermochemical conversion of low moisture-containing biomass under an oxygen-limited atmosphere, in a high temperature range (350–700 °C) and generally at atmospheric pressure [12]. While some authors refer to torrefaction and pyrolysis indistinctly when mild temperatures are used (both take place under an inert atmosphere), the first concept is generally used when the inert treatment is made at temperatures lower than 350 °C [13,14], even though the literature offers a flexible temperature range to stablish the boundary of both processes. Apart from the solid carbon product, non-condensable gases (and this involves a significant contribution for biomass) and condensable liquid (pyrolysis oil) are produced; the properties and distribution of phases for a given feedstock depends on operating parameters: temperature (mainly), pressure (if applied), residence time, particle size, and feeding of other non-inert gases [12]. The rate of heat transfer also significantly affects the distribution of phases, in such a way that fast, intermediate, and slow pyrolysis are differentiated. Normally, slow heating rates (10–30 °C/min) are used if the solid product (the char) is the target product to be obtained, since these heating conditions favor solid yield and C fixation [10]. This process, called slow pyrolysis, will be the one we will refer to in this review.

When biomass is the feedstock used to produce the char, then the solid product obtained by pyrolysis is usually referred to as biochar (although biochar could also be valid for a carbon material obtained by HTC). However, according to IUPAC [15] and the IBI [16], this name is preferably ascribed when the application aimed for the biochar is as soil amendment substrate to improve crop productivity. Also, in general, the term charcoal is used if the char is to be used as fuel.

2.1. Similarities and Differences between Both Processes

In pyrolysis and HTC, the degradation of the feedstock occurs mainly through the removal of volatile compounds by depolymerization of the feedstock. In both processes, reactions like decarboxylation, dehydration, decarbolynation, demethanation, intermolecular derangement, aromatization, or condensation take place [12]. This results in a gradual carbonization of the material at the expense of the removal of a high gas fraction (and characterized by a wide amount of compounds) in the case of pyrolysis and a small gas fraction (<5% and mainly composed of CO_2) in the case of HTC.

Researchers agree that the solid product obtained by pyrolysis and HTC exhibits a greater C content, more accessible porosity and greater grindability as compared to the feedstock [2–5,9,10]. In the case of HTC, its surface chemistry also makes it more pelletizable [17].

Both pyrolysis and HTC involve the production of a liquid product that can have highly valuable compounds. In the case of pyrolysis, this liquid is the result of condensation of high-molecular-weight degradation compounds and is often referred to as bio-oil or tar. In HTC, rather than a product, the PW that is obtained after filtrating the slurry is a consequence of the solvation of extractives in the water used as a reactant or produced during feedstock dehydration, and the dissolution of monomers from biomass polymers, acids, and diverse organic and inorganic compounds. In any of the processes, the phase distribution and their composition are affected by temperature (this being the most important influencing property), time, heating ramp, or particle size.

Most of the studies are consistent on the fact that high operating temperatures involve lower solid yield (SY) in both processes and enhanced C and energy densification [9–11]. Also, using longer times on HTC has a slight positive effect on solid yield, while this trend is not found in pyrolysis, unless an additional gas (like CO_2) is fed to the system.

Regarding the influence of the input material particle size, although the effect depends very much on the range considered, a smaller particle size in general involves faster kinetics and lower SY in the case of both processes. For pyrolysis, a greater diameter has been associated with a greater C capture [18]. Using a slower heating ramp has been shown to influence the phase distribution during pyrolysis (increasing the SY) and also favor C capture. This effect has been studied very scantily for HTC, and the few works on it show controversial results.

Finally, the influence of other parameters, like pressure, have been scantly addressed. Newalkar et al. (2014) [19] reported that increasing pressure in loblolly pine pyrolysis involved remarkable modifications on the pyrochar: it had a clear effect on the elemental composition (rising C proportion), and improved the material apparent surface, although a slight porosity widening was also observed. Pressure effect has been rarely investigated for HTC, since in general, these processes are made in tight autoclaves that guarantee thermodynamic autogenous pressure. However, in this aspect, it must be highlighted that the reactor void volume plays a role that should not be ignored (and is usually omitted). The void volume (or the volume of space that remains unoccupied after it has been filled with water and biomass) will determine the real thermodynamical state of the HTC mixture under processing conditions. In other words, the reactor void volume determines the specific volume of the system water+biomass, and hence its quality or title value (if it is under compressed liquid, superheated vapor, or mixture). For this reason, rather than the pressure, this is the parameter that should be studied, not only because it affects the HTC degradation extent, but also for safety reasons. Álvarez-Murillo et al. (2022) [4]

demonstrated this effect and developed a model in which they demonstrated how HTC kinetics are related to operating pressure.

In reference to the energy densification provided by the two processes, it occurs in both cases via decarboxylation (removal of O and increase in C proportion), although reaction conditions (especially temperature) influence its intensity. For pyrolysis, greater T causes a significant increase in HHV, whereas for HTC, although T is also the major factor, effects of other parameters have to be considered. For example, some compounds in process water (PW) are adsorbed on the HC (and this depends not only on T, but also on water acidity, biomass load, and time) influence its HHV; this is the case of compounds such as 5-HMF, whose energetic value is greater than the biomass composing the main molecules [20].

2.2. Surface Properties

One of the main differences between the carbon materials obtained by pyrolysis and HTC is their pore volume availability as well as their pore size distribution, and also their surface functional groups. These facts have been largely reported in the bibliography [10,21]. On the basis that the precursor and the processing variables will influence the final properties of the char, in general, HTC yields carbon materials with a very poor porosity (S_{BET} around 25 m^2/g) and which are, in general, mesoporous in nature; processing variables (temperature, time, and biomass to water load) does not seem to have a very significant influence on it [22]. The adsorption of degradation compounds from PW and/or their deposition on the HC surface blocks microporosity, and the pore volume is low and exhibits very slight changes at different times and under temperature conditions of the carbonization process. It is well known that the highly reactive degradation molecules at the liquid phase can combine, polymerize, and yield macromolecules that can deposit on the HC surface, contributing to SY, usually in the form of microspheres (secondary char) that grow in size and amount with residence time [23]. The knowledge on how this secondary HC is formed, as well as its properties and potential extraction, is today a hot topic of research because of the influence it can have on HC use, as it is in the case of soil applications, which will be addressed in Section 4.

In contrast, during pyrolysis, no secondary char is produced (pyrochar), since the degradation compounds do not remain at the solid interface but are dragged away with the carrier inert gas (only a small fraction of them condense as tars during the cooling period). In consequence, pyrolysis gives a cleaner surface, microporous material with apparent surface values ranging within a wide interval (50–400 m^2/g), mostly depending on feedstock and processing time and especially temperature (which has a relevant influence on both total pore volume and pore size distribution, in contrast to HTC). The removal of surface oxygen groups upon pyrolysis make BCs more resistant to degradation and microbial deposition, and more basic than HCs, although ageing can alter BC reactivity [11].

Another important aspect is surface chemistry. HCs have a variable degree of surface aromatic compounds depending on HTC conditions, and in general have a remarkable amount of oxygen containing groups. Some authors have investigated in depth the chemical features of the surface microspheres, and have reported that the core of the microspheres is hydrophobic, while the shell is hydrophilic [24]. In contrast, mostly due to the use of greater temperatures, pyrochars have a more ordered turbostratic structure, a greater aromatization degree, and a small amount of oxygen surface groups. In addition, in both cases, biochar and HC textural and chemical properties can be improved by subsequent physical and/or chemical activation processes to yield activated carbons (ACs).

A body of literature has focused on the comparative study of the adsorption performance of biochar and HC-derived ACs, including physiochemical properties and sorption possible mechanisms based on the type of adsorbent [25]. Although even after activation the pore volume availability in ACs from HTC is generally lower than in BCs, the acidic point of zero charge of HCs is beneficial for some adsorption processes in which non-dispersive and electrostatic interactions are preferred, as it is in the case of polar molecules

and cations [26]. In addition, the possibility of easily adding specific features to the HTC system makes this option very attractive, for example, to induce magnetism on the carbon.

2.3. Carbon Capture

Carbon capture should not be confused with carbon densification, and this is why both concepts have been included in different sections. Firstly, carbon densification is associated with the increase in the carbon proportion (%) that is found after the carbonization process, so it is appreciated when one compares the C (%) of the feedstock and that of the solid product. It is based on the rise in C (mostly at the expense of O removal), independently of the solid yield. Secondly, carbon capture does take the solid yield into account because it represents the ratio at which the amount of C of the feedstock readily remains in the solid product. It is usually calculated as:

$$C_{capture}(\%) = \frac{C(\%) \text{ in hydrochar or pyrochar}}{C(\%) \text{ in feedstock}} \cdot (100) \quad (1)$$

As previously described, pyrolysis can provide a greater rise in C (and high heating value (HHV)) on the char (in reference to the feedstock) than HTC. Devolatilization is greater upon pyrolysis, and it yields a large amount of gas products (mainly CO_2 and CO, and also traces of CH_4, C_2H_2, C_2H_6, and others) and tars composed of condensable hydrocarbon compounds, in a way that the net ratio of C/O removed is lower than in HTC [12].

However, if the focus is put on the amount of C that is retained on the char after the degradation in reference to the amount of C that the feedstock had (that is, the parameter C capture), then HTC offers a much advantageous result which can be further improved if the C extracted to the PW is added. In this context, biomass HTC can be seen as an effective way of recovering C from the atmosphere (the one grabbed by the plant via photosynthesis) in the form of HC and liquid, which led some authors call it "C capture" process, a global warming mitigation option. However, the persistence of C storage on HCs depends on its application [27], and will be further discussed in Section 4, where its degradability in soil is discussed and compared to biochar.

Very few works have been conducted using the same feedstock to compare the effect of pyrolysis and HTC and obtain the same SY to really infer differences in relation to C capture. The studies of Fuertes et al. (2010) [11], using the same corn stover, demonstrated that if HTC was made at 250 °C for 4 h and pyrolysis was performed at 350 °C (only heating and cooling steps), similar SY values (36% for HC and 35% for the BC) are obtained. From the elemental analyses of these materials, they obtained a slightly bigger C capture for the HC (67.8%) than for the biochar (64.5%).

2.4. Waste Disposal

Whereas both pyrolysis and HTC give products in the three states of matter, HTC gives a slurry that has to be filtered to recover the HC, while Pyro gives a dried char. That means HTC requires additional post-drying steps (although it does not use pre-drying, whereas pyrolysis does). Only by mechanical drying can 50% of the slurry water be removed, while the remaining would require thermal drying.

Process water management is one of the most important issues for HTC and will be further addressed in Section 5. In reference to the gas production, the bibliography agrees that it is below 5% w/w [17]. This is referred to as the initial feedstock mass, and it is mainly composed of CO_2, with the presence of CH_4 and H_2; on a continuous operation, this gas does not exit the reactor, but participates in the process providing additional gasification reactions. Also, the gas does not contain particulate matter. Opening the reactor after operation, however, would probably require the management of the HTC gas.

In the case of pyrolysis, the gas effluent accounts for a very significant share of the products (depending on the feedstock and operating conditions, the gas yield can be as high as 75%). Although this gas could be used for self-heating the reactor, it has to be

treated before being discharged to the environment because of its toxicity: compounds such as NOx, Cl, aromatics, dioxins, and particulate matter can be released in a different extent depending on feedstock properties and operating conditions [28]. This involves the use of costly gas cleaning strategies, such as particulate filtering, absorption, and adsorption processes. Feeding the exhaust gas to the reactor has the advantage of decreasing the volume of gas emitted, recovering heat, and also improving the porosity of the biochar by inducing activating effects (at certain temperatures, CO_2, CO, and other compounds can selectively oxidize the compounds blocking porosity).

2.5. Other Aspects

2.5.1. Potential Ash Tunning

An outstanding advantage of HTC as compared to pyrolysis is the ability of the former to modify the content and composition of the precursor ash, something that cannot be achieved by pyrolysis. This is especially important if the char is to be used as a fuel, for which a low ash quantity and specific ash composition is determinant on the behavior of a feedstock as a fuel; ash causes undesirable behaviors during combustion in a boiler, such as slagging, fouling, clinker formation, or corrosion.

In the case of pyrolysis, since a massive removal of volatile is produced and ash has no possible way to be eliminated during the process, the ash content of the char is always higher than that of the starting material, and the effect is more intense at higher temperatures [29]. Dissimilarly, in the case of HTC, the choice of processing conditions provides a spectrum of HCs with different ash properties. Subcritical water together with the acids that are produced in the first steps of HTC (such as acetic acid) help the solubilization of a part of the feedstock mineral composition. Leaching out and recovering of these elements in the PW for a given starting material is affected by several factors (mainly temperature and system acidity, but also time) [30]. In this way, greater temperature helps the extraction of minerals by facilitating bond cleavage, but also helps their precipitation as salts on the HC surface so that the net effect of this property has been reported as positive. The factor of longer times is also associated with an ash increase on the HC leading to enhanced adsorption.

Acid HTC processes have been proven to improve ash content on the HC as compared to non-catalyzed runs. Many studies have shown that acids such as HCl or HNO_3 can help in the leaching of specific ash components such as P, Mg, Ca, or Mn, and their recovery in the liquid phase has been achieved using different methods [31]. Benavente et al. (2021) [32] used HTC not only to reduce the ash content of biomass or extraction of specific elements, but also to tune up its composition by adding specific elements to the HC which, definitely, enhanced the control on the target ash properties (such as the melting point) [32].

2.5.2. Fate of Nitrogen

The N content of a feedstock can be seen as an advantage or a downside, depending on the application that is considered. If the HC is to be used as fuel, then a low N amount is preferred to avoid the formation of NOx, since the release of these compounds during oxidation is positively related to the N biomass proportion. In these cases, it is therefore advisable to provide the HTC reaction conditions that enhance the transference of N-containing compounds into the aqueous solution.

The N content of feedstock is not a sufficient predictor to devise the formation of NOx compounds; it has been reported that their emission upon oxidation of biomass and chars is influenced by the composition of the ash of a substance. Karlström et al. (2017) [33] demonstrated this by conducting analogous experiments with pristine and demineralized biomasses, in some cases previously subjected to torrefaction. These authors suggested that inorganics present on the feedstock have a role in $N/NO/N_2$ oxidation/reduction paths; for example, K has been reported to be effective in reducing NO to N_2. In this way, these authors demonstrated that the proportion of initial biomass N that remains as char-N in relation to the gas-N is affected by previous demineralization; this is interesting since HTC can modify the feedstock ash composition, as explained in the previous section. The

morphology and available internal area of the porous structure of the char remaining after devolatilization has also been indicated to have an influence on this equilibrium.

The way HTC affects the N content of a feedstock is quite complex and is determined by operating conditions. In general, greater temperatures will allow enhanced protein degradation and eventually, by Maillard processes, will involve a greater N migration to the liquid [34]. Also, studies report that NH_3 is preferably generated at low temperatures, and HCN is produced at high temperatures. However, time and biomass load also influence this effect, both helping the adsorption of N compounds back to the HCs. The fate of N in the case of feedstock subjected to pyrolysis is quite different and more foreseeable. Pyrolysis, as a means of utilizing biomass resources, converts fuel-N in biomass into N-containing compounds, such as pyrrole-N, pyridine-N, and nitrile-N. These compounds can be further decomposed into NOx precursors (mostly NH_3, HCN, and HNCO), which will cause air pollution after oxidation and emission [35]. If the targeted HC application is a soil improver, then a high N content might be an advantage, although the way it is bounded in the HC is important; this point is described in detail in Section 3.

2.5.3. Fate of Chlorine

The chlorine content of a feedstock can limit its potential use in specific applications, as it is in the case of materials to be used in combustion processes; Cl is associated with the emission of harmful compounds, like dioxins, with severe effects on living beings.

In this case, HTC offers the opportunity to promote the dechlorination of a feedstock, because water under certain temperature conditions can act as nucleophilic agent and favor OH-nucleophilic substitution reactions, enhancing the migration of Cl to the PW [36]. This requires, however, the use of a certain temperature and/or the addition of catalysts (organic solvents or alkaline compounds have been reported on the HTC system) [36,37], but can open the spectrum of materials to be used in bioenergy applications as solid fuels.

Treating PVC by pyrolysis would require the incorporation of post-treatment of the gas effluents and in addition is associated with very low solid yield values [28].

2.5.4. Process Improvement for HTC and Pyrolysis

Studies have demonstrated that HTC offers economic improvements in relation to pyrolysis [30,38]. However, making such an affirmation is conceited, since both processes yield different products with different values in the market and the variability of processing conditions significantly changes all target parameters of a viability study (e.g., the energy needed, inlet resources required, outlet products, valorization of effluents, or use in the process to improve overall efficiency). The thermodynamics of the two processes have not been comparatively studied; while there is consensus about the endothermal character of pyrolysis, HTC net enthalpy calculations show controversial results [39], as it will be described later in Chapter 3 [39].

The overall efficiency of both processes can be improved by including recovery of heat steps that also have other additional benefits. In this way, the recirculation of PW during HTC involves reducing the hydric footprint and reducing wastewater treatment needs, and at the same time, heat recovery can decrease external heat consumption.

PW recirculation also gives rise to a greater HC mass yield because of the enhancement of secondary HC production, promoted by a greater total organic carbon (TOC), chemical oxygen demand (COD), and organic acids of recirculated PW. While the bibliography agrees on the greater SY for cyclic use of PW on HCs, as compared single processes, the rise in the HHV of the HC is not found in all cases. For instance, Köchermann et al. (2018) [40] demonstrated while hydrocarbonizing sewage sludge that SY increased gradually after 11 cycles, although HC HHV did not show any remarkable change. In contrast, most of the authors agree on the enhancement of this parameter specially for the first recirculation cycle, and attribute it to the adsorption of specific compounds on the HC whose HHV is greater than that of cellulose [41]. Another advantage of using PW stands on the fact that it

allows the fostering of kinetics and thus the use of lower reaction times, as the hydrolysis steps that initiate HTC are enhanced by the acidic nature of PW.

In the same way that recirculating PW allows the recovery of heat, reusing high temperature fumes from pyrolysis also facilitates a decrease in thermal losses associated with the whole process. In addition, effluent gas feeding has been proposed as a way to improve biochar properties (C capture and porosity) and it yields a gas product that has greater calorific value because of enhancement of reactions like Boudouard, in which CO_2 is consumed to give CO [42].

3. HTC Process Modeling

Modeling and simulation play crucial roles in chemical and process engineering, allowing researchers and industries to design and enhance processes, achieving higher efficiencies, delivering resource savings, and reducing environmental impacts [43]. Reliable models offer the advantage of predicting a process's behavior without costly experimental campaigns and provide a deeper understanding of the underlying phenomena. In recent years, there has been a significant focus on the multiscale modeling methodology, which aims at bridging models and approaches that work at different time and/or size scales, obtaining predictive tools that lie on more solid bases [44,45].

HTC is not excluded from such a path: several articles published in recent years have provided contributions on modelling efforts. However, their prominence is still quite moderate compared to similar processes. This is evident in Figure 2, which shows the annual count of publications containing the terms "hydrothermal carbonization", "biomass gasification", or "biomass pyrolysis" on the scientific database Scopus (www.scopus.com) in the last decade. The graph also indicates the percentage of publications that also contain the words "modeling" or "simulation" (in both cases only considering the title, abstract, and keywords). HTC publications are experiencing the highest yearly growth rate, with an average of 21.4% that significantly outpaces the average 4.1% that all fields of science are experiencing [46]. Despite this growth, HTC modeling articles have, on average, accounted for a mere 3.4% and show no significant increase. Thus, nearly all HTC research is still conducted by experimental means. In contrast, biomass gasification is more implemented and well known, and sees nearly 1 in 4 articles focusing on modeling activities. This suggests that better modeling approaches could bolster HTCs standing, improve its understanding, and enhance investor confidence.

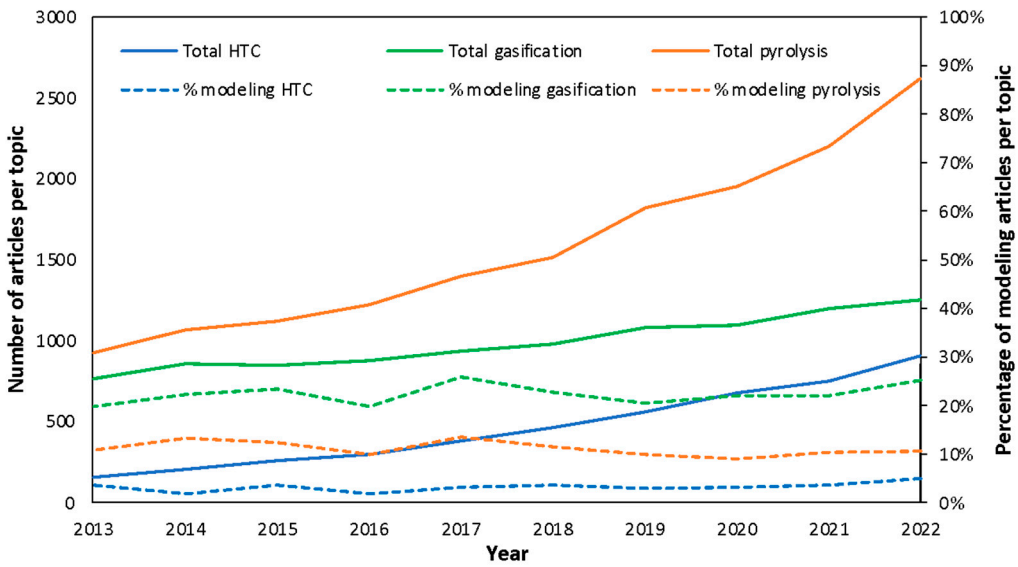

Figure 2. Number of yearly published articles and percentage of modeling articles on HTC, biomass gasification, and pyrolysis according to the Scopus database as of 18 August 2023.

The scarcity of efforts in HTC modeling is also reflected in the number of existing review articles that focus on this topic: as far as we are aware, the only ones are the 2021 work by Ischia and Fiori (2020) [47] and the 2022 work by Ubene et al. (2022) [48] (although others have also covered the topic with less focus [3,49]). In light of the recentness of these two reviews, the aim of this section is not to provide yet another comprehensive survey of the existing literature. Instead, it aims to offer a concise overview of the objectives and challenges associated with different modeling approaches applicable to HTC. Hopefully, this will guide researchers in shaping their future efforts in this domain.

3.1. Kinetic Models

At the smallest scale, HTC can be envisioned as molecules breaking apart and recombining due to chemical reactions. Developing predictive mathematical correlations that describe the rates and yields of these chemical reactions is a crucial endeavor. This task is instrumental in assessing the performance of the whole process. Advanced computational techniques such as molecular dynamics [50] may in principle aid this task: they are able to directly simulate molecules and their interactions, and have been applied to other biomass conversion pathways such as pyrolysis [51]. Nonetheless, they are still unviable due to their inherent difficulties and the high variability of molecules and reactions involved in HTC. Therefore, experimental campaigns have been the preferred approach. The already-cited review by Ischia and Fiori (2020) [47] has comprehensively outlined the progress and gaps in kinetic modeling of HTC, so only a succinct recall is provided here. Some related works have been published since the aforementioned review [52–56], but the overarching recommendations remain valid.

Following standard practices for homogeneous chemical processes, reaction rates in HTC are also expressed as the product of a temperature-dependent term (modeled through the Arrhenius equation) and another term that is a function of the concentration of reactants. The difficulties are mainly ascribable to two problems: the complex reaction pathway and the difficulties in correctly accounting for the reactants' concentration. These complexities have often resulted in overly simplified models or models exclusively valid for the specific experimental data used in their calibration. The following paragraphs discuss these difficulties in greater detail.

In contrast to other chemical processes, HTC is not fed with a pure, constant feedstock. Biomass is invariably a complex blend of various molecules, and its composition can vary significantly depending on its source. This inherent complexity has posed substantial challenges in understanding the kinetics of its conversion, even in more established pathways [57,58]. Significant breakthroughs have nonetheless been achieved through the study of idealized components, such as glucose or cellulose: their behavior in HTC is nowadays quite well understood, although a consensus on specific aspects is still lacking. However, when these components appear in mixtures, their behavior may change significantly. On the other hand, many studies developed kinetic correlations starting from real biomasses, with their findings having a narrower range of applicability, or even obtaining different kinetic parameters for the same feedstock due to the choice of the reaction scheme. Moreover, due to the high number of involved compounds, researchers have often resorted to lumped models that group different compounds into single classes (e.g., "gas" or "liquid") but do not elucidate the underlying processes. The possible catalytic effect of ashes [59,60] is also often neglected, thus remaining unclear. In summary, there remains a gap in having a comprehensive and universally applicable model capable of describing HTC mechanisms across a wide range of biomasses and operating conditions, and that can be scaled up reliably beyond laboratory settings.

Another aspect of the challenge lies in the mathematical formulation of reaction rates. The dependance on the concentrations of the involved compounds is often assumed to be linear, simplifying the development and use of the correlations. However, this does not often reflect reality: in some studies, it has been proven that many of the involved reactions are not linear, such the formation of secondary char from dissolved compounds [61]. The

presence of solid materials complicates matters further, as there is no uniform approach to incorporate a solid concentration into reaction rate correlations. In HTC, various solid materials are involved, including the initial biomass, primary and secondary char, and ash. Additionally, the assumption that reaction rates are independent of transport phenomena may not always hold true, as the porous nature of biomass and the use of non-stirred chemical reactors can influence kinetics.

Overall, increasing the accessibility of experimental data through readily available databases with well-documented operating conditions would greatly facilitate kinetic modeling. Standardized experimental procedures agreed upon by researchers could also help reduce the variability stemming from different lab methodologies. In summary, the main knowledge gaps in HTC kinetic modeling revolve around the need for comprehensive and versatile models that can handle biomass variability, account for complex reaction mechanisms, and scale up to industrial processes.

3.2. CFD Models

Moving to a larger scale, computational fluid dynamics (CFD) has become a fundamental tool for studying chemical reactors and various process units, with its significance expected to grow [62]. The fundamentals of CFD are relatively straightforward. Initially, the geometry of the targeted unit is defined and discretized into a numerical grid with the desired fineness. Subsequently, the specified equations are iteratively solved at each cell or point of the numerical grid to replicate the behavior of the unit over a specified time period. The main involved equations are local balances of mass, momentum (i.e., the Navier–Stokes equations) and, if relevant, energy. Moreover, additional closure equations also must be included to account for the phenomena that are deemed as relevant. If run properly, these simulations yield very detailed descriptions of the studied units, allowing observations unattainable through experimental tools, either entirely or in comparable detail. Researchers have harnessed CFD for the most diverse applications, such as the process industry, geotechnical scenarios, and even to study diverse aspects of the human body [63].

The application of CFD to HTC has thus far been quite limited. Only four relevant works have been published [54,64–66] since 2020, each with interesting findings but also significant simplifications. Another recent work [67] neglected instead HTC reactions, and discussed how natural convection affects the inner behavior of a hydrothermal reactor depending on the employed heating scheme.

This literature gap may be ascribed to the following main points: the use of batch reactors and the long duration of the process, the difficulties in obtaining adequate experimental data for the validation, the complexity of the involved physico-chemical phenomena (including the intricate and vast network of chemical reactions) and the difficulties in adequately specifying the solid (or slurry) phase. In the following paragraphs, these points are discussed in better detail.

In general, CFD simulations are rather demanding from a computational point of view. They operate by iteratively solving several equations on a large number of cell elements for each time step. To make the simulations faster, the Navier–Stokes equations are usually solved in a time-averaged form (called 'Reynolds-averaged Navier–Stokes', or RANS) that does not include the effects of turbulence. Nonetheless, very small time steps are still required (at least 0.01 s, but in several cases down to 10^{-6} s or less), depending on the time scale of the involved phenomena. Nonetheless, CFD simulations remain quite slow and are usually focused on the steady-state or time scales of few tens of seconds. This is problematic for HTC, which often operates in batch mode for an hour or longer. Even with larger time steps, conducting simulations to cover a standard HTC run can consume days. Considering a hypothetical steady state may also be unrealistic, since the vast majority of HTC reactors are operated in batch mode, due to their research-oriented purposes. An alternative, utilized for slow processes such as wastewater treatment [68], is to decouple the CFD equations from the kinetics and only solve the latter once a fluid dynamic steady

state is reached. This would indeed be effective in reducing the simulation time but may not allow the prediction of the interphase mass transfers. Parallelization (i.e., solving the equations on multiple computational cores) is helpful when the grid features a large number of elements, but this may not be the case for standard HTC reactors, which rarely reach large scales. Bench-scale continuous HTC reactors are currently lacking but may noteworthily aid CFD simulations, in addition to fostering the industrialization of the process.

To ascertain the accuracy of a CFD simulation approach, its results must be validated against experimental data. Ideally, these results should be available at as many times as possible and at different locations. For example, using the temperature from a single thermocouple or the yield of a product after a specific time is rather unsatisfactory. Ideally, it would be more desirable to have temperature data at different locations (ideally one or more profiles) and the yields or concentrations of the various products at different times. Obtaining such data is, however, often problematic from HTC experiments, which are performed in pressurized batch units that are not equipped for providing these data in such detail. In this context, more consistent, detailed, and transparent sharing of experimental data among research groups would be invaluable, as emphasized throughout this manuscript. Simultaneously, addressing the specific requirements of CFD simulations could benefit from innovative experimental methods capable of supplying real-time data during HTC operations.

In addition to the aforementioned local balance equations, simulating HTC also requires a plethora of closure equations. Most notably, including all the relevant chemical reactions and their rates is cumbersome and slows down the calculations, alongside the uncertainty issues detailed in the previous subsection. However, HTC also involves other phenomena that are usually not relevant for other systems. One of these is evaporation and other phase transfers [4]: their inclusion is mandatory to assess the gas pressure and yield, but such models clearly complicate the setup [69]. Furthermore, the evaporation models commonly applied in the literature were not originally designed for systems with such substantial temperature variations. In similar applications (e.g., tanks for liquefied gases), a relatively straightforward model like the Lee model [70] is employed to reproduce evaporation. This model predicts the evaporation rate by comparing the cell temperature to the fluid's saturation temperature, which is taken as a constant. However, in an HTC reactor water's saturation temperature would not be constant but rather depend on the water vapor partial pressure according to Antoine's equation. Other more advanced models exist [71,72], but it remains to be seen how reliable they are for HTC and if the added complexity is worth it. Other factors to be considered include surface tension and the dependence of the fluids' properties (mainly viscosity and density) on temperature. For water, a non-constant density is mandatory to reproduce natural convection in unstirred reactors: otherwise, water would not move, and its temperature would remain much less homogeneous than it is in reality. When simulating other devices, researchers often apply Boussinesq's simplification to facilitate natural convection in fluids with constant density by introducing a temperature-dependent volume force. However, this approach is advisable only when fluid temperature variations are limited, which is rarely the case in HTC reactors unless they are in a steady state. Some previous HTC studies simplified the CFD set-up by neglecting the presence of a gas phase above the fluid. Again, this would not allow natural convection to arise within the fluid, since it would not have room to expand. Given HTC's severe temperature and pressure conditions, accounting for potential non-ideality effects further complicates the simulation setup. In summary, several sub-models warrant further scrutiny before an established approach for simulating HTC can be devised.

Finally, the presence of solid biomass particles is worth considered separately. CFD was originally developed to study pure fluids, and accounting for the presence of solid particles presents notable complications. Two distinct scenarios necessitate separate assessment:

1. Uniform slurries. In scenarios where tiny solid particles are uniformly dispersed within a slurry and do not exhibit spontaneous separation from the water, the situation is somewhat simpler. Here, there is no imperative to treat water and solids as distinct

phases; instead, a single slurry phase can be employed. This also allows the employing of relatively simpler multiphase models, such as the "volume-of-fluid" (VOF) [73]. The rheology of the slurry is, however, often non-ideal due to the cohesive forces, and slurries have often been described as non-Newtonian fluids [74]. This is not too problematic per se, as there are several approaches to calculate the viscosity of non-Newtonian fluids [75]. However, while the viscosity of nearly all fluids is known to decrease when they are heated, sludges also lose their non-Newtonian behavior when hydrothermally treated [76,77], due to the breaking of biomass molecules. This effect has been reported multiple times, but the resulting rheology was only assessed after the slurry had been taken out of the reactor and cooled at ambient temperature. As far as we are aware, there has been no description of slurries rheology during the HTC process itself. To obtain a tool that is suitable for CFD simulations, there should be a mathematical relation linking the fluid's rheology with temperature and with its composition, which in turn changes when heated due to the degradation kinetics.

2. Biomass particles distinct from water. The other case, with macroscopic biomass particles, is typical, for example, of agricultural residues and there are more possibilities for its reproduction. As a first simplification, especially if their concentration is low, solid reactants and products may be assumed to be chemical species, allowing the use of simpler multiphase models, such as the VOF. Another simplified approach could be to assume that biomass particles do not move, and define the area they occupy as a porous zone. Instead, to actually model real granular solids, several approaches are available in the literature, but ultimately, the most viable ones are the following two: the two-fluid method (TFM), and the coupling of CFD with the discrete element method (CFD-DEM). The TFM [78] follows a Eulerian–Eulerian framework where both the solid and fluid phases are treated as interpenetrating continua. The behavior of the solid is reproduced through the kinetic theory of granular flows (KTGT), which involves numerous closure equations [79]. This approach is generally considered less reliable and more dependent on the chosen sub-models and parameters, and provides less-detailed results. At the same time, it is computationally more efficient (especially at larger scales) and is less restrictive in the definition of the solids properties and the numerical grid. The CFD-DEM [53,80] follows instead a Eulerian–Lagrangian approach: the fluid is a continuum, but solid particles are treated as discrete elements, with their trajectories being predicted by solving their Newtonian equations of motion, in addition to the various closure equations for the forces that they experience. The approach clearly provides more detailed results as it can yield the trajectories of all the involved particles and was often deemed as more accurate [81,82], but is much more computationally complex and is unviable if there are more than a few hundred thousand particles, especially for long simulation time. In the case of HTC (or of treating biomass in general), it may also be complex to describe how the particle properties (size, density, composition) may change due to the involved reactions. Despite the difficulties in modeling reacting solids [83], both approaches have successfully been applied for other types of biomass conversion processes [84–86], but never for HTC.

It has to be pointed out that both the TFM and the CFD-DEM still present some uncertain aspects even when dealing with simpler setups, such as the quantification of the biomass treatment processes in general or the treating of non-spherical and polydisperse solid particles. In summary, it appears evident that much work remains to be undertaken, but there are also many opportunities for pioneering breakthroughs in the field, which should be an exciting drive for researchers.

3.3. Plant-Scale Models and LCA

Widening the focus again, at an even higher scale, HTC can be simulated considering the whole plant. There are various open-source and commercial programs to perform this task, and nowadays they are irreplaceable in the chemical and process industry, since they aid the design and optimization of the plant, the operating conditions, and the resources.

In these programs, reactors and other unit operations are treated as zero-dimensional, with macroscopic material and energy balances being solved iteratively for the various units. The Leading Process Simulation Software (Aspen Plus®, Bedford, MA, USA) is the most known and utilized, including in the most recent studies focusing on HTC [87–89].

Embracing a multi-scale approach, these simulations could incorporate insights obtained at lower scales. Notably, the programs are equipped to include the reactions' mechanisms and rates. This is, however, often avoided due to the problems of HTC's kinetics and the increased computational complexity, and experimental product yields are inputted instead. The inclusion of kinetics also requires properly defining the reactor's volume and residence time. In cases where a chemical reactor's behavior cannot be adequately described as a continuous stirred tank reactor (CSTR), CFD simulations can prove valuable. They facilitate the development of an equivalent network of ideal chemical reactors [90], roughly including the effects of the fluid dynamics while only employing zero dimensional units.

HTC's thermal requirements deserve a particular mention: there is some uncertainty on the net enthalpy change during the process [39], which is expectable given the complexity of the involved reactions and the heterogeneity of the processable feedstocks. However, the process's energy needs must become very clear in order to assess its economic sustainability, commercialize it and properly designing the cascade of heat exchangers. The use of reaction rates, product yields, and thermal requirements in process simulators is yet another example in which the results obtained at lower scales are important, but the transfer of lab-scale data to the industrial scale must always be performed with care: oftentimes, the change in scale results in different limitations to the involved phenomena. In this sense, as stated elsewhere, campaigns comparing the performance of reactors of different sizes may be crucial to ascertain the scalability of lab-scale findings [91].

Finally, and at an even larger scale, life cycles analyses (LCA) are indispensable to assess the environmental sustainability and impacts of an HTC plant. A recent review [92] presents an overview of the achievements and challenges in the LCA of hydrothermal processes. The authors highlight the lack of study in this field, and stress the importance for future LCA works to also take into account the net energy demand and the impact of heavy metals and of greenhouse gases. In general, a key recommendation is to, once again, enhance the accessibility of detailed research data, as it greatly aids in configuring computational tools accurately. Making data more available also holds fundamental importance for non-physically based modeling approaches, such as those relying on statistical correlations or machine learning techniques [93], which have not been addressed within this discussion.

4. Effect of Hydrochar Products in the Soil

Except for functionalized HCs, the most widely considered utilization pathways apart from biofuel would be their soil applications, aiming mainly at soil improvement and carbon sequestration. The morphology (e.g., particle size, surface area, and pore structure) and chemical structure of HC provide the initial information on its potential effects on soil systems [94]. As described later in Chapter 6, these properties are mainly determined by feedstock characteristics and process conditions. However, the soil environment is a complex system, and the effect of HC introduction would also vary depending on several factors such as soil texture and pH, climate, land use, indigenous microbial communities, and more. In the following sections, we provide a summary of general aspects of HC soil application and suggest future research points.

4.1. Effects on Soil Parameters

(a) Physicochemical parameters

The introduction of HC into the soil would have an immediate impact on soil physicochemical properties. Inherited pH from the hydrothermal conversion process would directly impact on the soil pH. In general, the pH of HTC slurry obtained from biomass is around 4.5 or below [95], while the ones from anaerobically digested sewage sludge

generally have alkaline pH conditions [96]. Also, the proton-consuming activities of soil microorganisms might increase the pH by decreasing acidic metabolites [97]. Beneficial effects were shown mainly in degraded soils, for improving soil pH, cation exchange capacity (CEC, through high surface area and O-containing functional groups), electric conductivity (EC), and soil organic carbon (SOC) [71,98]. In general, it was reported that the hydrochar application improved soil porosity, decreased bulk density, and facilitated the formation of soil aggregates [99]. The porous structure of hydrochar and its hydrophilicity derived from oxygen-containing functional groups were beneficial in increasing the water retention capacity of the soil [100]. These beneficial effects are more evident in sandy soils than in clay and loamy soils [101]. In contrast, finer particles can block soil micropores and result in retarded water infiltration and retention [71]. In this context, the form of hydrochar application (e.g., post-processing methods: drying and pelletizing) and particle size may have a significant impact on the soil physical structure.

(b) Impact on soil organisms

Due to easily degradable carbon, the addition of HC to soil usually leads to increased soil respiration, enzyme activity, and microbial abundance [102]. However, the presence of HC in the soil may lead to a significant change in the bacterial and archaeological community. While HC application generally increased the abundance and diversity of bacteria and fungi, in some cases, a decrease in bacterial abundance was found [99]. This effect could be attributed to the acidic nature of HC, favoring fungi rather than bacteria. Generally, hydrochar, with its rough and nutrient-rich surface, forms a suitable habitat for soil microorganisms and protects them from leaching and predators [99].

4.2. Effects on Plant Growth

Both beneficial and detrimental effects on plant growth were observed from hydrochar application in soils. On the one hand, it could provide essential nutrients and improve soil properties. On the other hand, undesirable substances generated during hydrothermal conversion hampered seed germination and plant growth. In some cases, heavy metal contents in hydrochar inherited from its feedstock (e.g., sewage sludge and animal manure) need particular attention for its potential plant uptake and transfer through terrestrial food webs.

(a) Effects on plant-available nutrients

Nutrient contents in HC are mostly determined by its starting material and HTC conditions [103]. HC generally possesses plant nutrients, including N, P, K, Ca, and Mg. In some cases, hydrochar derived from manure, sewage sludge, and algal biomass is rich in phosphorus and/or nitrogen, and their potential application as slow fertilizer was reported [99,104–106]. It was also suggested that hydrochar with low nutrient contents could still provide beneficial impacts when used with conventional fertilizer by reducing the amount of nutrient which is lost through surface run-off [107,108]. Also, nutrients available in subsoils can be adsorbed on the porous surfaces of hydrochar and be slowly released over time, which increases the efficiency of plant uptake [109,110]. Richness in surface functional groups of hydrochar would facilitate ammonium (NH_4^+) and nitrate (NO_3^-) retention in soils through electrostatic attraction and pore-filling [111,112]. In contrast, the supplement of hydrochar with a high C/N ratio could facilitate microbial N immobilization, which leads to inhibition in early plant growth [113].

The potential of hydrochar as the nutrient source would have more importance in recovering phosphorus, which is a finite resource which experiences depletion at an alarming rate [114,115]. Phosphorus in hydrochar derived from sewage sludge is predominantly associated with multivalent cations such as Fe and Al [116,117]. These compounds are considered as moderately labile pools in soil for plant uptake [110]. It was reported that the hydrochar can act as a direct P source and also as a reservoir through adsorption when excessive P is supplied (e.g., fertilizer application), which is readily available for plants [106].

(b) Phytotoxic substances in hydrochar

Phytotoxic effects of hydrochar application are multi-variant phenomena consisting of the influence of soil properties, plant species, field settings, environmental conditions, and hydrochar characteristics [118]. Subsequently, researchers reported both positive and negative impacts of hydrochar application. Water-soluble phenols, furans, and organic acids could be the most representative by-products, resulting in acute phytotoxic effects [119]. The formation of these compounds can be attributed to the hydrothermal conversion of lignin, cellulose, and hemicellulose, which are the main constituents of plant-based feedstocks [120]. For the hydrochar materials derived from sewage sludge, the phytotoxic effects of other organic contaminants, including polychlorinated biphenyls, dioxins, and PAHs, as well as heavy metals, should be considered [119].

While some of the toxins in HC are organic substances built during the HTC process, heavy metals may be present in some input materials, like sewage sludge or other municipal organic waste [121,122]. Especially regarding the latter, caution is required; soil, as a finite and non-renewable resource, should not be additionally contaminated. To produce HC materials with more desired characteristics, the co-HTC of various feedstock blends could be an immediate solution [123]. Lang et al. (2018) [124] suggested that the co-HTC of swine manure and lignocellulosic biomass stabilized the heavy metal associated with hydrochar, decreasing the risk of heavy metal leaching. It was reported that the addition of corn cob into the hydrothermal treatment of swine manure (1-to-1 mass ratio) enhanced the nitrogen recovery and surface pore structure, which favors their application as fertilizers [125].

(c) Post-treatment options for hydrochar detoxification

Washing: Water washing of hydrochar prior to soil application can remove the amount of labile C in hydrochar, resulting in less phytotoxicity. Busch et al. (2013) [126] reported that hot water (100 °C) effectively eliminated the detrimental effect of hydrochar and facilitated plant growth in a greenhouse setting. In the repetitive washing experiments, the number of washing cycles was shown to have significant improvement, while the duration of washing did not. Three-fold washing of 1 h at a mixing ratio of 1 to 30 (hydrochar to deionized water) was sufficient to remove labile carbon adsorbed on the hydrochar surface. However, washing with water was not effective at removing water-insoluble organics (e.g., high-molecular-weight PAH 98.8 mg/kg) and resulted in inhibited germination [127]. Also, it should be noted that the available essential plant nutrient was lost during the washing processes [128].

Aging: Several ageing techniques were investigated for their impacts on the changes in hydrochar properties and potential implications. Natural ageing of hydrochar could be the simplest solution for remediating the phytotoxic effects of hydrochar. In the pot tests performed on two subsequent barley cultivations, the detrimental effect of hydrochar application in the first round was not observed in the second cultivation round. The authors attributed this to the microbial degradation of phytotoxic agents which is supported by the high O/C and H/C ratios indicating the abundance of labile carbon compounds [104]. The idea corresponds with similar results obtained from another research on barley cultivation, which suggested that the harmful substances were degraded or water-leached during the ageing period [129]. Also, ageing in the air could be an appealing option. Puccini et al. (2018) [130] reported that storing pelletized hydrochar under a free air exchange chamber for four months was effective at remediating inhibited germination. The idea can be supported by the recent publication that reported rapid changes in the chemical properties of process water even in freezing temperatures [131].

Composting: Microbial degradation of phytotoxic chemicals can be accelerated by composting techniques. Co-composting of hydrochar, green waste and horse manure eliminated germination and plant growth inhibition within four weeks of composting period without active aeration [126]. The beneficial effects of various co-composting blends were reported for green waste compost [132], organic fraction of municipal solid waste [133], fresh compost (with high microbial activity—substrates not specified) [134].

Al-Naqeb et al. (2022) [135] tested the cytotoxicity of methanolic extracts of hydrochar made of municipal organic waste after anaerobic digestion. Untreated hydrochar was compared to composted hydrochar and compost. The results showed that untreated hydrochar has a higher cytotoxicity than the hydrochar co-compost, which is in the same range as standard compost cytotoxicity. The authors conclude that composting hydrochar is a good step to eliminate the cytotoxicity of hydrochar.

4.3. Carbon Sequestration

Similarly to other SOC components that are generally considered reactive (i.e., prone to degradation) [136], hydrochar introduced into soil can decompose through microbial activity, releasing CO_2 into the atmosphere. Detailed processes of degradation and stabilization remain incompletely understood [137]. The beneficial effects of hydrochar soil application in carbon sequestration would depend on its long-term persistence over decades to millennia. High carbon content, thermal stability, and recalcitrance could be favored properties for efficient carbon sequestration in the soil [138,139].

Several methodologies have been implemented to estimate the carbon sequestration potential of biochar materials: (i) ultimate analysis (focusing on H/C and O/C ratio), (ii) proximate analysis focusing on fixed carbon and volatile matter, (iii) thermal stability indices based on real-time analysis of gas and vapors during high-temperature pyrolysis (e.g., 900 °C) of test samples using the pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) technique, and (iv) recalcitrance indices based on the fraction of carbon withstanding thermal oxidation measured by a combination of thermal gravimetric analysis and differential scanning gravimetry [139]. Among them, ultimate analysis becomes the most common approach, which provides an immediate estimate of the carbon sequestration potential. Higher contents of O and H in biochar (i.e., higher O/C and H/C ratio) indicate high aliphatic and less polyaromatic carbon content, which would lead to facilitated biotic degradation [140,141]. The majority of biochar materials (with exceptions for biochar from algal biomass and hydrochar with high H/C ratios) showed a close correlation between O/C and H/C ratios [142,143]. Based on the literature study, Spokas (2010) [144] coupled the O/C ratio with the expected half-life of biochar materials obtained through various laboratory studies on biochar degradation during its incubation in soil: an O/C ratio < 0.2 would indicate a half-life > 1000 years; an O/C ratio between 0.2 and 0.6 is for a half-life between 100 and 1000 years; a ratio greater than 0.6 is for a half-life < 100 years. Mostly, hydrochar showed intermediate to high O/C ratios ranging from 0.2 to > 1.7 [94,140,141].

However, this approach needs careful interpretation because most laboratory investigations are performed in idealized conditions, and other natural processes such as climate variability, infiltration, ozone and UV exposure, freeze–thaw cycling, or run-off are not considered [144]. It is advisable to perform field investigations over longer periods to obtain a more comprehensive understanding of hydrochar stability in a natural environment. To our knowledge, there is only limited research performed in field conditions. Lanza et al. (2018) [145] conducted a two-year field experiment to assess the degradability of biochar. Their findings estimated a half-life of 76–79 years for pyrochar and 49–61 years for hydrochar. In both cases, the degradation rate decreased over time, suggesting that more labile compounds are decomposed first, while the more stable fractions are more resistant to degradation. A similar result was reported by [146]. Around 1/3 of the initial hydrochar applied to a field lysimeter set-up was lost through leaching and decomposition within a year. However, the degradation rate of the remaining hydrochar slowed down significantly, having an estimated half-life of 19 years.

4.4. Priming Effect

With respect to the priming effect of hydrochar application on the degradation of original soil organic matter (SOM), the results are contradictory. Short-term studies found positive priming effects indicating that hydrochar application leads to an increased degradation of SOM [27,147,148]. Malghani et al. (2015) [146] carried out a one-year field

experiment and found a positive priming effect over the first three months, while the overall effect over the one-year period was negative. de Jager et al. (2022) [149] on the other hand, found a positive priming effect of hydrochar added to a podsol in a one-year experiment. The examination of the fate of hydrochar C showed interactions between particles of hydrochar with the original soil organic matter and indicated the possibility of incorporation into newly built aggregates.

Based on these results, it could be possible that priming effects may change over time. It has been shown that the degradation of hydrochar increases in the beginning when the less stable fractions decompose and slow down over time. Decomposition and soil respiration likely correlate with the abundance of soil microorganisms, which is affecting the degradation of SOM as well. Another factor is the effect of soil properties on the decomposition of hydrochar and SOM. The above-mentioned experiments were carried out on soils with different texture or pH. The meta-analysis of [150] for pyrochar showed that soil properties like the clay content affect the char decomposition as well as the priming effect. We therefore suggest long-term (field) studies on different soils in order to obtain better knowledge on effects like the stabilization of char by interaction with clay or the effect of soil pH on the decomposition of HC.

4.5. Contaminant Retention

Hydrochar has been suggested as a capable adsorbent in wastewater treatment processes based on its porous and reactive surface (i.e., rich in surface functional groups and polarity). Adsorptive removal of various contaminants was reported for heavy metals, dyes, pharmaceutical residues, endocrine-disrupting compounds, nitrates, phosphates, and sulphates [151]. It suggests the role of hydrochar in the soil as a contaminant barrier. Also, considering the fact that hydrochar is biodegradable and its recovery (i.e., separation) from the soil is unrealistic, more attention needs to be taken to the fate of non-biodegradable contaminants such as heavy metal and more recalcitrant organic contaminants retained in a soil–hydrochar matrix. They could be released into the soil and transported through plant uptake or infiltration into groundwater.

Isakovski et al. (2020) [152] investigated the immobilization and biodegradation of organophosphoric pesticides associated with hydrochar and pyrochar applied to river sediment. All carbonaceous materials slowed the migration of tested pesticides 4 to 18 times. Chlorpyrifos and chlorpyrifos-methyl were still being biodegraded. However, there was no visible degradation in the test for chlorfenvinphos. A similar result was observed from experiments targeting antibiotics (oxytetracycline). Hydrochar materials enhanced the microbial degradation of antibiotics and decreased their plant uptake [153]. The effect of biochar on organic contaminants varies and depends on the substance and its chemical structure. The selection of feedstock and HTC conditions affected the remediation performances of the soil–hydrochar mixture [152]. This would shed light on the application of hydrochar in the selective remediation or separation of organic contaminants. Also, it is of particular interest for the hydrochar derived from feedstock with potential heavy metal contamination (e.g., sewage sludge and animal manure). Yue et al. (2017) [154] observed an immediate and significant increase in heavy metal contents in soil amended by sewage sludge-derived hydrochar during 60 days of laboratory incubation. The authors suggested that the heavy metal contents embedded in the hydrochar were released as the hydrochar decomposed and were adsorbed by a soil matrix such as carbonates, iron oxides and clay minerals.

4.6. Discussion and Future Research Points

One of the most interesting and important phenomena in the soil–hydrochar matrix is the degradation of hydrochar. It is unavoidable, occurs over a long period spanning weeks to centuries at rates that change over time, and has various impacts, both in desirable and undesirable ways. As seen in the previous sections, degradation is accompanied by the release of nutrient contents embedded in hydrochar, which suggests its use as a slow-

release fertilizer (Section 4.2). Simultaneously, rapid decomposition limits its application for carbon sequestration (Section 4.3) and poses a potential risk of heavy metal contamination (Section 4.5) in the surrounding environment, particularly for the hydrochar derived from sewage-sludge, which generally has high contents of P and heavy metals.

In several research areas, it is stated that HC is composed of, at least, two different carbonaceous parts, which differ in their characteristics. Regarding HC degradation in soil, more labile carbon decomposes first at a significantly higher rate, and the recalcitrant carbon lasts for much longer periods. In a comparative investigation of conventional pyrochar and HC in field tests, a slowing down of the degradation rate was observed in both cases, but to a much smaller extent for pyrochar [145]. In water treatment research, the adsorption performance of hydrochar was improved by chemical activation, which removed the outer part. For instance, cold alkali washing of hydrochar (e.g., with 1 M KOH at room temperatures) was effective at removing the carbon layer deposited on the hydrochar surface and exposed the inner part, which provides improved surface areas with higher hydrophobicity [155–157].

More fundamental research on hydrothermal conversion processes has suggested the concept of primary and secondary char. Hydrochar is mainly composed of (i) primary char formed through solid-to-solid conversion of non-liquified remainders and (ii) secondary char generated through polymerization of dissolved organic substances through liquid-to-solid conversion which condenses on the surface of primary char [158,159]. The characterization of the secondary char is mainly based on its chemical extraction and subsequent analyses. Lucian et al. (2018) [159] provided important observations: (i) the secondary char is mainly comprised of organic acids, furfurals and phenols, which induce phytotoxic effects; (ii) the formation of the secondary char was most prominent at moderate reaction temperatures between 220 and 240 °C; at higher reaction temperatures, dissolved organics would be polymerized as the solid primary char; (iii) devolatilization rate of hydrochar was positively correlated with the higher secondary char contents, suggesting its responsibility for reactiveness. In contrast, Volpe and Fiori (2017) [160] reported higher thermal stability of secondary char based on its higher carbon content (lower atomic O/C ratio) than the primary char. Also, the methodological approach which identifies the secondary char as an extractable fraction would need careful consideration because, in harsh HTC conditions, it is likely that non-extractable primary char is generated through liquid–solid conversion processes. In-depth research on the hydrochar formation mechanisms would provide insights for developing more tailor-made hydrochar materials for its application in specific cases.

These results would have direct implications for soil–hydrochar interactions based on the strong correlation between thermal stability and biodegradability [161]. More comprehensive research under field-like conditions in the long term is essential. It is not only to obtain more information on hydrocar degradation in the soil, but also to examine the long-term effect of hydrochar on the soil under more realistic circumstances. Given that the soil–hydrochar interaction occurs in a much longer timespan than other reactions (e.g., combustion), the heterogeneous composition of hydrochar is of particular interest, resulting in responses in multi-stages as different char composites have different decomposition rates and characteristics. Because it is directly connected to climate change mitigation, a drastic surge in carbon permit price could be a driving force for future research. The prices of EU carbon permits has risen from EUR 3.5 to 76.1 per ton of CO_2-eq [162].

Specific research topics would include the following:

- As primary and secondary char decompose at different rates, identifying spatial distribution (i.e., proportioning) of nutrients and heavy metals in hydrochar composite would provide fundamental knowledge that facilitates subsequent research streams in both hydrochar production and application. Finer tuning of hydrochar products could be a more tailor-made solution in a given context.
- The effects of hydrochar biodegradation on its adsorptive performance are not yet known. If the degradation of secondary char in the soil–hydrochar matrix occurs at

a significantly higher rate than that of primary char, biodegradation would induce similar impacts as the chemical activation and provide a larger surface area. However, it has to be considered that the loss of rich surface functional groups (mainly O- and H-containing groups) would lead to an increase in hydrophobicity, resulting in a decrease in water holding capacity. Continuous monitoring of the hydrochar characteristics in the soil would provide crucial insights into long-term perspectives.

- The interaction between the soil–hydrochar matrix and other soil substances, such as chemical fertilizers and pesticides, would also change with the ageing of the soil–hydrochar matrix. This has to be examined in the long term. It might affect biogeochemical cycling and efficiency as well as the fate of pollutants.

5. Process Water Management and Valorization

During the thermochemical conversion of organic residues into HC, significant amounts of PW are generated. The PW quantity and quality largely depend on the specific conditions of the process, including the nature of the feedstock, the ratio of dry solids to water S/L, the temperature, the residence time, and other operational parameters (e.g., use of additives/catalysts). The management and valorization of this by-product are crucial for the overall sustainability and economic viability of the HTC process. While many investigations have delved deeply into the features of the HC, its energy potential, SY, and combustion traits, relatively few have explored the HTC PW with an aim to turn them from mere waste to valuable products such as chemicals, fuels, and energy [95,96,163–165]. The available studies indicate significant uncertainties surrounding the composition and potential uses of HTC process waters; therefore, further research is crucial to address challenges and optimize the recovery of valuable resources from the process water [8,160].

5.1. Process Water Characteristics/Characterization

Characterizing the HTC PW is essential for assessing its potential for valorization and determining the most suitable final treatment methods for its disposal. The analysis from existing studies underscores noticeable variations in the yields and the physical and chemical properties of PW. These variations stem from both the HTC process conditions and the attributes of the raw material. Such variability can affect the valorization process and may pose challenges when implementing this procedure at an industrial scale.

The liquid yield of the HTC process can vary within a very wide range (11–55% wt.) and tends to increase with higher temperatures and initial water quantity, which increase the breakdown and dissolution of organic substances during the HTC process [163,165]. As the reaction time increases, the liquid yield typically increases until a certain point in which the polymers dissolved in the process water interact to produce what is termed secondary char. This trend is more prominent at extended reaction durations [165].

Generally, PW possesses an acidic pH (below 4.5, even if higher values are reached when feedstocks with elevated buffering capacity are used) and a dark color, from yellowish to dark brownish with decreasing temperature. PW contains high concentrations of organic matter and a relative abundance of nutrients (N, P, K) as a result of the dissolution and decomposition of organic matter during the thermochemical conversion. The carbon/nutrient quantity and speciation are strongly dependent on the treated feedstock and process operating conditions and give rise to different opportunities for material and/or energy recovery according to a biorefinery approach. While most heavy metals are concentrated in the hydrochar, a portion can still be detected in the HTC process waters, posing an environmental concern. Another element of impact is the presence of potentially toxic organic compounds such as phenols, furfurals, pesticides, PAH, pharmaceutical compounds, and several Maillard products produced following the interaction between carbohydrates and proteins [8,95,163,166].

According to the discussion reported above, PW from HTC possess inherent value allowing for several valorization possibilities; however, the intrinsic variability on the chemical and physical properties of this by-product is a limiting aspect in the definition of

the optimal valorization pathway, and more studies are deemed necessary to fully exploit the biorefinery potential of HTC. Figure 3 represents the different ways of managing HTC PW, which are described in the next subsections.

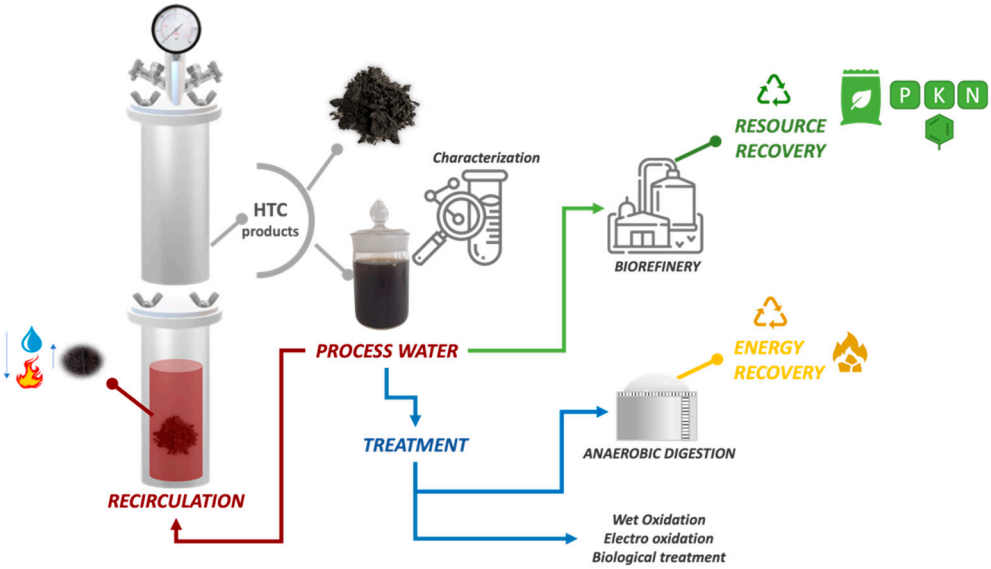

Figure 3. Methods for the management of HTC process water.

5.2. Management of Process Water through Recirculation

In an industrial-scale HTC facility treating relatively dry feedstocks, ensuring a consistent supply of water and suitable management of PW could present significant operational hurdles. Recirculation of process water, i.e., the reuse the process water generated in one cycle of HTC as the reaction medium in the next cycle, has gained significant attention as a strategy to reduce water usage, and manage the produced wastewater, leading to substantial cost savings in the HTC plant but also boosting the system's overall efficiency [163,167]. Studies have indeed shown that process water recirculation is the most effective means of heat recovery, with the potential to slash external heat demands by a factor of ten [168]. Further, recirculating HTC process water enhances the reaction mechanism, primarily because the liquid is inherently acidic and warm—two attributes known to expedite HTC reactions [96,167,168]. For instance, the presence of acetic acid in process water might accelerate the HTC kinetics when recirculated, possibly allowing for reductions in both pressure and temperature conditions. The quality of the produced HC also seems improved by recirculation: evidence suggests that factors such as hydrochar mass yields, carbon percentage, hydrophobicity, and therefore dewatering properties, and HHVs can all see improvements when process water is recirculated in the HTC treatment. Moreover, degraded sugar byproducts from biomass polymers found in the HTC process water could embed themselves into HC's porous makeup, potentially enhancing the solid's energy density. PW recirculation is not applicable in the HTC treatment of wet biomasses like raw digestate and sewage sludge, due to the high moisture content of such waste. Still, it can be recirculated as liquid source in another HTC or Co-HTC process to circumvent some limitations of specific feedstock such as the substantial need for water, improving the process feasibility and paving the way for numerous future research opportunities to delve deeper into this method [8].

Still, open questions remain, such as to what extent water recirculation in HTC process reduces the overall water consumption and how the quality of the produced process water and hydrochar evolve as a function of operating cycles. The specific reduction in water usage can depend on several factors such as the type of biomass used, the HTC operating conditions, and the extent of water recirculation practiced. The repeated use of process water in the HTC process can lead to changes in its quality, with an accumulation of dissolved

organic and inorganic compounds that should be taken into account in view of choosing the optimal final treatment or valorization process that must necessarily occur after a certain number of recirculation steps. Some studies [167,168] suggest that the pH decreases with each cycle due to the accumulation of acidic compounds. The chemical oxygen demand (COD) and total organic carbon (TOC) of the process water tend to increase with each recirculation cycle, as more organic matter is dissolved from the biomass [8]. Certain organic compounds like phenols and organic acids can accumulate in the process water over multiple cycles. These could have implications for the toxicity and final management of the process water. Also, the concentrations of nutrients such as nitrogen, phosphorus, and potassium also tend to rise with each cycle, which could potentially increase the value of the process water as a fertilizer.

5.3. PW Valorization through Energy Recovery via Biogas Production

Lately, numerous research efforts have investigated the synergistic opportunities between HTC and anaerobic digestion to optimize the utilization of organic by-products. Specifically, anaerobic digestion has been suggested as a strategy to transform the substantial organic content in process water into biogas [8,95,165], thus supporting the thermal requirements of HTC via biogas combustion on one hand, and mitigating the environmental implications of discharging HTC PW on the other. Promising outcomes regarding biogas production and methane concentration in the biogas were documented for process waters derived from various feedstocks. Factors such as HTC process temperature, residence duration, starting feedstock properties, nutrient levels, the acclimation of the inoculum, and its buffering ability are the primary determinants affecting the efficacy of valorizing HTC process water through anaerobic digestion (AD). A deficiency of nutrients in HTC process water, coupled with high levels of toxic compounds and elevated organic loading rates, can hinder the AD process. Merzari et al. (2019) [95] determined that using HTC on sewage sludge at temperatures between 180 and 200 °C and reaction durations spanning 60–90 min offers a balanced approach considering HTC energy usage, hydrochar yield and valorization, HC dewatering capability, and biogas generation from PW.

Numerous researchers indicate that, from the perspective of managing process waters produced by HTC treatment applied to feedstocks such as sewage sludge and agricultural digestate, an optimal implementation system involves integrating an HTC plant with a wastewater treatment plant and an anaerobic digestion plant, respectively. However, for a large-scale integration of the HTC process within a wastewater treatment plant, further research is necessary. This would involve examining the impact of HTC PW on the stable functioning of anaerobic digestion, taking into account the behavior of emerging contaminants and understanding the long-term implications of persistent and harmful compounds that might accumulate throughout the system.

5.4. PW Valorization through Resource Recovery

Currently, treating and valorizing HTC process waters through resource recovery, especially focusing on nitrogen and phosphorus, presents significant challenges. Given its rich nutrient profile and the presence of soluble alkali elements, the HTC liquid could serve as a potential liquid biofertilizer for agricultural crop production or as a nutrient-rich medium for algal cultivation, aiming to decrease cultivation expenses and enhance the overall sustainability of the process. The reaction conditions ensure it is pathogen-free, and heavy metals are predominantly captured in the hydrochar. However, to capture commercial interest, the effluent needs enrichment processes to intensify its nutrient content [169]. This paves the way for phosphorus and nitrogen recovery opportunities, by combining HTC or Co-HTC plants with technologies dedicated to reclaiming these elements.

The HTC liquid fraction also contains additional valuable compounds that can be recovered and valorized according with a biorefinery strategy. Chemicals such as formic acid, lactic acid, furfural, phenol, guaiacol, acetic acid or acetol, among others, hold significant commercial value, and extracting them from the liquid phase presents an

intriguing avenue to investigate [165]. Merging emerging technologies for treating aqueous solutions with HTC could be advantageous in reclaiming or concentrating these chemicals. Membrane technologies, for instance, are examples of methods that can be paired with hydrothermal carbonization to concentrate the liquid phase by eliminating water. Such integration could offer a promising biorefinery approach for effluent enhancement.

5.5. PW Treatment

As previously mentioned, PW is often viewed as a challenging byproduct to handle, and this represents a primary obstacle for large-scale HTC implementation. The effective management of this liquid byproduct necessitates, on one hand, the exploration of all potential valorization avenues for material and energy recovery. On the other hand, there is a need to establish robust treatment methods for its eventual disposal. Suggested methods for the ultimate disposal of PW encompass anaerobic digestion, aerobic processing, and wet oxidation [170,171].

Because of the suitability for managing the high organic load of easily biodegradable compounds like acetic acid, the application of anaerobic digestion for the treatment and energy valorization of process water has been extensively researched. Based on existing findings in the literature, anaerobic digestion offers a promising approach to decrease the organic burden while also facilitating extra energy recuperation. An HTC temperature close to 200 °C seems to yield the most energy recovery and optimal PW treatment. Methane potential values from AD ranging roughly between 200 and 350 N mL CH_4/g COD_{added} have been documented, corresponding to a COD reduction of 60% up to over 80%. However, these results must be enhanced to make it a more environmentally viable solution for handling PWs. While AD is an established technology, its tailored use for PWs warrants deeper exploration, particularly focusing on boosting methane yields and simultaneously reducing the high COD of these liquid residues. This presents a significant hurdle, necessitating considerable research before AD can be seamlessly incorporated with HTC, particularly with reference to the synergistic outcomes of the co treatment of PW and other raw organic residues [166].

Compared to anaerobic digestion, the application of aerobic processes in treating HTC PW has not been widely explored. However, aerobic treatment might offer benefits, especially in the elimination of persistent compounds like polycyclic aromatic hydrocarbons (PAH), phenols, N-heterocyclic compounds, or melanoidins [170]. Combinations of anaerobic and aerobic processes have been studied by Weide et al. (2019) [172], reaching a strong reduction in the PW organic load. However, additional treatments are suggested to allow for the final discharge, such as ozone treatment, precipitation, and flocculation. Releasing into municipal WWTPs should be thoroughly assessed, considering the load and the quantity of refractory compounds present in the process water. Due to high residual carbon content, the use of HTC process waters as an external carbon source in standard nitrification and denitrification procedures has been suggested by some authors [172]. Yet, this facet warrants exploration in upcoming studies, particularly concerning any inhibitory effects on nitrifying and denitrifying bacteria [173].

Techniques designed for the treatment of aqueous wastes with a high organic content, such as industrial discharges or landfill leachate, have been eyed for pollutant elimination in PW. In this context, wet air oxidation stands out due to its proven efficiency at a full-scale in significantly reducing COD [166]. Among advanced technologies, electrochemical process such as electro-oxidation (EO) could facilitate the destruction of organic compounds with no addition of chemicals and therefore with no production of toxic by-products in the treated PW [171].

However, considering the characteristics we discussed earlier regarding PW, treating them to remove existing pollutants can create favorable opportunities for developing solutions aligned with the circular economy model, smoothly integrating with the recovery of energy, nutrients, and/or valuable chemicals.

6. Strategic Feedstocks for Pyrolysis and Hydrothermal Carbonization

Biomass selection for each unit of biochar production is a critical step in order to align with the strategies of sustainable development for the local communities and local businesses [174]. Research on diverse biomass has experienced a dramatical growth, driven by the demand for high-quality biochars with enhanced capabilities and adaptability [175].

6.1. Animal Manure

Animal manures are produced in the amount of 3.12 to 7 billion metric tons per year globally, and they are traditionally used as a fertilizer for producing food and feed crops [176,177]. However, the development of concentrated animal feeding operations (CAFOs) has resulted in the production of a large amount of animal manure often exceeding the local soil and crop demand for nutrients. Inadequate storages and over-application of nutrient rich manure in large quantities near CAFOs impose a serious threat to the environment such as eutrophication and greenhouse gas emission. It also increases the pressure for growers to safely dispose surplus manures. Research studies reported in the literature suggest that with proper management practices and technologies, manure has a role to play in generating renewable fuels and other valuable coproducts. Anaerobic digester has been used to produce renewable natural gas from manure [178]. Hydrothermal carbonization (HTC) can be used as a manure conversion technology for producing value-added solid (i.e., hydrochar) and liquid products. This chapter reviews such research studies involving various applications of hydrochar and HTC process liquids from animal manures.

6.1.1. Physico-Chemical Characteristics of Animal Manures

Physico-chemical and thermal characteristics of animal manure are widely different depending on species, housing, feeding, handling, and storage conditions. Poultry and feedlot operations produce a mixture of manure, bedding, waste feed, and underly soil. These mixtures of manure and other materials are considered to dry with moisture contents generally less than 50%. When the mixtures contain soil, the ash contents are high, which negatively impacts the heating value (Table 1). In contrast, dairy and swine feeding operations typically produce dilute solid streams composed of discharged wash water, manure, urine, and undigested feed. The characteristics of these dilute solid streams depend on growth stage of animals, type of manure handling collection system (i.e., flush, pull-plug, or pit recharge), and amount of added water. While the moisture contents of these wet manure streams are typically higher than 95%, those of dewatered steams are less than 75%. The volatile solid fractions of dairy and swine manure streams are generally higher than that of dry manure waste streams [179].

Table 1. Physico-chemical and thermal characteristics of animal manure streams.

	Dry			Wet			
Parameters	**Poultry Litter**	**Feedlot Manure (Unpaved)**	**Feedlot Manure (Paved)**	**Dairy Manure**	**Swine (Pit Recharge)**	**Swine (Flush)**	**Swine (Dewatered)**
MC (%)	7.5–41.4	19.81	20.27		98	96.18	
VM ($\%_{db}$)	40.3–74.3	33.77	64.6–76.7	63.4–83.8	68.7	68.6–83.8	61.3–73.6
Ash ($\%_{db}$)	16.9–43.9	58.73	15.4–20.2	14.8–22.9	31.3	16.2–19.6	20.9–26.7
FC ($\%_{db}$)	5.7–15.8	7.5	7.9–15.2	4.5–13.7		11.9	5.6–12

Table 1. *Cont.*

	Dry			Wet			
Parameters	**Poultry Litter**	**Feedlot Manure (Unpaved)**	**Feedlot Manure (Paved)**	**Dairy Manure**	**Swine (Pit Recharge)**	**Swine (Flush)**	**Swine (Dewatered)**
C ($\%_{db}$)	22–42.1	21.7	43.1–45.1	40.8–46.5	45.7	44.7–57.0	31.0–47.4
H ($\%_{db}$)	3.8–5.2	2.62	5.2–5.5	5.3–5.5	6.5	5.9–9.7	5.2–6.0
N ($\%_{db}$)	2.6–3.7	1.94	2.4–3.1	2.3–2.6	3.5	2.1–4.1	4.1–5.3
S ($\%_{db}$)	0.5–0.7	0.42	0.4–0.7	0.3	0.4	0.31	0.9–1.7
O ($\%_{db}$) (diff.)	27.1–34.8	14.6	27.7–32.5	27.2–33.2	31.4	29.2–38.2	25.3–26.
HHV (MJ/kg)	9.2	6.3	13.4	17.6	17.2	18.2–22.9	19.5
Refs	[180–184]	[185]	[182,185]	[7,181,182]	[180]	[180,186]	[7,182,183]

MC = moisture content; VM = volatile matter; FC = fixed carbon; C = carbon, H = hydrogen; N = nitrogen; O = oxygen; S = sulfur; HHV = higher heating value.

6.1.2. Carbonized Animal Manure Characteristics

When raw animal manure streams are carbonized with (hydrothermal carbonization) or without water (pyrolysis), phyco-chemical, and thermal characteristics of the carbonized solids are widely different. The characteristics of the animal manure-based chars depend on complex array of conditions such as types of animal manure, solid–liquid ratios, exposure to liquid water, and reaction temperatures and times. However, our understanding of the complex interaction of these conditions taking place during HTC process is still very limited. Only a few regression models exist for predicting hydrochar properties based on raw feedstock characteristics and process conditions [187–189]. Table 2 shows the characteristics of various animal manure-based hydrochars and pyrochars. The solid products from pyrolysis or HTC of animal manure resemble natural coals more closely than chars from dry pyrolysis (hereafter referred as pyrochar) than that from HTC (i.e., hydrochar). Pyrochars also usually have a higher carbon and fixed solids and lower hydrogen and volatile matter than hydrochars (Table 2).

Table 2. Physico-chemical and thermal characteristics of pyrochar and HC derived from animal manure streams.

Process Condition	Raw Material	VM ($\%_{db}$)	FC ($\%_{db}$)	Ash ($\%_{db}$)	C ($\%_{db}$)	H ($\%_{db}$)	N ($\%_{db}$)	O ($\%_{db}$)	Refs.
P350	swine	31.7–49.8	17.7–26.6	32.5–41.8	51.5	4.9	3.5	11.1	[182,183,190]
H210–250	swine	54.0–59.8	12–15.2	21.1–34.5	66.0	8.4	3.5	22.2	[183,186]
P350	poultry	33.5–42.3	27.0–30.8	30.7–35.7	51.1	3.8	4.5	15.6	[182,183,190]
H250	poultry	39.2–39.8	14.8–17.3	42.9–46	39.1–45.8	3.1	3.1	9.0	[183,191]
P350	dairy	53.5	23.2	24.2	55.8	4.3	2.6	18.7	[182]
H170	dairy	66.14	13.41	20.45	40.97	5.09	1.69	23.64	[182,192]
P350	cattle	47.9	23.5	28.7	53.3	4.1	3.6	15.7	[182]
-	coals	32–34.8	55.7–57.7	9–12.1	56.6–78.8	3.6–4.9	1.0–1.7	4.7–8.8	[183,193]

P = pyrochar; H = hydrochars; VM = volatile matter; FC = fixed carbon; C = carbon, H = hydrogen; N = nitrogen; O = oxygen; Numbers after the first letter show reaction temperature in °C (Ex. H210-250 = HTC at 210–250 °C).

6.1.3. Potential Applications for Animal Manure Hydrochar

Ducey et al. (2017) [194] reported that HTC temperatures as low as 150 °C at autogenic pressures was sufficient to result in both pathogen kill and complete elimination of microbially derived DNA based on studies using animal mortality spiked with high

levels of the model microorganism Escherichia coli (Ec), carrying a high copy plasmid, designed to simulate an antimicrobial resistance gene (ARG)-harboring pathogen. This study revealed that HTC can be used as a biosecure treatment option for animal manure, and its byproducts such as hydrochar and process liquid can be used without concern of biological contamination to energy, soil, and other environmental applications.

Ro et al. (2019) [183] compared the combustion characteristics of manure-based hydrochar and pyrochar to that of fossil coal. Hydrochar showed two distinctive combustion stages, while pyrochar and fossil coal showed a single stage. Based on characteristic combustion kinetic properties, temperatures, and ash contents, they suggested that up to 10% hydrochar or 20% pyrochar can be blended with coal to achieve combustion characteristics similar to fossil coal.

Ro et al. (2016) [181] compared the potential of a swine manure-based pyrochar and hydrochar in improving soil fertility. They reported that the swine manure-based hydrochar improved soil fertility by providing abundant nutrients to plants yet reduced the water-polluting potential by not releasing N, P, and K in leachate. In contrast, the pyrochar amended soil leached significant amount of nutrients suggesting potential contamination of ground and surface water bodies if applied in soil. More research is needed to fully understand about the plant availability of the nutrients in manure-based hydrochar and the mechanism to withhold nutrients within the hydrochar-amended soil matrix.

Manure-based hydrochar showed remarkable ability to remove both water soluble and insoluble organic pollutants in water by adsorption. In contrast, pyrochar made of the same manure feedstock was effective in removing only insoluble pollutants [195,196]. The hydrochar showed much higher sorption capacity than pyrochar toward organic pollutants with wide range of water solubilities; acetaminophen (water solubility, Sw = 12.9 g/L) to most insoluble pyrene (Sw = 0.01 g/L). The high adsorption capacities of the hydrochar toward both soluble and insoluble compounds might be attributed to the complex surface functionalities of hydrochar as reported by [197]. The dominant component of swine manure pyrochar was aromatics, whereas that of swine manure hydrochar was alkyl moieties consisting of O-alkyl, O-CH_3, NCH, and COO/N-C==O groups. The aromatic cluster size of hydrochar was smaller than those of pyrochar. They claimed that these complex surface chemical functionalities of hydrochar might explain its ability to sorb both water soluble and insoluble compounds, while pyrochar with mostly fused aromatics only sorbed insoluble compounds.

6.2. Lignocellulosic (Plant) Biomass

One of the most abundant biomass is lignocellulosic (plant) biomass, which is structured by three main components such as cellulose, hemicellulose, and lignin [198,199]. Its structure and compositions are influenced by soil quality and weather conditions [200]. The annual production of lignocellulose biomass is about 181.5 billion tons globally, out of which only 8.2 billion tons is used in various application areas [201]. Lignocellulosic biomass is classified into four common groups such as (1) agricultural/crop residues, (2) energy crops, (3) forest residues, and (4) industrial or municipal solid wastes [202,203].

Lignocellulosic biomass is well known as fuel for heat-needed activities (e.g., cooking, heating) in developing countries, while this type of biomass is employed as a sustainable alternative to the ecosystem in developed countries [204]. Both thermochemical and biochemical processes have been explored in order to convert this type of biomass into value-added products [205].

6.2.1. Physico-Chemical Characteristics of Lignocellulosic Biomass

Biomass is known as hydrocarbon materials containing carbon, hydrogen, and oxygen, along with minor quantities of nitrogen, sulfur, and various minerals [206], which exhibits a predominant elemental composition on a dry mass basis, comprising approximately 30–40% oxygen, 30–60% carbon, and 5–6% hydrogen, with variations influenced by the ash content [207,208]. Properties of various lignocellulosic biomass are listed in Table 3.

Lignocellulosic biomass contains typically 20–40% of hemicellulose, 40–60% of cellulose, and 10–25% of lignin [209]. Those components are degraded under different range of conversion temperatures. Cellulose is a glucose polymer, consisting of linear chains of glucopyranose units [210,211], which is degraded at 240–350 °C [212]. Hemicellulose is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylose, and arabinose [210,211]. The degradation of hemicellulose is found in the temperature range of 225–315 °C [213]. Lignin is a group of amorphous, high-molecular-weight, chemically related compounds [210,211]. Due to its very complex structure, it is more challenging to decompose lignin compared to hemicellulose and cellulose [213]. Kruse et al. (2018) [214] also reported that there is no complete conversion for lignin at low HTC temperatures, especially less than 200 °C, but the degradation occurs slowly at a broad temperature ranging from 250 to 500 °C [215].

Table 3. Physico-chemical and thermal characteristics of different lignocellulosic biomass.

Lignocellulosic Biomass	MC (%)	VM ($\%_{db}$)	FC ($\%_{db}$)	Ash ($\%_{db}$)	H/C (-)	O/C (-)	Refs.
Coconut fiber	n.a.	80.9	11.0	8.1	1.4	0.7	[216]
Eucalyptus leaves	n.a.	79.2	10.3	10.5	1.6	0.7	[216]
Miscanthus	n.a.	87.5	11.7	0.8	1.5	0.7	[217]
Empty fruit bunch	n.a.	78.7	15.3	5.9	1.7	0.8	[218]
Pine wood meal	n.a.	87.3	12.4	1.2	1.8	0.8	[219]
Corncob	n.a.	81.1	17.5	1.4	1.6	0.7	[220]
Cornstalk	n.a.	n.a.	n.a.	4.6	1.6	0.7	[221]
Tamarix ramosissima	n.a.	n.a.	n.a.	4.4	1.6	0.7	[221]
Sugar beet	n.a.	75.4	18.5	6.2	1.6	0.6	[222]
Bark	n.a.	66.8	25.5	7.7	1.3	0.4	[222]
Corncob residue	n.a.	78.6	17.2	4.2	1.6	0.8	[214]
Hyacinth	n.a.	52.9	6.7	40.4	2.2	0.6	[223]
Wood sawdust	n.a.	83.1	9.5	7.4	1.7	0.6	[117]
Bamboo	n.a.	80.0	17.6	2.4	1.7	0.7	[224]
Primary sewage sludge	n.a.	68.6	3.9	27.5	1.9	1.1	[225]
Wood chip	4.6	56.9	40.0	3.1	n.a.	n.a.	[184]
Sugar beet pulp	6.9	75.4	18.5	6.2	n.a.	n.a.	[222]
Bark	7.0	66.8	25.5	7.7	n.a.	n.a.	[222]
Oak	5.8	79.1	14.6	0.5	0.1	0.8	[226]
Pine	7.6	79.9	12.3	0.3	0.1	0.7	[226]

n.a. = not analyzed; MC = moisture content; VM = volatile matter; FC = fixed carbon; C = carbon, H = hydrogen; O = oxygen.

6.2.2. Properties of Carbonized Solids (from Pyrolysis and Hydrothermal Carbonization) Derived from Lignocellulosic Biomass

Different carbonization process leads to the change in pH of HC and pyrochar (P). Wiedner at al. (2013) [227] found in their study on various biomass that the pH of hydrochar increased with an increasing HTC temperature (4.7 at 220 °C and 5.4 at 280 °C), while the pH of pyrochar maintained a relatively high pH value of, for example, 7.7, 9.8, 10.6, and 10.5 for samples produced at 350, 500, 650 and 800 °C [228]. HCs showed a lower increase in ash content compared to pyrochar, for example, 50 to 471 g/kg (pyrochar) and 46 to 513 g/kg (HCs) [227]. The HHV of HCs increases with an increasing HTC temperature, while the pyrochars remains a stable HHV with increasing pyrolysis temperature (Jian et al., 2018). This leads to a better combustibility of HCs at the heating rate of 20 °C/min compared to that of pyrochar [228]. Proximate and ultimate analysis of different lignocellulosic biomass are presented in Table 4.

Regarding the surface area, Garlapalli et al. (2016) [229] found in the results that pyrochar at 800 °C had a 5.5 times larger surface area than HC at 260 °C, and 2.5 times larger than a mixture of pyro-HTC. The adsorption capacities for methylene blue, iodine, and copper are higher by using HCs, suggesting the predominant role that surface function-

alities may have on the adsorption performance of HCs; however, the capacity of copper adsorption was better by using pyrochar correlated to the surface area from 1.8 m^2/g (350 °C)–122.6 m^2/g (800 °C) [228].

With respect to the safety in soil application, Wiedner et al. (2013) [227] found that pyrochars have higher proportions of PAH fractions than HCs, but pyrochars have lower total PAH amounts than HCs.

Table 4. Physico-chemical and thermal characteristics of pyrochars and hydrochars derived from different lignocellulosic biomass at various process conditions.

Lignocellulosic Biomass	P and HC	MC (%)	VM ($\%_{db}$)	FC ($\%_{db}$)	Ash ($\%_{db}$)	C ($\%_{db}$)	H ($\%_{db}$)	N ($\%_{db}$)	S ($\%_{db}$)	O ($\%_{db}$)	Refs
Wood chip	P250	3.96	59.1	38.3	2.6	62.8	7.41			25.8	[184]
	P500	7.74	14.2	80.3	5.6	81.9	4.03			6.0	
Sugar beet pulp	s-H200	4.6	61.0	32.0	7.1	67.3	3.6	4.2	0.1	24.8	[222]
	w-H200	4.1	66.2	21.2	12.6	61.3	5.4	5.3	0.1	27.8	
	w-H250	4.7	51.8	35.7	12.5	71.1	7.6	1.7	0.9	17.1	
	w-H250	3.9	50.0	38.1	12.0	72.2	7.1	2.7	1.2	18.0	
Bark	s-H200	6.0	56.1	37.3	6.6	69.0	3.1	1.5	0.1	26.3	[222]
	w-H200	10.0	56.1	35.1	4.7	64.4	3.1	1.5	0.1	27.5	
	w-H250	3.7	50.6	43.2	6.2	70.8	6.1	0.1	0.6	21.3	
	w-H250	4.4	45.2	46.9	7.9	72.2	6.0	0.4	0.7	17.7	
Algae	H200	n.a.	n.a.	n.a.	0.3	66.3	7.9	7.3		18	[230]
	H250	n.a.	n.a.	n.a.	0.2	48.9	9.1	7.9		16.5	
Corncob	P350	n.a.	32.2	65	2.8	76.5	4.2	n.a.		12.9	[220]
	P400	n.a.	24	72.3	3.7	80.1	3.7	n.a.		8.8	[230]
	H230	n.a.	67.2	31.3	1.5	n.a.	n.a.	n.a.		n.a.	
Coconut shell	P350	n.a.	28.6	49.9	21.5	n.a.	n.a.	n.a.		n.a.	[190]
	P500	n.a.	16.7	55.5	27.8	n.a.	n.a.	n.a.		n.a.	

P = pyrochar; HC = hydrochars; n.a. = not analyzed; FC = fixed carbon; s = solid; w = water; C = carbon; H = hydrogen; N = nitrogen; S = sulfur; O = oxygen; Numbers after the first letter show reaction temperature in °C (Ex. H200 = HTC at 200 °C).

6.2.3. Potential Application of Carbonized Solid (Pyrochar and HC) Derived from Lignocellulosic Biomass

Biochar (e.g., pyrochar and HC) is considered as a promising adsorbent for pollutants in wastewater and exhaust gas [21], e.g., Cd removal from aqueous solution [231]; nitrobenzene removal in aqueous and soil phases [232]; etc.

Pyrochar exhibits potential for enhancing the remediation of polluted environments with appreciable adsorption capability of Pb and atrazine, reported at 100% and 77%, respectively [233]. Pyrochar also enhanced protein catabolism by increasing leaf proteolytic activities, and on the other hand, by enhancing protein anabolism [234].

HC may not be suitable for soil amendment without proper treatment [102,235,236], because high total PAH concentration is found in HC [229]. An increase in emissions of NH_3, CO_2, and CH_4 from soil was found for HCs, although it decreased N_2O emissions compared to un-amended soil [237]. The KOH-treated wheat straw, corn stalk, and sawdust HC were found to be effective for the sorption of cadmium in aqueous solutions, resulting in 2–3-times-higher sorption capacities compared to that of their unmodified counterparts (30.40–40.78 mg/g vs. 13.92–14.52 mg/g) [11].

7. Conclusions

This study addressed the current state of the art on the strategic research issues relating to HTC technology, thus allowing us to obtain the following conclusions:

Technology comparison (pyrolysis vs. HTC): More studies comparing pyrolysis and HTC of a given feedstock are needed. Whereas the convenience of using one or other process depends on the type of feedstock, a better comparative understanding of the specific expected target products that can be obtained from them is essential to make a successful

choice of experimental designs towards a given application. Also, research should be conducted on the strategic combination of these two processes to lower energy input or to obtain particular features on the final carbon material that would not otherwise be possible using the two processes separately.

HTC process modelling: Modeling tools could provide substantial aid in the industrialization of HTC, favoring the fundamental comprehension of the involved phenomena, facilitating the scale-up of reactors and optimizing plant schemes. At present, the modeling activities on HTC are, however, quite lacking, with most of the published works being primarily devoted to experimental activities. Before models can be applied more extensively, some doubtful aspects must be clarified. To achieve this, there is a need for more established reaction pathways and kinetics, clearer and more versatile mathematical descriptions of the reacting media's rheology, and more certainty on the process's overall energy demand. All these targets can be aided by a wider and more standardized sharing of experimental data, which thus far has been quite limited and unmethodical. Such data would also help perform LCAs and tune machine-learning techniques.

Hydrochar as soil improver: A large number of research projects have been carried out on the effect of hydrochar on soil properties, organisms, and plants, as well as on the behavior of nutrients and pollutants in soil. The effect depends not only on the input material and process parameters of HTC, but also on the soil properties themselves, adding a lot of complexity to the issue. Some knowledge is available on the influence of the HTC input material on the soil pH and thus on adsorption processes, as well as on the influence of HC on the soil water regime. The influence on plant growth is contradictory, depending on the effect of the release of nutrients and growth-inhibiting substances from the HC. For these and other processes, the rate of degradation of HC is one of the key parameters. The easily degradable fraction of hydrochar promotes the activity of soil organisms, while the question of whether the less degradable fraction leads to carbon sequestration is still under discussion. Predictions of the rate of degradation based on laboratory or short-term field experiments result in a wide range of timespans. Lab experiments to better understand degradability processes and the possible effect of primary and secondary hydrochar are essential for a better understanding of degradation processes, in combination with long-term field experiments under realistic conditions. This knowledge is a prerequisite for a more insight on the effect of HC on soil organisms as well as on nutrient flows and the release of pollutants.

Management of HTC process water: More research on PW composition as a function of operating parameters is needed and the means of valorizing it to extract valuable compounds and guarantee a proper management. Its high organic load makes PW suitable for anaerobic and aerobic digestion processes, the latter being less studied. Other classical water treatment techniques could also be applied, but studies on their techno-economic feasibility, are scarce. In addition, PW recirculation in HTC processes is beneficial and brings out greater SY, more favorable kinetics and thermal balance; in this aspect, extraction of specific compounds before reusing PW has been scarcely addressed so far.

Biomass selection for HTC: Various types of biomass have been used as initial feedstocks in thermo-chemical conversion; however, biomass selection based on its properties and the final desired products (pyrochar and hydrochar) is still undeveloped. Therefore, a high demand for investigation of biomass selection for final products in different application areas needs to be considered in further research. Manure properties with high nutrient and moisture contents make it a good candidate for HTC; studies have proved that it can facilitate a very efficient capture of nutrients on the PW, and the organic matter could further be transformed into stable compounds, which can be used in soil. On the other hand, lignocellulosic biomass with different moisture contents is also well converted into hydrochar, which contains high energetic properties being suitable for combustion. However, it is still under consideration for soil application due to the presence of PAH and aromatic compounds. It is important for post-treatment methods to be addressed to improve those properties of hydrochars for soil application.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy14020247/s1, Figure S1: HTC research needs and actions, as identified from OCDE Workshop ("Innovative Hydrothermal Systems to Valorize Agricultural Residuals: Roadmap towards implementation—achievements and barriers").

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