









Review

Advances in Research and Technology of Hydrothermal Carbonization: Achievements and Future Directions

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Abstract: Hydrothermal carbonization (HTC) has emerged as a pivotal technology in the battle against climate change and fosters circular economies. Operating within a unique reaction environment characterized by water as a solvent and moderate temperatures at self-generated pressures, HTC efficiently converts biomass residues into valuable bio-based products. Despite HTC's potential—from the management of challenging biomass wastes to the synthesis of advanced carbons and the implementation of biorefineries—it encounters hurdles transitioning from academic exploration to industrial implementation. Gaps persist, from a general comprehension of reaction intricacies to the difficulty of large-scale integration with wastewater treatments, to the management of process water, to the absence of standardized assessment techniques for HTC products. Addressing these challenges demands collaboration to bridge the many scientific sectors touched by HTC. Thus, this article reviews the current state of some hot topics considered crucial for HTC development: It emphasizes the role of HTC as a cornerstone for waste management and biorefineries, highlighting potentialities and challenges for its development. In particular, it surveys fundamental research aspects, delving into reaction pathways, predictive models, analytical techniques, and HTC modifications while exploring HTC's crucial technological applications and challenges, with a peculiar focus on combined HTC, wastewater integration, and plant energy efficiency.

Keywords: hydrochar; modeling; hydrothermal humification; nutrient recovery; co-HTC; anaerobic digestion; analytical techniques; energy analysis; concentrated solar energy

1. Introduction

In a historical period driven by the urgency of addressing climate change and environmental issues, hydrothermal carbonization (HTC) has emerged as a thermochemical

technology for establishing biorefineries and implementing principles of a circular economy. Due to its distinctive reaction environment, using water as a solvent and operating at relatively moderate temperatures (typically between 180–250 °C) and self-generated pressures of 10–50 bar, HTC distinguishes itself by efficiently converting biomass residues and wastes into highly valuable products while serving as a waste management strategy [1]. The resulting products mainly consist of a solid phase rich in carbon, known as hydrochar (HC), and a liquid phase abundant in organic compounds, referred to as HTC liquor or HTC process water (PW).

While HTC research started with the conversion of substrates like sugars or common lignocellulosic biomass, in recent years, there has been a deep interest in merging it with treatment strategies. Indeed, HTC is well-suited for valorizing challenging-to-manage biomass with high heterogeneity: the thermochemical environment is aggressive enough to cause a deep reorganization of the initial substrate and concentrate difficult compounds in one of the phases (typically liquid or solid) resulting from HTC. This has led to an internal split in HTC research, with one path studying “simple” substrates like sugars for producing advanced carbons [2] and the other path focusing on waste treatment, where the final hydrochar is mainly used for coal co-combustion [3] or soil amendment [4]. The waste stream path opened up a more direct industrial application of HTC, meeting treatment needs. Typical wastes include urban waste such as sewage sludge [5] and food waste [6,7], digestates [8,9], organic waste from the zootechnical sector such as manure [10,11] and the agro-industrial sector such as fruit processing residues [12], as well as emerging substrates like algae or medical wastes [13]. For instance, algae were converted via HTC to recover biofuels and chemicals [14–16], removing some dyes [17] and also promoting plant growth [18].

In the past 10–15 years, there has been a constant growing interest in HTC marked by significant progress in both fundamental research and technological applications. Research efforts have substantially enhanced our understanding of the intricacies of the HTC process, unraveling numerous underlying conversion mechanisms which are inherently complex [19]. Simultaneously, extensive work has been dedicated to applying HTC within the realm of waste management and using hydrochar in various applications [20]. However, despite the fervent amount of academic research, HTC remains a niche in biomass conversion technology. While the first operational industrial-scale plants were set up around ten years ago (like the Ingelia[®] plant in Valencia/Spain and the Terranova[®] plant in Jining/China), the current worldwide scene counts only a few plants worldwide [21]. The moment of finalizing the many efforts made until now to transit from theoretical applications to industrial plants can arrive if we face some indispensable challenges. HTC’s interdisciplinary nature, bridging many sectors, like waste management, with their new frontier technology [22], along with material science, chemistry, and agronomy, offers advantages in terms of leveraging established concepts. However, there is a risk of sectoral polarization without an efficient exchange of information among these diverse fields, limiting the common knowledge.

While there exists a general comprehension of HTC mechanisms, the intricate nature of the reaction environment and feedstocks still presents a significant area that lacks complete understanding. This knowledge gap offers research opportunities to delve deeper into the formation mechanisms of hydrochar and its derivative compounds. Shedding light on these reaction mechanisms is vital not only for advancing scientific knowledge, but also for optimizing products and tailoring process conditions to produce specific outputs. Moreover, modeling at many levels, from kinetic to statistical to plant simulations, is still lagging despite its importance for the optimization and design of the process, and increases attractiveness to investors despite other technologies. Furthermore, the assessment of HTC products lacks standardized assessment techniques, resulting in a hydrochar undefined for regulations, particularly when derived from waste sources, presenting challenges in uniform evaluation. Moreover, there is a certain hesitancy to modify HTC chemically, often maintaining water as the sole solvent or refraining from combining vastly different

substrate types (such as plastics), thereby restricting its potential for advanced applications. Technologically, the integration of HTC with wastewater treatment plants offers a unique opportunity to harness its efficiency, reducing sludge volumes and enhancing overall plant performance. However, complete integration faces challenges due to the absence of proper regulations and the production of PW, leading to certain issues. The liquid waste, often disregarded despite its high organic carbon content and chemical oxygen demand, raises potential environmental concerns, which in turn dissuade industries from adopting this approach. There is also a general scarcity of comprehensive analyses and limited data sharing regarding large-scale plants, notably in economic and energy analyses. This lack of data restricts opportunities for further advancements in this domain, particularly on a larger scale.

In this context, this article reviews various critical topics aimed at advancing the field, summarizing the current state of the art and presenting suggestions and challenges for further development. The article dives into two core facets of HTC, exploring topics that center around both fundamental research and technological development. Specifically, Section 1 addresses topics concerning fundamental research, commencing with an overview of reaction pathways and extending to models utilized in predicting hydrochar properties and analytical techniques. It also touches on some boundary concepts for HTC—hydrothermal humification and fulvification—where the HTC chemistry is modified to produce high-quality substances mainly for agricultural applications. Section 2 delves into the applications and technological aspects of HTC. It reviews the potential synergies in treating different substrates through co-HTC, particularly in conjunction with wastewater treatment plants. These plants typically encompass an anaerobic digestion compartment aimed at biogas production. Notably, the HTC PW is recirculated back into this system to augment the biogas yield and potentially recover macronutrients (like P, N, and K) beneficial for the agricultural sector. The section concludes by discussing considerations on the energy efficiency of HTC plants, incorporating an energy analysis conducted on a continuous pilot plant located in Switzerland.

Thus, this work intends to offer an overview of HTC, focusing on research and technological applications. Each topic shows its state of the art, with suggestions to fill the gaps in basic and applied knowledge to try to advance the research and development of HTC. Actually, this scientific contribution is an outcome of the OECD workshop that took place in May 2023 in Seoul (Republic of Korea), where the authors had the chance to meet, become familiar, and exchange ideas.

2. Around the Fundamentals

This section delves into the intricate realm of hydrothermal biomass conversion, exploring its multifaceted aspects, from reaction pathways to predictive models to analytical techniques. It begins by unraveling the complexity of reaction pathways in biomass conversion, elucidating mechanisms like primary and secondary char formation following biomass hydrolysis and dissolution (Section 2.1). Then, it provides details on models predicting hydrochar properties, encompassing artificial intelligence, statistical models, and mechanistic approaches, highlighting their predictive accuracy and potential applications (Section 2.2). Additionally, it investigates analytical techniques utilized in hydrothermal conversion studies, aiming for standardized characterization of HTC products (Section 2.3). Finally, it delves into the boundaries of hydrothermal conversion, expanding into humification and fulvification processes (Section 2.4). The differentiation of these processes delineates their chemical boundaries and product traits, shedding light on their potential applications within agricultural and environmental contexts.

2.1. Reaction Pathways

The hydrothermal conversion of biomass entails enormous complexity. The intricacy spreads at different levels, from the variability of the substrate to the chemistry involving the interaction of biomass with hot, pressurized liquid water. Pressurized hot water, repre-

senting the connotate of the “hydrothermal” environment, has properties and a chemistry completely different from ambient conditions, acting macroscopically as a non-polar solvent and keeping its polar structure at the same time [23,24]. Biomass is an obnoxious substrate: heterogeneous, seasonal, degradable, and with a highly variable composition. In addition, hydrothermal processes suit the treatment of heterogeneous substrates in the waste management field, welcoming biomasses which were ignored up to a few years ago—algae, sewage sludge, and organic wastes, for example. Thus, apart from the constituents of lignocellulosic biomass, a multitude of other constituents, like oil, proteins, organics, and metals, enter the story. The result is a highly complex environment, where each component, with its structural and chemical properties, interacts with the others and with hot liquid water via heterogenous and homogenous reactions. This is a fantastic playground for researchers, who started to dig into the basic mechanisms of hydrothermal conversion around 20 years ago, with the pioneering works of Japanese [25,26] and European-based researchers [27–30]. Complicit in the intrinsic complexity of the reaction environment, the hydrothermal conversion of biomass is still not fully understood, with several mechanisms being unclear, leaving space for further research. Indeed, the multicomponent nature of biomass limits our ability to understand precise reaction pathways. Despite this complexity, a general approach to understanding the mechanisms can assist with process optimization and scaling up: tailoring process conditions can maximize the production of target compounds and minimize energy inputs to the process. Moreover, deeper comprehension of these mechanisms is pivotal for synthesizing advanced carbon materials, where understanding the structure of the final materials is crucial for producing platform molecules or custom-designed chars. Indeed, the material synthesis from hydrochars is a well-established field of research. Hydrochars have some unique properties compared to biochars, such as easy tunability (for example, by adding different components) and functionalization thanks to the abundance of oxygenated functional groups, which makes them green candidates for material applications [4]. Hydrochars are currently being investigated for energy storage applications, for example, as graphite replacing lithium-ion batteries or starting material for composite electrode supercapacitors [4].

2.1.1. Reaction Mechanisms in HTC

In the realm of macro-mechanisms, we can identify some common pathways according to the phase: solid-to-solid, solid-to-liquid, liquid-to-liquid, and liquid-to-solid. Biomass can proceed via a solid-to-solid route, forming the primary char, and a dissolution phase, resulting in a spectrum of compounds within the liquid phase. Dissolved compounds can further degrade into the liquid phase or undergo repolymerization into secondary char via a liquid-to-solid path. Both solid phases and dissolved organics can form gas. The detailed mechanisms involve a multitude of reactions, often including hydrolysis, decomposition, recombination, and aromatization. Generally, the prevalence of one mechanism or a specific reaction highly depends on the initial substrate’s composition and operating parameters. Thus, the relative abundance of microconstituents—macromolecules such as carbohydrates, lignin, lipids, proteins, and potentially metals—becomes pivotal for subsequent stages. Figure 1 shows a reaction scheme of carbohydrate-rich feedstock. The interplay of operating conditions, encompassing temperature, duration, biomass-to-water ratio, pH levels, possible presence of catalysts, and heating/cooling intervals, is critical in shaping the process. Below are some details on the mechanisms.

Primary char formation. Primary char forms via the solid-to-solid conversion of biomass. This mechanism occurs in the inner layers of biomass particles and is similar to torrefaction/pyrolysis [19]. Primary char has a structure and morphology that resembles that of the parent biomass, which undergoes bulk carbonization reactions that rearrange the inter- and intramolecular structures. Reactions include dehydration, deoxygenation, decarboxylation, and aromatization. This mechanism results in carbon densification and a higher number of aromatic structures that confer an improved thermal stability to the material [31,32]. In the

case of lignocellulosic biomass and wastes, primary char predominates the final fraction of hydrochar due to the limited amount of soluble precursors.

Dissolution of biomass into the liquid phase forms a multitude of compounds. The initial dissolution mainly occurs via hydrothermal hydrolysis and consists of the partial depolymerization of biomass macromolecules into their monomers. It generally requires an excess of water surrounding the material, and it begins in a lower temperature range than other reactions. For example, in lignocellulosic biomass, the degradation starts with the hydrolysis of glycosidic bonds of the carbohydrates. The hemicellulose degradation starts at lower temperatures than cellulose due to its branched, non-crystalline structure. Monomers of cellulose and hemicellulose are sugars (mainly hexoses and pentoses), which are highly soluble in water. Lignin hydrolysis requires harsher conditions than carbohydrates due to its highly branched and aromatic nature, and therefore, its degradation is mild over the HTC range [33,34]. It depolymerizes into its monolignols and derivatives. Then, other constituents also hydrolyze: lipids, for example, present in algae or organic wastes, hydrolyze to free fatty acids and glycerol, and proteins to amino acids. Generally, biomass degradation is a kinetically slow step compared to reaction steps occurring in the homogeneous (liquid) phase [35].

Degradation of soluble compounds. The degradation of soluble compounds involves their further decomposition within the liquid phase, often resulting in the creation of an acidic environment that facilitates self-catalysis of biomass hydrolysis. For example, the increased concentration of H⁺ ions can weaken hydrogen bonds within the cellulose chain, promoting its cleavage [36]. Elevated temperatures cause monosaccharides to decompose into alcohols, furanic acids, and short-chain fatty acids. Under severe conditions, lignin monomers can rehydrate into acids, furans, and aldehydes, potentially forming alcohols and ketones. Simultaneously, proteins break down into amines, short-chain fatty acids, and aldehydes, with fatty acids undergoing esterification to become long-chain fatty acids [37]. When temperatures approach the liquefaction range (i.e., around 280–300 °C), reactive fragments may recombine into larger molecules, such as long-chain fatty acids, contributing to biocrude formation. Additionally, the presence of amino acids might activate Maillard reactions, hindering the formation of repolymerized solids and promoting biocrude formation. Furthermore, certain organics undergo adsorption on the hydrochar surface, acting as a sink for dissolved compounds [38].

Secondary char formation. Secondary char likely forms from polycondensation reactions involving intermediates dissolved in the liquid phase. This mechanism entails a conversion from liquid to solid, where intermediates engage in a sequence of polymerization and condensation reactions. Deriving directly within the liquid phase, secondary char often features a spherical morphology with nano/microscale domains, exhibiting physical–chemical properties distinct from the initial substrate. Indeed, its final properties mainly depend on operating conditions, such as process severity, concentration of intermediates, and pH of the reaction environment, often to a greater extent than the original substrate: Once the precursors are released in the liquid phase, secondary char formation proceeds independently from its original source. The composition of intermediates contributing to secondary char formation significantly hinges on the substrate: Hydroxymethylfurfural (HMF) for carbohydrates, phenolic fragments from lignin, and fatty acids from lipidic substrates [37]. For instance, HMF undergoes polycondensation and cross-linking, creating a furan-like structure. The intra-reactivity of functional groups, like hydroxy and aldehyde groups, accompanies a volume increase and enhanced hydrophobicity, leading to precipitation of nanoparticles that gradually enlarge in diameter. Various theories have attempted to elucidate the formation of carbon spheres, encompassing nucleation [30], coalescence [39], and hydrophobic ripening [40], yet a definitive theory remains elusive. For instance, Modugno and Titirici [41] recently proposed an approach based on MALDI techniques to identify specific monomers contributing to hydrothermal carbon formation. Notably, understanding the formation mechanism could finally provide a holistic theory and facilitate the tuning of parameters for material science applications [19]. Indeed, secondary char, taking the

form of carbon nano/microspheres, has gained significant attention as a precursor for synthesizing advanced carbons, occupying a well-established research domain. Apart from their distinctive morphology, these nano/microspheres possess intriguing characteristics such as a high concentration of functional groups, excellent tunability, and potential photoluminescence—properties that make them appealing as precursors for advanced carbon synthesis. To date, the majority of research on secondary char as a precursor of advanced carbon has primarily centered on derivatives originating from carbohydrates [42]. This focus likely stems from their high presence in biomass and their compatibility with HTC conditions, as they are easily converted into carbons.

Carbon dots represent a third solid phase achievable through hydrothermal conversion. Typically, they possess diameters smaller than 10 nm and exhibit distinct properties such as photoluminescence alongside crystalline domains, positioning them as candidates for high-tech applications. Owing to their colloidal nature, they disperse within the liquid phase. Although HTC is a recognized synthetic production approach for carbon dots [43–45], their formation remains not fully understood [2]. Current explanations involve nucleation as well as evolution mechanisms that include interactions with the gas phase.

Gas production. Both the solid and the liquid phases undergo reactions like decarboxylation and decarbonylation, which lead to gas formation: mainly CO₂, with a minor amount of CO [2]. Gas yield increases with process severity, but at limited extents compared to other thermochemical processes, making the gas phase often neglected.

2.1.2. Suggestions for Future Works

Research has notably advanced in untangling the fundamental aspects behind HTC over the years. The complexity is enormous, and addressing some specific points could lead to a deeper understanding of the mechanisms, aiming to formulate holistic theories and customize operating conditions to tailor the target products. In particular:

- Developing a robust theory explaining the formation of carbon nano and microspheres, mechanisms that are still not unanimously recognized. Shedding light on their formation could significantly contribute to a comprehensive understanding and offer insights into customizing operating conditions to achieve desired products. This need for clarity in mechanisms applies similarly to carbon dots, whose recovery could significantly enhance the appeal of HTC. Notably, carbon dots possess crystalline domains, a feature scarcely observed in carbon spheres. A more detailed investigation into the fate of carbon throughout the hydrothermal pathway could facilitate the development of overarching theories, contributing to a broader understanding of the process.
- Investigating in more detail the effect of pH, solvent polarity (for example, mixing water with other solvents), and the addition of catalysts. There is a notable lack of literature exploring modifications in the hydrothermal environment beyond acidity studies. Understanding the effects of specific additives could assist in tailoring operating conditions and optimizing parameters, especially for multicomponent biomasses characterized by inherent variability that can be utilized in co-hydrothermal conversion. Furthermore, identifying certain additives could render hydrothermal conversion a compelling synthesis process, not only for hydrothermal carbons but also for various chemicals or platform chemicals.
- Performing tailored experiments following some target compounds (for example, a specific chemical) along kinetic parameters such as, for example, time and temperature. This approach could establish guidelines for a biorefinery operation and provide kinetic data essential for refining and calibrating advanced models of kinetics and processes.
- Expanding basic research on substrates beyond conventional biomasses is pivotal. The domain of waste management offers diverse feedstock, including plastic, bioplastic residues, and metals within waste materials. Their treatment has the potential to generate products distinct from those derived from traditional hydrothermal conversion substrates. This exploration could broaden the spectrum of potential end-products

and reveal the interplay among these varied products, as well as widen the range of potential materials of interest.

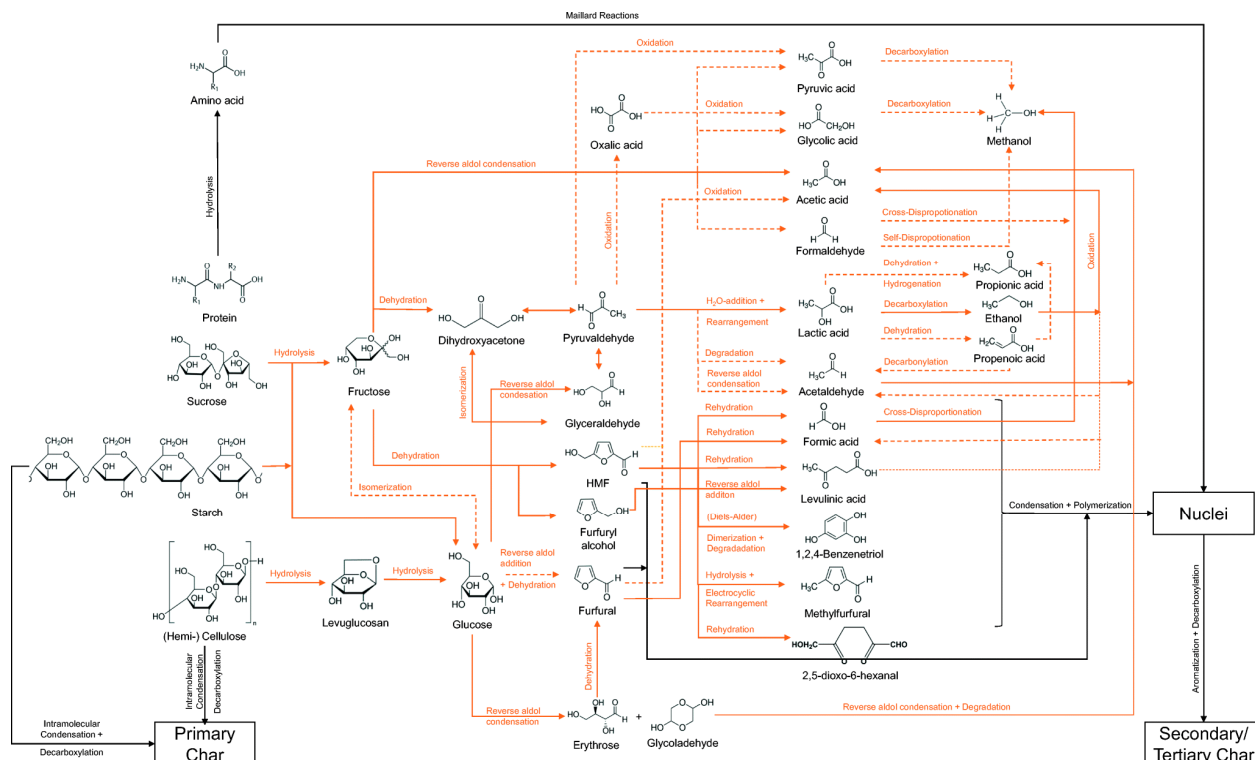


Figure 1. Reaction pathways of relevant organic components from the HTC of carbohydrate-rich biomass. The formation of gases is not shown. Image reproduced with permission from Wust et al. [46].

2.2. Models Predicting Hydrochar Properties

Hydrochar is the most widely studied product generated from the HTC of organics. Much of this interest is a result of the many possible applications in which it may be used, including as a soil amendment, solid fuel, adsorption medium, and energy storage [32,47–49]. The composition and structure of hydrochar have been well characterized for a variety of feedstocks carbonized over a wide range of reaction conditions [50]. As a result, significant efforts over the past decade have been focused on developing models to predict several hydrochar properties based on feedstock characteristics and carbonization conditions. These models have been developed using artificial intelligence/machine learning algorithms and statistical approaches, as well as more mechanistic approaches based on reaction pathways and kinetics. In this section, we report a short review on the state of the art of current models.

2.2.1. Current Artificial Intelligence/Machine Learning and/or Statistical Models

Table 1 highlights some representative efforts associated with the use of artificial intelligence/machine learning and/or statistically based models to predict hydrochar properties. As shown, a variety of different modeling algorithms have been used, each predicting different hydrochar properties with acceptable levels of accuracy. Recently, Zhang et al. [51] conducted a review of similar models and reported that the R^2 values with the models they reviewed were greater than 0.80, with most of the models having R^2 values greater than 0.90. It is important to note that these types of models are most often developed with large datasets (>100 points, see Table 1) populated with data obtained from the literature. As a result, these models generally have wide applicability, which is a distinct advantage associated with this approach. Exceptions to this exist in a few cases in

which the models were developed using data only from a specific study (see Table 1). In these instances, model applicability is more limited. An important element of many of these modeling efforts is the inclusion of an analysis regarding parameter (or feature) importance. This type of analysis is impactful, as it can be used to understand the relative importance of different input variables on the output [51], which has the potential to improve our understanding of carbonization processes and aids in the prioritization of future modeling and experimental efforts related to property prediction.

When using artificial intelligence/machine learning and/or statistical models, hydrochar properties related to energy-based applications, such as higher heating value (HHV), energetic retention efficiency (ER), and solid yields, are commonly predicted (Table 1). Hydrochar combustion for energy generation is a popular route for hydrochar valorization, so the focus on energy-related properties is not surprising. These properties appear to be predicted accurately with these models. What is important to note, however, is the lack of studies linking work associated with hydrochar combustion and feedstock and carbonization conditions. This represents an important knowledge gap. Work by Ischia et al. [6] highlighted the potential need for hydrochar processing (e.g., removal of adsorbed organics) for efficient energy generation. Understanding and including this information in future modeling work is necessary to obtain predictions that have more impactful and meaningful results. Significant use of artificial intelligence/machine learning and/or statistical models has also been dedicated to predicting both the ultimate (e.g., C, H, O, N) and proximate (e.g., ash, volatile matter) properties of hydrochar. Being able to accurately predict these hydrochar properties is also quite valuable when considering hydrochar's use options. Hydrochar's nitrogen and phosphorus contents have also been predicted and used to provide a preliminary assessment of its potential applicability for use in soils. It is important to note that, although these elements may be important when considering hydrochar's application to soils, previously published studies indicate that other hydrochar properties, which have not been considered in current models, may also play a role in soil applications [38,52,53].

2.2.2. Current Mechanistically Based Models

More mechanistically based models have also been developed and used to predict hydrochar properties. In the majority of these models, reaction pathways were proposed, and reaction kinetics (most commonly assumed to be first-order) were used to model the carbonization processes. Román et al. [49] reviewed and described several of these models. In terms of hydrochar properties, solid yields and, most often, carbon content are predicted. This modeling approach is quite valuable for understanding carbonization mechanisms. Bevan et al. [54] recently provided a mini-review of efforts modeling carbonization reaction kinetics, with particular attention paid to the proposed reaction pathways. Several kinetic models have been reported in the literature for a variety of feedstocks, including kitchen waste [55], coconut shells [56], grape marc [57], and olive trimmings [58]. Bevan et al. [54] developed and evaluated kinetics models to predict the carbon distributions in the solid, liquid, and gas phases resulting from the HTC of cellulose, hemicellulose, and lignin. They demonstrated that, from their kinetic model, they were able to accurately predict carbon distribution from carbonization data collected from the literature (106 experimental data points).

Predictions of hydrochar properties have also been made using models based on the severity factor. In this approach, the effects of temperature and time are combined into a single factor that defines the overall reaction severity based on a coalification model reported by Ruyter in 1982 [59]. Such an approach has been proven to be valuable in predicting some hydrochar properties [60]. Suwelack et al. [61,62], for example, used the severity function to predict hydrochar yields and different elemental ratios associated with the hydrochar (H/C and O/C). Guo et al. [63] combined reaction severity and the dose–response function to correlate severity factors with hydrochar yield, carbon, and energy content. More recently, Spitzer et al. [64] correlated the severity factor with yield

($R^2 = 0.88$), carbon content ($R^2 = 0.85$), and HHV ($R^2 = 0.90$), illustrating its utility in providing insight into hydrochar properties.

2.2.3. Suggestions for Future Works

The sections above highlight the efforts made to date in developing models to predict hydrochar properties. However, important knowledge gaps remain. Models connecting important hydrochar properties and/or characteristics with their intended use are lacking. Developing models that can be used to make this connection represents an important and pressing need in the HTC area.

One of the challenges in developing such models is a lack of data identifying the important hydrochar properties associated with different intended uses. Experiments aimed at identifying and validating such information are needed. Because it is likely that more than one factor may influence hydrochar use in a specific application, the generation of application-specific indices in which multiple factors, and thus their relationships, are described may be most beneficial. Pairing experimental data and modeling approaches may aid in the generation of these indices. Once such information is gained, the development of robust models that predict how feedstock properties and carbonization conditions may be used to generate hydrochar with properties conducive to its application in specific uses can be achieved. These types of models are greatly needed to guide the design and implementation of industrial-scale processes.

2.3. Analytical Techniques Adopted for HTC

The HTC of biomass results in three distinct phases: the hydrochar, the HTC liquor abundant in organics, and a gas phase, each of them requiring specific analytical techniques for their assessment and valorization. A proper and detailed characterization is the baseline to perform any kind of study, from fundamental research to application. Moreover, fine-tuning their properties under optimized reaction conditions becomes crucial for product optimization. For example, hydrochar could be applied for soil amendment [85], environmental remediation such as heavy metal stabilization [86], carbon sequestration [87], and alternative fuels as a capacitor [87–89]. Each application necessitates a tailored set of analytical techniques to ensure top-notch quality. Then, the HTC liquor, comprising a wide array of compounds like organic acids, phenolics, furans, and other volatile substances [76], demands meticulous characterization to assess its management and potential recovery. This liquid product finds utility in diverse areas, from agricultural use as a nutrient-rich liquid fertilizer to bolster soil properties and crop growth to energy applications like biofuels or refined fuels [90]. Finally, the gas phase, often overlooked, can exhibit varied yield and composition, potentially containing carbon dioxide, methane, hydrogen, and volatile organic compounds [88]. Despite its dismissal, characterizing this phase is crucial, especially for evaluating overall process efficiency.

Below, we review the current analytical techniques adopted in HTC, emphasizing their strengths and drawbacks.

2.3.1. Current Status of HTC Analysis

Currently, the characterization of HTC products relies on instrumental analysis using spectroscopy, electrochemical analysis, chromatography, and other miscellaneous analytical methods. The complexity of reaction mechanisms involving diverse feedstock composition and HTC products requires a holistic understanding using various analytical techniques. Analytical techniques used to characterize HTC products and the information they provide are summarized in Table 2 excluding electrochemical analysis. In HTC studies, electrochemical analysis was mainly conducted to evaluate the potential for use as a new material in energy-related applications such as batteries, supercapacitors, and fuel cells [49,91]. It measures the electrochemical properties of hydrochar, including electrical conductivity, capacitance, charge–discharge behavior, and electroanalytical activity [88,92].

Table 1. Representative studies illustrating the use of artificial intelligence/machine learning and/or statistical models in predicting hydrochar properties.

Feedstock ¹	Specific Model ²	Data Source	Input Parameters ³	Predicted Parameters ³	Prediction Quality	Parameter Importance	Source
Variable	ANN combined with PSO	296 data points from lit.	EC, PC, temp, time, SLR	Yield, HHV, ash, dehydration degree, decarboxylation degree	R ² > 0.83	Yes	[65]
Variable	DTR, SVR	536 data points from lit.	EC, PC, temp., time, WC	Yield, HHV, PC, EC	R ² > 0.88	Yes	[66]
Variable	SVR, RF	248 data points from lit.	EC, PC, temp., time, WC	Yield, HHV, ER, ED	R ² > 0.88	Yes	[67]
SS	MLP	138 data points from lit.	EC, PC, temp., time, WC	N	R ² > 0.87	No	[68]
SS and LCB	XGB, RF	221 data points from the lit.	EC, PC, temp., time, SLR	C, H/C, O/C, N/C, HHV, Yield, FR, ER	R ² > 0.83	Yes	[69]
Variable	RF, SVM, DNN	248 data points from lit.	EC, PC, temp., time, WC	Yield, HHV, C, CR, ER, N/C, H/C, and O/C	R ² > 0.88	Yes	[70]
Municipal sludge	RF, GBT, ANN	246 data points from lit.	EC, PC, temp., time, WC	HHV, CR, ER	R ² > 0.84	Yes	[71]
Variable	ANN, RF, XGB, GBDT,	169 data points from lit.	SSA, pH, adsorption, dosage	Adsorption capacity	R ² > 0.86	Yes	[72]
Variable	RF, SVM, XGB	333 data points from lit.	EC, PC, HHV _o , temp, time, SLR	Yield, ash, C, HHV, ER	R ² > 0.83	Yes	[73]
Variable	graph-based GP	302 data points from lit. and exp	EC, HHV _o , temp, time, SLR	Yield, HHV, ER	R ² > 0.73	Yes	[74]
SS	MLP	70–110 data points from lit.	EC, temp., time	HHV, yield	R ² > 0.94	No	[75]
Variable	GEP, MISO-ANN, MLR	115 data points from lit. and exp.	PC, temp, time	Yield, ER, HHV	R ² > 0.96	No	[76]
Variable	E-SVM, SMA	281 data points from lit.	PC, EC, WC, time, temp	Yield, HHV, C	average R ² of 0.94	Yes	[77]
Poultry litter	hybrid ANN-Kriging	21 data points from exp.	Temp, time	Inorganic phosphorus recovery and carbon recovery rate	R ² > 0.91	Yes	[78]
SS	MLR	45 data points from lit.	EC, PC, temp, time, R	EC, PC	R ² > 0.84	No	[79]
SS	RF	109 data points from lit.	PC, EC, temp, time, pH, WC	P	R ² > 0.92	No	[80]
Variable	RF	1429 data points from lit.	PC, EC, CC, solids, temp, time	Yield, HHV	R ² > 0.90	No	[81]
CHLPL	Scheffe polynomial model	41 data points from exp.	Cellulose, hemicellulose, lignin, protein, lipid	Yield, HHV, ER, MCE	R ² > 0.89	No	[82]
Variable	MLR, RT, RF	475–649 data points from lit.	PC, EC, CC, solids, temp, time	Yield, C, HHV	R ² > 0.46	Yes	[50]

Table 1. Cont.

Feedstock ¹	Specific Model ²	Data Source	Input Parameters ³	Predicted Parameters ³	Prediction Quality	Parameter Importance	Source
Variable	RF, SVM, XGB	333 data points from lit.	PC, EC, HHVo, temp, time, SLR	Yield, Ash, C, HHV, ER	R ² > 0.83	Yes	[73]
Variable	MLR, RT	500 data points from lit.	SLR, temp, time, R, HHVo, H/C, O/C, PI, IR, fuel ratio, CC	Yield, HHV	R ² > 0.8	Yes	[83]
Food waste	RSM	20 data points from exp.	Temp, time, SLR	PC, EC, yield, HHV, ED, ER, EMC	R ² > 0.17	No	[84]

¹ CHLPL = cellulose, hemicellulose, lignin, protein, and lipid; LCB = lignocellulosic biomass; SS = sewage sludge; ² ANN = artificial neural network; DNN = deep neural network; DTR = decision tree regression; E-SVM = ensemble support vector machine; GBT = gradient boosting tree; GEP = Gene Expression Programming; GP = genetic programming; MISO-ANN = multiple-input single-output artificial neural network; MLP = multilayer perceptron; MLR = multilinear regression; PSO = particle swarm optimization; RF = random forest; RSM = response surface methodology; RT = regression tree; SMA = slime mode algorithm; SVR = support vector regression; SVM = supporting vector machine; XGB = eXtreme Gradient Boosting; ³ CC = chemical composition (cellulose, hemicellulose, lignin, ash); EC = elemental composition (C, H, O, N); HHVo = higher heating value of the feedstock; IR = reactivity index; PC = proximate composition (ash, volatile matter, fixed carbon); PI = polarity index; R = severity factor; SLR = solid to liquid ratio; SSA = specific surface area; WC = water content; CR = carbon recovery; ED = energy densification; EMC = equilibrium moisture content; ER = energetic retention efficiency; FR = fuel ratio; HHV = higher heating value; MCE = moisture content of wet hydrochar cake.

Table 2. Analytical methods used for characterization of hydrochar, liquid, and gaseous substances generated by HTC.

	Analytical Method ¹	Characterization	Information
Spectroscopy	UV-vis	Specific light-absorbing groups (chromophores)	Composition and reactivity of light
	FT-IR	Functional groups (aliphatic, aromatic)	Specific chemical bonds
	AA, ICP-OES, ICP-MS	Metal element	Metal element
	NMR	Chemical environment of atom	Arrangement of atoms; electronic environment around the nuclei
	Raman	Vibrational modes	Identification of carbonaceous structure and defects
Chromatography	XRD	Crystalline structure	Mineral phases and crystallinity
	GC-FID, GC-TCD, GC/MS	Volatile organic compounds	Volatile organic composition
	HPLC-UVD, HPLC-PDA, HPLC/MS	Non-volatile organic compounds	Non-volatile organic composition
	IC	Ionic compounds	Ionic composition
Miscellaneous analysis	TGA, DSC	Weight loss as a function of temperature	Thermal stability and decomposition behavior
	SEM, TEM	Morphology, porosity, surface features	Surface condition at micro- and nano-scale
	BET	Specific surface area	Adsorption capacity and reactivity
	Proximate analysis	Moisture content, volatile matter, fixed carbon, ash content	Combustion behavior and energy content
	Ultimate (elemental) analysis	Carbon, hydrogen, nitrogen, sulfur, oxygen	Elemental composition, reactivity, and stability
	Bomb calorimetry	Heating value	Energy potential
	TOC	Total organic carbon	Carbon transformation and conversion efficiency

¹ UV-vis = Ultraviolet-visible spectroscopy; FT-IR = Fourier-transform infrared spectroscopy; AA = atomic absorption spectroscopy; ICP-OES = inductively coupled plasma optical emission spectroscopy; ICP-MS = inductively coupled plasma mass spectrometry; NMR = nuclear magnetic resonance spectroscopy; XRD = X-ray diffraction spectroscopy; GC-FID = gas chromatography flame ionization detector; GC-TCD = gas chromatography thermal conductivity detector; GC/MS = gas chromatography mass spectrometry; HPLC-UVD = high-performance liquid chromatography ultraviolet-visible detector; HPLC-PDA = high-performance liquid chromatography photodiode array detector; HPLC/MS = high-performance liquid chromatography mass spectrometry; IC = ion chromatography; TGA = thermogravimetric analysis; DSC = differential scanning calorimetry; SEM = scanning electron microscopy; TEM = transmission electron microscopy; BET = Brunauer–Emmett–Teller surface area analysis; TOC = total organic carbon analysis.

In theory, spectroscopy uses the interaction between matter and electromagnetic radiation (light) to measure absorbance at the wavelength of maximum absorbance as a function of the concentration. Absorbance is proportional to the concentration of the chemical species that absorb light [93]. UV-Vis spectroscopy examines the absorption of light in the ultraviolet (UV) and visible (Vis) regions of electromagnetic radiation. Different compounds absorb light at different wavelengths due to their electronic states. Fourier-transform infrared spectroscopy (FT-IR) is employed to detect functional groups presented in the products. Different chemical bonds and functional groups in a molecule absorb infrared light at specific frequencies due to vibration transitions. Nuclear magnetic resonance (NMR) spectroscopy is used to analyze the molecular structure of organic compounds. Atomic nuclei absorb radiofrequency radiation in a magnetic field. Raman spectroscopy measures molecular vibrations to identify the molecular structure. It detects the intensity and wavelength of inelastically scattered light from a molecule. Atomic absorption spectroscopy (AA) and inductively coupled plasma–optical emission spectroscopy (ICP-OES) are used to determine the heavy metal contents [94]. X-ray diffraction (XRD) shows the crystal structure and degree of crystallinity. XRD measures the diffraction patterns of X-rays scattered by the atoms in crystalline structure interacting with X-rays [94].

Chromatography consists of the separation of compounds in a mixture by a partition between a stationary phase and a mobile phase. A mixture carried by a mobile phase moves at different velocities through the stationary phase so that each compound is separated at the stationary phase, leading to separation [15]. Chromatography hyphenated to various detectors effectively and efficiently enables the separation, identification, and quantification of a mixture in HTC samples. Gas chromatography (GC) is used to separate and identify the individual volatile organic compounds based on different volatilities and polarities. Depending on the purpose of the analysis, it can be coupled with different detectors, such as a mass spectrometer (GC-MS), flame ionization detector (GC-FID), and/or thermal conductivity detector (GC-TCD) [94]. High-performance liquid chromatography (HPLC) is used for mostly non-volatile organic liquid samples to separate, identify, and quantify. MS and/or UV-Visible detectors are hyphenated with HPLC [94]. Ion chromatography (IC) measures the separated ion retained on a stationary phase. Qualitative and quantitative analyses provide detailed information about HTC products with high accuracy and precision [93,94].

Usually, miscellaneous analysis includes electrochemical analysis, thermal analysis, separation, microscopy, precipitation analysis, and colorimetric analysis [95]. Elemental analysis is conducted to determine the elemental composition regarding carbon, hydrogen, oxygen and nitrogen amounts (sometimes also sulfur and trace elements). Proximate analysis includes moisture content, fixed carbon, ash content, and volatile matters. Thermogravimetric analysis (TGA) confirms the thermal stability and decomposition temperature, while differential scanning calorimetry (DSC) is useful for investigating the thermal behavior of the component. Rheological analysis is conducted to understand the viscosity and fluid behavior of HTC samples. Scanning electron microscopy (SEM) is used to examine morphology and surface structure, while transmission electron microscopy (TEM) shows a detailed image of the internal structure and its morphology. The surface area and porosity of the hydrochar can be measured through BET surface area analysis.

Obviously, these physicochemical analyses provide the fundamental information and significant insights into the composition of the three phases generated via HTC. However, standardization of the characterization method is lacking, and analytical results are too limited to be comparable. These will become the topics of future research.

2.3.2. Strengths and Limitations of HTC Analyses

Among the strengths of the analytical techniques used for HTC, we can highlight:

- *Comprehensive characterization of HTC products.* HTC reaction generates three different products with various physico-chemical properties. Analytical techniques such as GC/MS, HPLC, and NMR provide detailed information about the chemical compositions and structures as well as the physical and chemical properties associated with reactivity [95]. For example, Yu et al. [95] showed that the conversion of poplar leaves and rice straw as real biomass was conducted via the HTC process, and the comprehensive characterization was performed using elemental analysis, SEM, N₂ adsorption/desorption, FT-IR spectroscopy, and XPS. This confirmed that the HTC produced various shapes and sizes of hydrochar at different HTC reaction temperatures. Based on data obtained from analytical techniques, the relationships of diverse types of biomass with their HTC products can be evaluated in terms of advanced carbonaceous materials, new adsorbents, bio-fuels, energy storage systems such as electrode materials for supercapacitors, and green catalysts [49].
- *Combination of qualitative and quantitative data.* Qualitative analysis of HTC involves non-numeric values, which are characteristic of the products at various reaction conditions, while quantitative analysis numerically assesses the HTC process. Qualitative data include chemical compositions and structure determined by XRD spectroscopy for inorganic compounds present in product and organic compounds in the product measured by NMR spectroscopy, surface morphology of hydrochar (porosity, pore size distribution, surface roughness) investigated by SEM and BET analysis, functional

groups (hydroxyl, carboxyl, aromatic) confirmed by FT-IR influencing reactivity and adsorption properties, hydrochar and liquid properties (color, texture, viscosity, homogeneity), and environmental impact (sustainability, ecological implications). Data, on its own or combined, would provide insights into its potential and utilization. Quantitative analysis of HTC includes elemental analysis, determining the contents of carbon, hydrogen, nitrogen, oxygen, and sulfur for the energy content and environmental impact; chemical oxygen demand and biological oxygen demand, assessing the organic impact on environment; ion chromatography; high-performance liquid chromatography/mass spectrometry (HPLC/MS); and total organic carbon analysis, measuring organic and inorganic contents in PW. To quantify the HTC process, computational models have been investigated to predict and optimize HTC reaction parameters. Kinetic models, statistical models, and computation models are used to compute activation energies and reaction rates, to optimize HTC reaction parameters, and to simulate the full scale of an HTC reactor, respectively [49,96].

- *Sustainability approaches.* The understanding of the whole process of HTC reaction including characterization of HTC products generated by various types of biomass, energy consumption and/or generation which relates energy efficiency, values of new products generated by the reaction, and environmental impact is all related to sustainability in materials, energy, and environmental aspects [2]. In other words, HTC can be envisaged as a sustainable manufacturing process, a pathway for wet residues to decrease their environmental impact, and a technological and synthesis route to synthesize materials [49].

The negative attributes of HTC analysis for characterization are detailed below.

- *Analytical challenges.* A comprehensive analysis of all HTC products has not been achieved yet. It is impossible to measure all necessary properties using a single analytical technique; rather, multiple analytical methods need to be utilized for a complete analysis. Since analyses of solid hydrochar have been actively studied, bio-oil, processed water, and gas analysis is more challenging because their compositions are complex. Even though standard procedures may be available for a certain property (e.g., cetane number for biodiesel as an indicator of diesel combustion and quality compared to that of the regular diesel), other properties, such as lubricity, are seldom mentioned [94]. Opportunities exist for the development and advancement of standard methods for HTC characterization and property measurement.
- *Expensive and professional requirement.* Most analytical instruments, e.g., NMR, GC/MS, and ICP-MS, are expensive and require a professional who has obtained the specific theory and training. The use of these sophisticated analytical instruments is mandatory for achieving accurate and meaningful results on studies of HTC reactions. However, they are costly to purchase, calibrate, operate, and maintain. In particular, it is necessary to understand the theory behind and learn about sample preparation, sometimes involving complex procedures, data interpretation, instrumental operation, laboratory safety, and troubleshooting. Sample preparation includes simple processes such as washing, drying, grinding, and sieving and complicated processes such as liquid–liquid extraction, distillation, ionic exchange, and chromatographic separation [93,94]. Researchers who are trained in the specific instrument know how to operate the instrument, identify the limitations, and inform critical decisions from feedstock to industrialization.
- *Lengthy procedure.* Generally, instrumental analysis with high accuracy is time-consuming. Prior to running the analytical instruments, the sample preparation procedure is mostly conducted due to the complexity of the samples produced through HTC reactions. For example, the metal contents present in hydrochar could be measured by ICP-OES or ICP-MS. After the HTC reaction is completed, hydrochar is separated from the liquid and digested in a hot acid so that inorganic substances are dissolved in the acidic liquid [94]. Depending on the application, rapid assessment with efficiency becomes prioritized.

2.3.3. Future Directions for HTC Analysis

Diverse physicochemical properties rely on biomass feedstock, reaction temperature, and residence time. HTC products exhibit various properties suitable for different applications of the challenges that the world needs to unravel, such as energy, the environment, and sustainability. With increasing studies on the characterization of HTC products in the areas of agricultural advancement and alternative energy, there is still room for improvement in the future.

- *Standardization of the analytical method.* The lack of standardized analytical methods might hinder the comparative studies of the process. The development of standardized sample preparation and analysis of feedstock and products should be prioritized for the uniform understanding of the HTC process and products based on the reliable comparison of results from various studies. Pretreatment or post-processing, such as chemical activation, pyrolysis, and blending, are often necessary to generate competitive materials. Moreover, the need for in situ analytical methods is growing due to the size scale-up of the reactor, even for the pilot scale. Furthermore, characterization of liquid and gaseous products is critical to fully utilizing the HTC reaction.
- *Interdisciplinary collaboration.* Interdisciplinary approaches are imperative to address these multifaceted challenges in HTC research. Experts in chemistry, engineering, soil science, and economics can collaborate to suggest and understand the whole process and the values of HTC technology by providing integrated models, including raw materials and end products. By combining expertise from various fields, a comprehensive, long-term study and field-scale application can evaluate the benefits of HTC products and processes in mitigating greenhouse gas emissions and enhancing carbon sequestration. Future research should be focused on the potential of HTC products as a sustainable feedstock for further reactions or raw material for energy storage systems and material synthesis. Material sustainability can be provided based on a comprehensive understanding of physicochemical properties as well as economic assessment. Waste reduction and resource recovery from HTC reaction could be achieved through environmental remediation and waste treatment. Municipal solid waste and wastewater sludge treatment require scaling up the HTC process. It is associated with technical, economic, and regulatory implementations. At this point, life cycle assessments (LCA) need to be incorporated to evaluate the environmental impact of the entire process of HTC reaction. As a result, HTC can be integrated into sustainable energy resources and agricultural practices associated with a broader impact on climate change.
- *Integration of data.* The collective data on qualitative and quantitative information is important in order to understand HTC reactions, including the chemical composition, structure, and reactivity of hydrochar, liquid, and gaseous products. Value creation from HTC data automatically demands a data-sharing platform [97]. Through this platform, the researchers interact with other researchers at different locations on the same topic by depositing, searching for, using, and sharing data. To set up a data-sharing platform, there are some key components to be considered, such as data-sharing purpose, permission of accessibility, guidelines of users, quality and format of data, consistent and configurable metadata, etc. A more detailed process would be beyond the scope of this paper. In addition, the scattered data obtained from various conditions of HTC reaction and properties of HTC materials could be leveraged so that researchers might use machine learning algorithms and computational modeling to predict HTC products and optimize the process.

Therefore, the challenges associated with the analysis of HTC exist, but provide opportunities for solutions and innovation for future problems. Especially, understanding of the feedstock influence, reaction mechanisms, and analysis of feedstock and HTC products, including physicochemical properties and life cycle assessment, would provide full insights into HTC applications. The future direction comprises analysis standardization, interdisciplinary collaborations, and integration of data for computational modeling and

machine learning applications. Data-driven approaches are key factors for collecting data from researchers worldwide. Future efforts to integrate HTC into various areas in material synthesis, energy storage, waste treatment, environmental remediation, and sustainability are inevitable in the process of valorizing the HTC technology.

2.4. At the Boundaries of HTC: Humification and Fulvification

The HTC process operates within a temperature range of 180–250 °C, under auto-generated pressures that vary depending on temperature, biomass type, specific reactions occurring, and the production of gaseous by-products. A notable characteristic of this process is its auto-neutralizing effect, leading to a rapid reduction in pH and facilitating the polycondensation of aromatic compounds like furans and phenols [98]. This results in the formation of the so-called secondary char [99], which polycondensates on the surface of the primary char. However, not all the aromatic compounds formed during the HTC process polycondensate on the surface of the hydrochar; some remain in the process liquid [100,101]. The presence of these compounds in the process liquid significantly affects its properties over time. It has been observed that there is a marked reduction in sugars, phenols, total organic carbon (TOC), chemical oxygen demand (COD), and inorganic compounds in the process liquid during storage, even in samples stored at −18 °C. A noteworthy aspect of this change is the formation of precipitates, which occurs through the condensation and polymerization of phenols [102]. Moreover, knowledge about HTC process liquid remains quite limited. For instance, Becker et al., in their 2014 study, found that for eight varied lignocellulosic feedstocks, a mere 10–50% of the total organic carbon (TOC) could be accounted for, even after analyzing the major organic components [103]. This aligns with findings from Marzban in 2022, which showed that in the process liquid, organic acids, sugars, and aromatics accounted for only about 25% of the TOC, with 11% attributed to humic acid, leaving the majority of the TOC composition unidentified [102].

To minimize the presence of phytotoxic substances, such as phenols and organic acids [104], that may hinder the immediate application of HTC products for seed germination and plant growth, several treatment strategies such as storage and rinsing with water [104], along with chemical processing methods [105], have been proposed. However, it is essential to overcome these challenges with economically viable adjustments during the production phase to maximize the utility of hydrochar and its associated process liquids. In response to the limitations of HTC products, a new process known as hydrothermal humification (HTH) has been recently introduced within the HTC process boundary, in which the reaction occurs under a moderate to strong alkaline media and produces artificial humic acids (A-HAs) [106–108] while significantly reducing the aromatic compounds in both solid and liquid products [98].

The increasing demand in agriculture for humic substances and the scarcity of natural coal-related resources like lignite and leonardite, which are traditionally used for the mass extraction of humic substances, is driving research into hydrothermal production methods for A-HAs [109]. A-HAs are becoming more popular for soil enhancement due to their eco-friendly qualities, acting as biostimulants and conditioners that influence plant development, adjust soil pH, mobilize nutrients, and enhance water retention [109–111]. Ongoing research highlights their effectiveness in boosting nitrogen efficiency and reducing nitrogen pollution [112], as well as enhancing soil carbon sequestration and restoring soil health [113]. The use of A-HAs in combination with phosphate fertilizers has been shown to improve soil microbial activity and phosphorus uptake by plants, contributing to the reduction of phosphate unavailability for the plant [114,115]. The significant benefits and applications of A-HAs in sustainable agriculture have led the International Union of Pure and Applied Chemistry (IUPAC) to select the production of artificial humic matter from biomass as one of the top ten emerging technologies in 2021 [116].

2.4.1. Differences between HTC and HTH

The key distinction between HTC and HTH lies in the chemistry of the process. In HTH, the base amount is enough to prevent rapid pH reduction caused by organic acids resulted from auto-neutralizing reactions. Instead, furanic compounds, phenols, and organic acids undergo condensation and polymerization, forming A-HAs. The precise chemical boundary between HTC and HTH was unclear until Vitalii et al. (2022) delineated the humification–carbonization interface [98]. They discovered that sufficient KOH must be added initially to prevent a quick drop in pH into the acidic zone. The KOH quantity is determined by the biomass carbohydrate content, such as cellulose and hemicellulose. When KOH is less than 1 equivalent of these carbohydrates, the process remains in the HTC phase, featuring rapid aromatic condensation on cross-linked hydrochar. With KOH content between 1 and 2 equivalents, the process transitions to HTH. This condition facilitates complete lignin breakdown into phenol, catechol, and guaiacol, which are then condensed with acids and furans and polymerized to form macromolecules such as A-HAs.

Exceeding two equivalents of KOH relative to carbohydrates introduces a new concept: hydrothermal fulvification (HTF). Figure 2 shows the biomass degradation pathway during the HTC, HTH, and HTF processes, as suggested by Tkachenko et al. [98]. The HTF process is marked by a notable absence of furan derivatives and a significant presence of lactic and succinic acids. In the Van Krevelen diagram, HTC products exhibit lower H/C and O/C ratios, indicative of dehydration reactions and increased aromaticity. Conversely, the humification boundary, marked by increased KOH, yields higher O/C and H/C ratios. Fulvification, occurring after two equivalents of KOH, results in the highest O/C and H/C ratios and more demethylation reactions, reducing methyl groups, particularly $-\text{CH}_3$, as confirmed by two-dimensional ^1H - ^{13}C gradient heteronuclear single quantum coherence NMR analysis. This analysis also revealed reduced complexity and size in the HTF soluble products compared to those from HTH [1]. Different analyses such as X-ray photoelectron spectroscopy (XPS), FTIR, and pyrolysis–gas-chromatography/mass spectrometry (Py-GC/MS) analysis have revealed the similar chemical composition of A-HAs and natural ones [106].

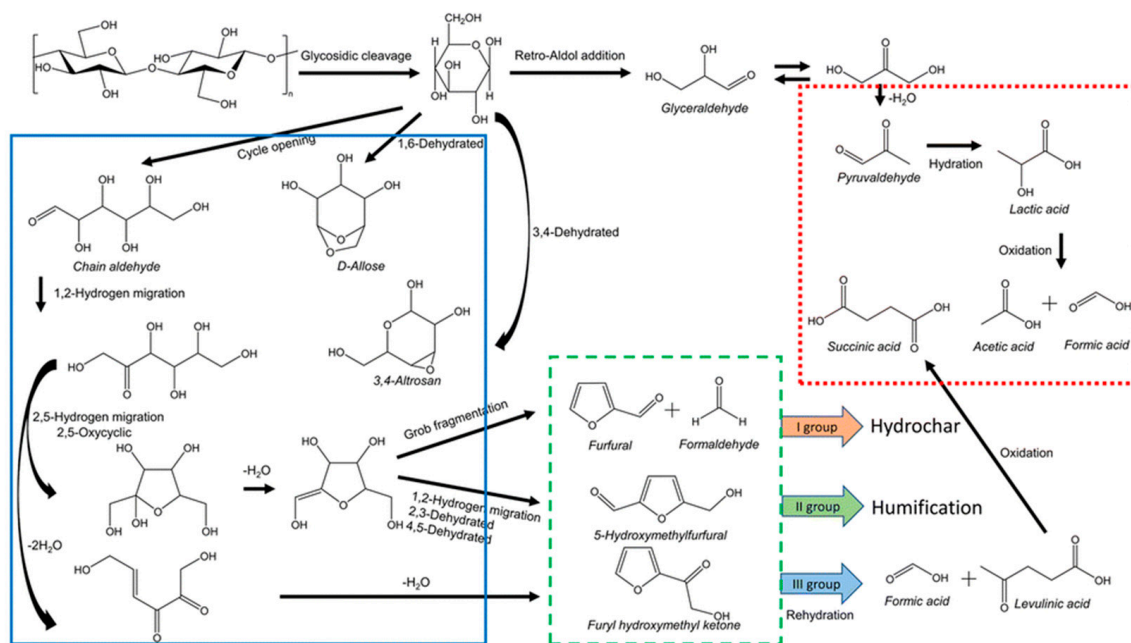


Figure 2. Degradation pathways of biomass through base-catalyzed retro-aldol addition and acid-catalyzed dehydration during HTC (group I, when the KOH content was less than 1 equivalent of the carbohydrates), HTH (group II, when the KOH content was between 1–2 equivalent of the carbohydrates), and HTF (group III, when exceeding 2 equivalents), suggested by Tkachenko et al. [98].

Compared to HTC, the solid products of HTH and HTF have lower carbon content due to ash accumulation, primarily potassium, affecting the solid product [98,117], while the TOC content in their process liquid is significantly higher than HTC. Since the higher heating value (HHV) correlates with hydrochar's carbon content [74], increased KOH reduces the carbon in solids, thus lowering the HHV. Consequently, solid products from HTH and HTF are unsuitable for biofuel applications, instead being more applicable to agricultural, soil, and environmental uses. These products are more hydrophilic compared to HTC products, making solid-liquid product separation challenging, yet in scaled applications, such separation is unnecessary, and the entire slurry may be directly applied to the soil. Additionally, the hydrochar produced via HTH and HTF processes adsorbs a portion of the humic substances, enhancing its functional groups, which broadens its environmental application scope [107]. However, their lower BET surface area, compared to HTC hydrochar, may require further activation for enhancement [118,119].

2.4.2. Suggestions for Future Works

To conclude, despite the advancements in HTH and HTF processes, there remains a significant scope for future research, particularly in optimizing these processes for a broader range of applications and understanding their full potential in agricultural and environmental contexts. For example, process parameters such as time, temperature, and biomass-water ratio should be optimized to increase the yield of A-HAs for a wide range of biomasses and biowastes. Indeed, all the research and process optimization that has been carried out so far for HTC, except for the biofuel application of hydrochar, can be repeated for HTH and HTF processes. In addition, identifying more cost-effective alternatives to KOH, such as lime or combustion ashes, could render these processes more economically feasible. Although research to date has utilized KOH to elucidate the chemical principles underpinning HTH and HTF and to unveil these innovative processes, the high concentrations of KOH used, especially in the process liquid, may lead to corrosion. Consequently, it is imperative to investigate less corrosive agents, including ammonium hydroxide and carbonates, to assess their potential in facilitating the production of A-HAs in comparison to KOH. This means that feedstocks like digestate manure, characterized by a high concentration of ammonium and buffering capacity, could inherently provide the conditions needed for humification and fulvification reactions to occur, eliminating the need for additional alkaline agents. Nevertheless, it is crucial to monitor the initial and final pH levels of the process. If the process ends up with a final pH that is near neutral, the formation of A-HAs should be studied through extraction and characterization from both solid and liquid products. The potential of HTF products in enhancing plant growth in hydroponic systems or germination, as well as their toxicity assessment compared to HTC and HTH products, requires further investigation. Recycling HTH and HTF process liquids into anaerobic digestion for methane production, or bioactivation methods like composting, could significantly improve their agricultural utility. Additionally, research previously focused on the application of natural humic substances can now be repeated using A-HAs, as hydrothermal processes provide an accelerated and sustainable method for their production and synthesis.

3. Applications and Technological Challenges

Section 3 explores the practical and technological challenges encountered in HTC, offering insights into the technological landscape and the domain's inherent challenges and implications. It discusses the potential synergies in treating different substrates through co-HTC (Section 3.1), particularly in conjunction with wastewater treatment plants (WWTPs), as explained in Section 3.2. These plants often include anaerobic digestion compartments aimed at biogas production, with HTC PW being recycled to enhance biogas yield and potentially recover macronutrients beneficial for agriculture, such as P, N, and K (as delved in Section 3.3). Then, it concludes with Section 3.4 by discussing the energy efficiency of HTC plants, addressing the energy-intensive nature of HTC. In particular, it reports an

energy analysis conducted on a continuous pilot plant located in Switzerland and some unconventional concepts where HTC energy needs are provided via concentrated sunlight.

3.1. Co-HTC: Mixing Wastes to Improve HTC Process or Products

HTC has found a reputed place among the thermochemical routes for managing wastes, especially in the case of wet organic wastes. As previously described, HTC is a cost-effective process that can work with moderate heat needs as compared to processes like pyrolysis. However, in the frame of sustainable management of wastes, aspects related to the energy associated with gathering and transporting feedstocks to the processing place have to be considered; otherwise, the favorable energy balance of the process would not be so advantageous as a whole. Also, the seasonal efficiency of the plants has to be taken into consideration, and for this, its operation during a high fraction of the year is necessary. For these reasons, the overall “green character” of an HTC plant will only be interesting if the reactor can process wastes that are within a regional diameter and also if it can work with different feedstocks (bringing independence to pruning seasons, for example) or mixing them (so that operation under high capacity is guaranteed). This view can envision HTC plants as central hubs for regional biorefinery [120].

The fact that HTC technology should not be limited to single feedstocks is not new; today, only some HTC plants use unique feedstock and are mainly associated with wastewater treatment plants. Most HTC pilot and industrial plants can work with various raw materials, and some adopt mixtures of feedstocks. Understanding the potential of waste mixtures (co-HTC) to yield products of equivalent quality compared to singular runs is critical, as it has the potential to enhance the efficiency of HTC for certain substrates. Additionally, alterations in the physicochemical properties of process waters (PW) modify the chemical pathways in HTC degradation, leading to the discovery of catalytic or inhibiting effects.

Co-HTC has increasingly attracted the attention of the scientific community, especially during the last decade, which has witnessed a growth in the share of co-HTC-related papers concerning HTC studies from 2.3% to 4.8% (search made in Scopus using the following keywords: hydrothermal carbonization and co-HTC). The literature encompasses findings ranging from studies investigating the inherent process modifications to research focusing on enhancing the properties of hydrochars (either as a blend or separately for each feedstock, depending on the scenario). Below, we review the current state of co-HTC and give some possible suggestions for its future development.

3.1.1. Changes Induced on HTC Process: Comparing Single and Co-HTC Processes

Co-HTC can foster some HTC reactions, helping in the conversion of specific wastes not undergoing significant decomposition in the subcritical range. This issue is the case, for example, of polyvinyl chloride (PVC) HTC, which hardly gives a high-quality hydrochar (HC) because of the slow organic carbon conversion rate and the existence of aggregation processes. In addition, inefficient dechlorination can yield a solid product that is inadequate for combustion due to potentially harmful polychlorinated biphenyls and dioxin emissions [121]. Previous studies have reported that dechlorination efficiencies using OH-nucleophilic substitution with water acting as a nucleophilic agent are only achievable at high temperatures (beyond 235 °C [122]). Several works have demonstrated that incorporating lignocellulosic biomass into PVC during HTC facilitates dechlorination processes and degradation reactions [121,123].

The increased concentration of HCl in the PW also benefits process kinetics, enhancing the carbonization of both PVC and biomass. Consequently, the calorific value of the final hydrochar improves compared to the one obtained from a mixture of hydrochars derived from individual processes. Additionally, the dechlorination performance is notably enhanced by biomass molecules, following the sequence of lignin > cellulose > hemicellulose [13]. This improvement is not limited to PVC dechlorination; the presence of HCl is advantageous for

demineralizing the biomass. As a result, the final hydrochar exhibits a lower ash content than that achieved through individual processing.

Demineralization is a common target when combining biomass with PVC materials. However, tracking the actual effect can be challenging due to the frequent addition of other acids to the system [121]. Nevertheless, this approach has exhibited success across various materials, like pomelo peels [124], pinewood sawdust [123], and others. Similarly, exploring this method involved mixing coal with PVC to demineralize the fossil feedstock [125]. Investigations into coal and biomass co-HTC for this purpose have also been undertaken [126], along with studies involving animal manure [127] or sewage sludge [128]. Additionally, magnetization of Fe-containing wastes via HTC can be achieved by introducing a lignocellulosic feedstock into the system. This effect was studied by Gu et al. [129], who found co-HTC as a way to upgrade iron sludge by adding biomass leaves. Their research revealed that Fe cations were released to PW. This facilitated the role of iron sludge as a nucleophile, catalyzing biomass degradation and contributing to ash reduction in the hydrochar. At the same time, the hydroxyl groups from biomass fragments participated in reduction reactions to transform ferrous iron into ferric one and form Fe_3O_4 (magnetite); this enabled the iron waste to be removed from the blended slurry using a magnet.

3.1.2. Improvements in HC Properties of Specific Feedstock by Co-HTC

The studies on co-HTC can be classified into two main groups: first, those examining the HCs derived from each feedstock, particularly if they can be physically separated; and second, those that directly consider the slurry as the product, often referred to as co-hydrochar (co-HC). In the first group of studies, we try to evaluate the benefit of the derived HC in comparison to the one that would have been obtained by a single HTC, and find effects like additional enhancement of decarboxylation, modification of combustion parameters, increase in secondary char formation, or migration of specific elements from one feedstock to the other HC [130]. In the second group, we directly evaluate the properties of the solid product as a whole and generally compare it to the HC that would have been obtained from one of the feedstocks, especially regarding any property that has improved.

The studies from the second group comprise the vast majority of the references found in the bibliography, and a wide variety of results are available. Most studies agree that there is a greater prominence of cluster formation and repolymerization reactions due to a higher concentration of HTC degradation products when more than one feedstock is used. This means that overall solid carbon recovery is achieved through co-HTC [131]. Such outcomes are expected when the total biomass load to water is increased by adding another feedstock.

In general, a high proportion of these studies focuses on combustion behavior. Co-HTC can provide greater calorific values because of the enhancement of secondary char formation, lower ash content associated with demineralization, better or worse values of ignition and burn-out temperature, and modification of activation energy values depending on the feedstock and operating conditions [121,124]. Another highlighted benefit of co-HTC in the specific case of feedstock containing Cl (like PVC) is that the HCl emission during the combustion of co-HCs (if biomass is added to the HTC process) is almost 100% minimized, as compared to the PVC HTC alone [123].

3.1.3. Changes on HTC Process Water by Co-HTC

While most of the works published on co-HTC have focused on the modifications of HC properties, the few studies conducted following the changes in PW show inspiring results. In terms of nutrient recovery, for example, mixing wastes has been shown to improve the extraction of the N or P to different extents, depending on the processing conditions. He et al. [132] found that using HCl-catalyzed co-HTC of food waste digestate and yard waste improved nutrient recovery: N was doubled, while a 129-fold extraction was found for P, as compared with single food-waste HTC.

Shan et al. [133] investigated the co-HTC of sewage sludge and spent mushroom substrate and revealed that N improved extraction efficiencies above 60%, as calculated from each waste. These authors tested the quality of their co-HTC PW as a liquid fertilizer for growing the species pakoi using hydroponic systems and found that the biomass yield obtained was 140% greater than that found when PW from single sewage sludge was used.

3.1.4. Research Needs in Co-HTC

The benefits of using blends of wastes in HTC processes are highly dependent on processing conditions, and identifications of the optimal parameters have scarcely been made. While temperature is often indicated as the primary factor in HTC degradation reactions, certain studies highlight that the waste 1/waste 2 mass ratio is equally critical in achieving synergistic effects [124]. This highlights the necessity of systematic investigations into this parameter's influence. Indeed, what initially manifests as positive effects can potentially shift to negative outcomes, hindering degradation reactions when one waste is excessively added in the presence of the other. For example, this problem arose in the co-HTC of PVC with pomelo peel: adding too much biomass resulted in a high concentration of biomass degradation fragments that covered the former waste and impeded its decomposition [124]. The same result was reported by Zhang et al. [123], who associated the lower conversion of PVC under high loads of pinewood waste with the formation of clusters or aggregates between biomass fragments and PVC surface, observed by SEM micrography. Shen et al. [13] found this tendency during co-HTC of lignin and plastic medical wastes. Hence, interactions between variables require studies via response surface methodology techniques or similar.

Catalytic co-HTC can potentially improve the degradation of blends of specific substrates. However, most studies employed commercial acids or bases, and green solvents should be evaluated. Moreover, in most of these studies, there is no clarity regarding the assignment of the effects to the "additional" feedstock added or to the catalysts; blank runs to confirm reaction pathways are also required.

Another hot topic for research in the co-HTC context that has rarely been addressed is related to the recirculation of PW obtained from co-HTC. The few works that have simultaneously investigated it have concluded that co-HTC leads to a surplus of solid yield compared to the sum of solid products obtained by individual HTC, and this effect is more intense at lower temperatures. In this way, larger C recovery of the HC from enhanced repolymerization and combination reactions, usually attributed to PW recirculation runs, was fostered due to the greater concentration of fragments for co-HTC [134].

On the other hand, there is a lack of research investigating the compositions of PW from co-HTC. Zhang et al. [123] found that PW from co-HTC was very different from that obtained by HTC of individual feedstock and evidenced interactive interactions between the respective decomposition fragments, including dehydration of biomass-derived compounds like 5-HMF, aromatization, and repolymerization. Finally, the meaning of the word "synergy" does not seem to be defined in the same way by researchers working on co-HTC, and the results are often confusing: It sometimes refers to the increase in a target parameter of co-HCs as compared to the one HC that would be obtained from one of the feedstocks; on other occasions, it constitutes the comparison of the property in the co-HC with the relative proportion found on any of the feedstock HC.

Therefore, co-HTC holds the potential to enhance degradation processes, especially demineralization, dechlorination, and the production of hydrochars, with enhanced specific combustion parameters or other desirable properties. The strategic combination of feedstock has shown promising outcomes, but systematic studies are needed, since the effect of operating parameters and/or the addition of catalysts significantly affects the potential synergies. Further research into the chemical reactions among the degradation products derived from diverse mixed feedstocks is crucial for a comprehensive understanding of co-HTC pathways, especially in contrast to single-feedstock processes.

3.2. Integrating HTC with Wastewater Treatment Plants

Wastewater treatment is a critical process in ensuring the protection of the environment and public health. Wastewater treatment plants (WWTPs) are integral components of urban infrastructure designed to manage and treat sewage and industrial wastewater. Traditional methods employed in WWTPs often involve multiple stages, including primary settling, biological treatment, and secondary settling, to remove contaminants and stabilize organic matter. However, these processes are energy-intensive and may not be sufficient to address the growing challenges posed by increasing wastewater volumes and stricter environmental regulations [135].

In recent years, HTC has begun to be integrated in WWTPs in order to treat sewage sludge and other residues derived from these plants. This integration offers several advantages, such as the reduction in organic matter, stabilization of the sludge, pathogen inactivation, and the generation of valuable products. In this section, we will explore the application of HTC in wastewater treatment plants, as well as its potential benefits and limitations.

The integration of HTC into WWTPs represents a pivotal stride towards sustainable waste management and resource recovery. HTC's synergistic relationship within this context offers multifaceted solutions to the persistent challenges of waste disposal, resource scarcity, and environmental impact mitigation.

3.2.1. Advantages of Integrating HTC with WWTPs

The transformative potential of HTC integrated into WWTPs lies in its capacity to offer several advantages in this context. HTC offers a practical solution to the persistent challenge of sludge management in WWTPs. Wastewater treatment plants generate substantial quantities of sludge (around 45 million dry tons per year [136]), which requires costly disposal or further treatment [137]. HTC significantly reduces the volume of this sludge [138] by converting the organic matter into a stable, carbon-rich material. On average, studies conducted on anaerobically digested sewage sludge have reported a solid yield (mass of hydrochar/mass of feedstock \times 100 on dry basis) of around 60%, varying according to the severity of the process [139]. It is noteworthy that higher severity (higher temperature and longer duration) tends to result in lower solid yields. For instance, a solid yield of 47.1% was reported by Berge et al. [140], who worked on digestate from sewage sludge at high-severity conditions (250 °C-20 h), while 93.9% was found by Kim et al. [141] for lower-severity conditions (180 °C-1 h). Hydrochar is easier to handle and dispose of, thereby alleviating the financial and logistical burdens associated with sludge management. An important aspect of integrating HTC into wastewater treatment processes is its impact on sludge dewaterability. HTC significantly enhances the dewatering process by reducing the moisture content of sludge [138,142], thereby transforming it into a more stable and less voluminous solid product. This enhancement not only cuts down on management and disposal costs, but also facilitates more efficient energy recovery from the sludge. In 2024, Hämäläinen et al. [138] discussed how the HTC process, when integrated into a centralized biogas plant for sewage sludge treatment, enhances the dewatering efficiency. They highlighted that HTC effectively reduces the moisture content of the sludge, resulting in a significant decrease in the volume of the solid product. As the hydrothermal temperature increased, Zhong et al. [142] demonstrated the improved solid-liquid separation performance of hydrochar produced from municipal sludge at various temperatures (180–300 °C), which was attributed to increased hydrophobicity of the sludge particles during the HTC process.

HTC has the potential to transform WWTPs into more energy-efficient facilities. The carbonaceous material produced during the HTC process can be exploited as an energy source [48]. As with other treatments, by utilizing the hydrochar as a renewable fuel or as a co-firing agent with other fuels, WWTPs can reduce their dependence on external energy sources and, in some cases, even become self-sufficient in terms of energy. This energy recovery aspect aligns with broader sustainability goals and reduces the carbon

footprint of wastewater treatment. Energy can be recovered from both hydrochar and PW. It is well known that HTC condenses energy into a solid product, as demonstrated by several authors who have shown the combustion properties of hydrochar [143–145], reporting higher heating values (HHV) in the hydrochar in the typical region of lignite (15–25 MJ/kg). In addition, energy can be also recovered by the anaerobic digestion (AD) of both hydrochar and PWs for the production of biogas [141,146,147]. The viability of employing the HTC method following the AD process (and vice versa) to reduce sludge disposal quantities (or digestate) and amplify biogas production has been proven by numerous authors [143,145,148]. During HTC, the production of volatile fatty acids (VFAs) occurs, while the more resilient components undergo hydrolysis. This process facilitates biological conversion when HTC is utilized as a pre-treatment for AD. Consequently, integrating AD with HTC stands as an appealing option [148–151].

Nutrient pollution, especially excess phosphorus and nitrogen in wastewater effluents, poses environmental risks such as eutrophication in water bodies [152]. HTC has the potential to recover and recycle these essential nutrients from wastewater streams [153]. The hydrochar and the PWs produced can be processed to extract valuable phosphorus and nitrogen compounds, which can then be used as fertilizers [138] or in other applications. This not only reduces nutrient pollution, but also contributes to the circular economy by closing the nutrient loop within the wastewater treatment process. Rathika et al., in 2024 [153], reported that the PW derived from HTC of sewage sludge contained substantial concentrations of nitrogen and phosphorus, reaching up to 2091.68 mg/L and 40.51 mg/L, respectively.

In the context of wastewater treatment, the presence of harmful pathogens in organic waste and sludge poses a significant concern for both environmental safety and public health. HTC involves elevated temperatures and pressures, which effectively deactivate pathogens present in organic waste and sludge [154,155]. In the study of Ducey et al. [154], HTC processing effectively eliminated pathogens as well as microbial DNA at temperatures of 150 °C and 200 °C in bovine bones and tissue. The pathogen inactivation is a crucial safety aspect of HTC-treated materials. It ensures that the resulting hydrochar is free from harmful microorganisms, making it safe for various applications. Additionally, it enhances the overall safety of WWTPs by reducing the risk of pathogen transmission during handling and disposal.

Hydrochar produced through HTC of sewage sludge has the potential to sequester carbon for extended periods, contributing to climate change mitigation efforts [156]. When applied to soil, hydrochar can serve as a long-term carbon sink [157], reducing the net CO₂ emissions associated with wastewater treatment.

3.2.2. Challenges, Considerations, and Future Directions for HTC in Wastewater Treatment

The implementation of HTC in wastewater treatment plants is not without challenges and considerations.

One of the primary challenges lies in the optimization of the process. HTC's efficiency can be influenced by factors such as feedstock composition, temperature, pressure, and residence time [48]. Achieving optimal performance for WWTPs under different conditions requires extensive research and development. The properties of the HTC products are strongly dependent not only on the operative parameters, but also on the feedstock composition. For example, while HTC holds promise for nutrient recovery from wastewater streams, its efficiency may depend on the specific wastewater composition (availability, concentration, and state of nutrients), which may define the fate of the nutrients. Moreover, the sustainability of the recovery processes should be considered. In their life cycle assessment (LCA) study on the HTC of sewage sludge, Mannarino et al. [158] evaluated various scenarios and valorization pathways for HTC products. Their findings indicated that scenarios incorporating phosphorus recovery generally yielded the poorest performances. As a result, they suggested that future research efforts should focus on refining process conditions to mitigate the impact of this procedure.

Integrating HTC into existing WWTPs may require substantial capital investment, which can be a barrier, particularly for smaller facilities or regions with limited financial resources. Comprehensive cost-benefit analyses are necessary to assess the economic feasibility of adopting HTC technology. In the recent study of Bacci di Capaci et al. [149], the authors performed an LCA proposing six different scenarios for a WWTP. The results show that integrating HTC leads to the generation of a valuable product (hydrochar), while the conventional layout is associated with high sewage sludge disposal costs. Finally, scale-up challenges should not be underestimated. Transitioning from laboratory or pilot-scale HTC systems to full-scale WWTPs can present engineering complexities. Ensuring consistent and reliable operation at larger scales demands meticulous engineering design and consideration.

Another barrier to the full integration of HTC into WWTPs may be represented by the lack of a specific regulatory framework, which may require the establishment of new regulations and standards. This gap in the regulatory landscape potentially affects the technology's adoption.

Lastly, while HTC reduces sludge volume, it still produces residual materials, including PW. Proper handling and disposal of these residuals are vital to prevent potential environmental impacts. PW may be treated in the same WWTPs, but the presence of unwanted and potentially toxic compounds produced during HTC may have negative impacts on WWTPs functioning. Farru et al. [157] reported that PWs have negative effects on nitrifying bacteria, posing an issue for those plants where a nitrification stage is present.

While HTC holds promise for wastewater treatment, several challenges need to be addressed for its widespread adoption. Additionally, research is ongoing to explore the integration of HTC with other treatment processes to achieve optimal results, as has been reported in several studies [149].

3.3. Resource Recovery from Process Water

Proper treatment of the highly organic aqueous phase derived from the HTC process is incredibly challenging for HTC technology. The aqueous phase in the HTC process, here referred to as PW or post-processing liquid, is a result of the thermal conversion of organic feedstock in an aqueous environment under elevated temperature and pressure conditions, which may exceed more than 75% of the substrate [159]. Its characteristics can indicate high total organic carbon (TOC) and chemical oxygen demand (COD) values due to the significant content of organic matter [160,161]. It may contain organic and inorganic compounds, mainly carbohydrates, proteins, and short-chain organic acids, e.g., acetic, propionic, benzenoacetic, and butanoic acids; phenolic, furanic, alkene, aromatic, and aldehydic compounds [162]; dissolved organic matter; nitrogen (40–70%); phosphorus (50–70%) [163]; and potassium [164]. Moreover, the PW is rather acidic, except that derived from the HTC of sewage sludge, and it has high conductivity. In addition, it has to be emphasized that, depending on the feedstock and feedstock-to-water ratio, the PW can be a major product in terms of volume, e.g., in the case of sewage sludge, where the final PW might account for as much as 90% of HTC products. Therefore, on an industrial scale, PW disposal is a crucial problem in determining the cost of investment. For this reason, the extraction of valuable compounds or resource recovery is one of the hottest topics in managing PW disposal.

3.3.1. Extraction of Valuable Compounds

Knowing the content of organic matter, phosphorus, and nitrogen is essential when HTC PW is intended for soil improvement. Accordingly, McCaughy et al. [164] have been working on micro- and macronutrient recovery in hydrothermally carbonized septic tank waste (septage), and they discovered that about 70% of available nitrogen reached the liquid phase as nitrate or ammonia. Furthermore, the higher the temperature of the HTC process and the longer the residence time applied, the more ammonia was recovered in

the PW, e.g., at 260 °C, 1400 mg/L was obtained. The formation of ammonia was probably because of the deamination of amino acids from organic raw septage.

A possible scenario consists of recovering ammonia by stripping it with air, as suggested by Huang et al. [165] when carbonizing chicken manure. Phosphorus, conversely, was found to be higher in the PW than in the raw feedstock, but decreased with the rising temperature of the HTC process due to adsorption on the hydrochar surface. In addition, the presence of micronutrients in the hydrothermal PW ensures its potential for liquid fertilizers, as heavy metals are below the detection level. Similar trends were found in the HTC of sewage sludge under the same conditions. However, for sewage sludge, over 10 times more nitrogen and 5 times more phosphorus and potassium were found. Therefore, it was determined that different factors can influence the solubilization of phosphorous and nitrogen from organic feedstock during HTC within the PW, including temperature, residence time, solid loadings, the origin of feedstock, and pH. For instance, Ekpo et al. [166] stated that an acidic environment enhanced the solubilization of nitrogen and phosphorous during the HTC process. This was also confirmed by Dai et al. [167], who observed that the acidic environment of the HTC process promoted the release of a higher concentration of total N and ammonia.

Phosphorus is a crucial element for agriculture. Its recovery from the HTC PW is a promising technology realized sustainably and omits the risk of eutrophication caused by an uncontrolled discharge of phosphorus [168]. The presence of phosphorus in the HTC PW is notably abundant, especially when the process involves treatment by an acid catalyst. It can be recovered from the liquid through a struvite precipitation process, which also facilitates nitrogen removal [169]. Struvite, despite its poor water solubility, is considered a valuable slow-release fertilizer that might be applied in agriculture [170,171]. Struvite fertilizers also reduce the need to use primary raw materials such as phosphate rock for fertilizer production [172,173]. Struvite precipitation has been discussed in a few studies on different HTC feedstocks. Numviyimana et al. [174] focused on the HTC liquid derived from dairy wastewater containing a high load of iron and dissolved phosphorus. They extracted phosphorus using oxalic acid and subsequently removed iron, successfully enabling struvite precipitation to produce a crystal fertilizer. In contrast, Crossley et al. [175] employed a combination of HTC, nanofiltration, and struvite precipitation, achieving a 75% recovery of total phosphorus from spent coffee grounds as solid struvite. Moreover, they achieved a recovery of 92.8% of concentrated aqueous phosphorus by adjusting the pH via nanofiltration for the HTC PW. Regarding sewage sludge, Aragón-Briceño et al. [176] conducted a study investigating the potential for struvite production. They explored six scenarios involving energy and economic evaluations of HTC combined with anaerobic digestion, using three types of sludge and two different temperature regimes for the HTC process. The study revealed that considering struvite production within the whole system could yield economic benefits. Chen et al. [177] recovered phosphate through vivianite crystallization from HTC PW derived from acidic kitchen waste. Vivianite has applications as a slow fertilizer and in industrial raw materials [178]. In particular, they found that the inorganic and organic impurities caused a reduction in vivianite purity, but when the Fe(II)/P ratio increased to 2 at a pH of 6, phosphate removal reached 98.2%. Zhao et al. [179] studied microalgae, *Spirulina platensis*, and *Chlorella vulgaris* using HTC and discovered that the PW was rich in phosphate–phosphorus that, after alkaline treatment, led to 85% of the total phosphorus recovery in the form of struvite.

3.3.2. Algae Cultivation and Recirculation of Process Water

PW obtained from HTC using various biomass wastes has shown successful applications in microalgae cultivation. For example, Tsarpali et al. [22] investigated the HTC process of lipid-extracted algae and observed that the resulting PW featured rich nitrogen content and other elements. These elements hold potential for cultivating *Chlorella vulgaris*, aiding in enhancing lipid productivity while concurrently purifying the PW by removing harmful substances.

PW obtained through HTC from various biomass wastes has been effectively utilized in microalgae cultivation. Tarhan et al. [180] conducted a study on the growth rate of *Chlorella minutissima* and *Botryococcus braunii* microalgae cultivated using diluted PW obtained from the HTC of olive and orange pomace, yielding positive results. However, when this same PW was used in the cultivation of *Chlorella sorokiniana*, adverse effects on microalgae growth were observed due to the presence of toxic compounds in the water. Interestingly, it was noted that despite these effects, the biochemical content of the microalgae remained unaffected by the type and concentration of the PW, indicating its potential use in cultivation [181]. Additionally, Du et al. [182] adopted an intriguing approach by recycling PW from algae hydrothermal carbonization, utilizing it for further cultivation. The algae exhibited accelerated growth and simultaneous removal of certain toxic compounds, and displayed increased richness of the carbon, hydrogen, and lipid content.

Stemann et al. [183] conducted a study on the impact of organic carbon PW recirculation derived from hydrothermally treated poplar wood chips (over 19 cycles). They found that recirculation led to an accumulation of organic acids, catalyzing a dehydration reaction that enhanced the dewaterability of the feedstock. Additionally, this process facilitated the creation of new solid products through the polymerization of the recirculated reactive substances.

Several researchers have investigated the recirculation of PW from different feedstocks across various cycles, primarily aiming for high-quality solid fuel production. For instance, Chen et al. [184] recycled PW four times from the HTC of sweet potato, Wang et al. [185] conducted twelve recycles of PW using laminaria, and Ding et al. [186] performed five cycles of PW from the HTC of rice husk at different temperatures. All of these studies reported enhanced yields, improved properties, and increased energy recovery of hydrochar. He et al. [187], employing two cycles of PW from acid-catalyzed HTC of food waste digestate, not only produced biofuel, but also synthesized hydroxyapatite, a slow-release fertilizer, by converting complex calcium and phosphorus compounds. However, in the case of sewage sludge, unlike lignocellulosic biomass, the recirculation of PW led to a 15% increase in energy recovery, yet the resulting hydrochar did not meet the criteria for high-quality solid fuel [188]. Notably, despite the advancements, many studies investigating PW recirculation have not delved further into the utilization or treatment of the remaining PW.

3.3.3. Energy Recovery

The high organic matter content of the PW enables energy recovery via anaerobic digestion and methanogenesis. Gaur et al. [150] investigated the energy recovery from PW using anaerobic fermentation and found that biomethane production was influenced by the parameters of the liquid and the intensity of the HTC reaction. The maximum energy return achieved from PW was 83%. Marin-Batista et al. [189] worked on the PW from the HTC of cow manure and obtained a higher methane yield for PW than for dairy manure, proving that HTC is a promising technology for dairy manure. Periyavaram et al. [190] worked on the HTC of food waste and the biomethane potential of PW and PW-enhanced hydrochar. For the mixture of PW and hydrochar, the methane yield increased by 35.5%, indicating that hydrochar stimulated microorganisms to induce higher methane production. Aragón-Briceño et al. [191] proved that solid loading influenced resource recovery, not only in hydrochar, but also in PW from sewage sludge, and the concentration of carbon, nitrogen, and phosphorus compounds increased the biomethane potential (228–301 mL CH₄/g COD).

3.3.4. Guidelines for Future Research Interest

In conclusion, resource recovery from PW holds substantial promise within HTC. However, the existing research predominantly concentrates on carbon recovery, phosphorus, and nitrogen. Yet, PW contains additional compounds that offer the potential for recovery and valorization. However, the current understanding of these compounds re-

mains relatively limited compared to the aforementioned elements, and also in comparison to the research focusing on solid products derived from HTC [192].

Accordingly, a profound, reliable report on these compounds' determination, reaction mechanism pathways, treatments, and valorization can be considered as a future research prospect. The type of feedstock and HTC conditions greatly affect the composition and behavior of the resulting HTC PW. However, correlations between them are scarce: detailed chemical characteristics of PW derived from different feedstocks are required. Furthermore, special attention should be focused on anaerobic digestion or other methods of PW treatment in terms of energy recovery. Conducting toxicity tests on PW can ascertain its viability as a soil fertilizer.

While much research occurs at the laboratory level, transitioning these technologies to an industrial scale requires the validation of methods for extracting valuable compounds and energy from PW. The technology must be user-friendly, efficient, and cost-effective to entice investors and position HTC as a promising method. In summary, future research should concentrate on pioneering valorization pathways, elucidating mechanisms, detailed analysis of chemical and physical attributes, life cycle assessments, and techno-economic evaluations to expedite the industrial application of this (pre)treatment method.

3.4. Energy Efficiency in HTC

HTC is a full-fledged green route for a bio-based future. However, to be sustainable in an ample view without forgetting being attractive and convincing in choosing HTC, we need to address energy consumptions. The mild operating conditions apparently only demand little energy: HTC requires a non-indifferent amount of energy, making the process potentially energy-intensive compared to other biomass valorization strategies like anaerobic digestion, composting, or pyrolysis [193]. Indeed, energy has to be provided to: (1) heat both the biomass and the water, which is present in a high percentage (from 70 to 95%, in mass) and is characterized by a specific heat capacity higher than the solid phase; and (2) sustain the process during the constant-temperature phase, compensating for heat losses and possible endothermic reactions, as even if HTC is slightly exothermic [194], the system has to face heat losses.

The investigation into energy demand remains limited, with few studies dedicated to comprehensive energy optimization of the entire HTC process. Current plant designs typically rely on heat recovery from internal streams. For instance, in integrated setups, heat is derived from either the combustion of biogas generated through anaerobic digestion or a portion of the hydrochar. Limited attention has been given to exploring the potential integration of HTC with renewable energy sources, such as solar power. Below, we present an example outlining potential energy recovery strategies within an integrated HTC pilot plant for wastewater treatment. Additionally, we delve into unconventional concepts concerning the integration of HTC with concentrated sunlight.

3.4.1. Potential Energy Savings and Recovery in a HTC Pilot Scale Plant

A great advantage of HTC is the improved filterability of the slurry compared to most input materials, which significantly reduces the energy required for drying the resulting hydrochar (HC) before combustion. Escala et al. [195] found that the mechanical dewaterability of HC compared to the untreated sewage sludge, which served as an input material, increased up to 70% instead of 30% dry matter (DM) content. Their comparison of the energy needed to dry one ton of untreated sewage sludge with 9% DM with the energy required for HTC, dewatering, and drying of the same amount of sewage sludge on a lab scale resulted in saving 99.6 kWh of thermal energy and 8.5 kWh of electrical energy via the HTC process.

As discussed previously, several studies have found promising results regarding HTC with subsequent combustion of HC in combination with anaerobic digestion of the PW concerning energy [176,196,197]. Models of industrial-size HTC have been developed, and simulations have given insight into optimal conditions [198,199], but it is difficult to find

published data on energy use and yield for pilot or industrial-size HTC plants. Findings from laboratory studies cannot necessarily be extrapolated to large-scale plants. In the HTC-Berlin project, the carbonization of sewage sludge was investigated simultaneously on laboratory and pilot scales [200]. While the laboratory data provided promising results regarding energy savings, problems with the efficient feeding of the input material into the reactor, as well as with the mechanical dewatering of HTC slurry, occurred on a larger scale, resulting in the HTC treatment losing its energetic advantage over the conventional process.

The results collected by a Swiss study at a pilot-scale plant showed more promising results [201]. The core of the project was a constantly operating HTC facility with a reactor volume of 1 m³. The energy potential and the fuel characteristics of the hydrochar were tested with raw sewage sludge as input material. A mass flow of 275 kg/h sewage sludge (DM = 9.5%) was fed to the reactor, corresponding to 26 kg/h dry matter. The results showed a mass distribution after the process of 79% of DM in the HC and 21% in the PW when running the HTC at 200 °C for 4 h. A DM content of nearly 70% of the carbonized raw sludge could be achieved by mechanical filtering with an industrial-size batch press suitable for apples. Despite the high ash content, the calorific values of the HCs from the campaigns were comparable to wood, with an HHV of 18.7 MJ/kg, which is in the lower range of the typical 15–25 MJ/kg. HTC in laboratory experiments with sewage sludge, as summarized by Ipiales et al. [202] in their review paper, resulted in an HHV of HC of 14.5–18.5 MJ/kg [176,203]. Concerning energy recovery in the hydrochar, the results of [6] were 78.4% in the range found by the laboratory measurements, with 57.4–84.9% [202].

Gasification and pyrolysis tests carried out by Mehli et al. [201] with combustion equipment that was not optimized for HC showed that the emissions of NO_x, SO₂, and dust clearly exceeded the limits given by the Swiss ordinance on air pollution control. The authors suggest using a combustion system optimized for hydrochar along with suitable flue gas cleaning.

Table 3 shows the energy input and output, as well as the thermal efficiency and the plant efficiency per ton of fresh sewage sludge (DM 5%), as input material for two examples. The energy efficiency parameters are defined as follows: (i) thermal efficiency = ratio between the thermal energy contained in the hydrochar produced and the thermal energy for production; and (ii) plant efficiency = ratio between the thermal energy contained in the hydrochar produced and the sum of the thermal energy, electrical energy, and thermal energy contained in the input material [198]. In Table 3, example “a”, the material was first concentrated to 9.5% DM using a thickening decanter. After HTC at 200 °C with a residence time of approximately 4 h, the slurry was dewatered to 68.5% DM and dried to 90% DM using a fluidized bed dryer. The energy input was composed of 86 kWh_{th}/t and 13 kWh_{el}/t for the HTC process, 3 kWh_{el}/t for mechanical dewatering, and 11 kWh_{th}/t and 1 kWh_{el}/t for drying the HC. The output of electric and thermal energy of a combined heat and power plant was calculated for the HC. The calculations for energy efficiency were made based on the measurements obtained in this study and agreed quite well with the modeling predictions of Lucian and Fiori [198] for input material with lower DM at a medium process temperature and residence time.

Table 3. Input and output of electrical and thermal energy per ton of raw sewage sludge (5% DM) to HC used in a combined heat and power plant, as well as energy efficiency, defined as the ratio of energy input to energy output (see text for details).

Example	Energy Input		Energy Output		Energy Efficiency	
	Electrical	Thermal	Electric	Thermal	Thermal	Plant
	kWh _{el}	kWh _{th}	kWh _{el}	kWh _{th}	-	-
a	17	97	46	66	2.13	0.55
b	11	45	46	66	4.58	0.65

Based on these results, Mehli et al. [201] suggested using a decanter centrifuge to concentrate the input material to 15% DM to optimize the process. As shown in Table 3, example “b”, this change would result in a decrease in the input energy for the HTC process by 52 kWh_{th}/t and 6 kWh_{el}/t and an increase in the energy efficiency. The energy input for dewatering the raw sewage sludge was assumed to stay the same. However, the authors stated that the assumptions made for predicting example “b” were rough and must be verified. Additional promising sewage sludge reduction technologies were summarized by Ferrentino et al. [204] in their recent review paper, along with information on the efficiency of the methods, the energy consumption, and the costs, which could be helpful for better estimations. Based on the results of their project, a potential reduction of 23% in electricity consumption and 61% in heat consumption when using HTC to produce combustible material compared to conventional sewage sludge treatment was determined by Mehli et al. [201]. During the project, the consumption of input energy was reduced via heat recovery and optimized pre-heating of the input material. Further energy savings of 20–25% through additional measures are expected.

Further research on the pilot or even industrial scale is needed to improve the processes. Apart from optimized heat recovery, efficient dewatering of the input material or the HTC slurry has the highest potential to increase the energy efficiency of HTC on the pilot or industrial scale. Lucian et al. [205] reached a DM of 80–89% after acidic conditioning, centrifugation, and optimized filtration.

As discussed in Section 3.3, additional energy recovery is possible from the anaerobic digestion of the PW. The recovery was tested by Mehli et al. [201], with limited success. Their findings agree with other studies [196,197] stating that problematic substances in the PW lead to limitations in anaerobic digestion effectiveness. Laboratory experiments showed that only a fraction of the theoretical methane production could be achieved with PW, and the production was delayed by several weeks compared to the control samples containing cellulose [201]. The authors assume that not only do elements like phenols and N-, O-, or S-heterocycles hinder anaerobic degradation, but high levels of long-chain fatty acids and condensation products of amino acids (melanoidins) also play a role in inhibition. Merzari et al. [196] found that microorganisms adapted to some of the toxic substances in the PW. The authors suggest further investigations into the microbial community and the optimization of the HTC process regarding the quality of both HC and PW. The expected energy recovery of PW was 20.9%, in the range of laboratory measurements obtained in other studies (of 6.7–23.5%) [176,203].

Depending on the potential energy yield from PW, it is worth thinking about other possibilities to valorize the PW. Section 3.3 addresses the positive effect of acidification during the HTC process on the phosphorous recovery in the PW and the possibility of producing fertilizers like struvite from it. Regarding optimal resource management, it is important to consider the contents of HTC products for appropriate utilization. Sewage sludge, for example, is rich in plant nutrients, but also contains heavy metals (HM), which poses a challenge. If the HTC process can be controlled in such a way that the HM remains in the HC, but the nutrients end up in the PW [206], the energetic use of the HC makes more sense than its application in agriculture, while the return of the nutrients from the PW into fertilizers is desirable.

3.4.2. Towards the Zero-Energy Plant: HTC Sustained by Solar Energy

HTC requires proper optimization to achieve a fully green biorefinery. Despite its significance, there exists a general disinterest in the energy efficiency of HTC plants. The challenge is heightened by the necessity for high temperatures in the HTC reactor, and it is especially pronounced in large-scale applications. In these cases, using renewable electricity, which theoretically could be more easily generated, faces inherent technological barriers in meeting these required temperatures [193]. Hence, as shown in the previous section, energy sourcing often leans towards thermal methods, mainly from the combustion of natural gas or biogas (possible solely through integration with anaerobic digestion), combustion

of hydrochar, or from the recovery of waste heat. These solutions represent an excellent premise for improving energy efficiency without a significant investment in design and optimization. However, in an ideal energy scenario, this approach could undergo further optimization. Indeed, despite considering biogas or hydrochar as “renewable” due to their derivation from biomass or waste, relying on this classification or, worse yet, hiding CO₂ certificates does not negate the specific emission of greenhouse gases (GHG) associated with the use of such biofuels in combustion. Meanwhile, waste heat streams could be directed to some other utility, improving the energy efficiency of the entire plant. Therefore, the path toward sustainability inherently involves the integration of HTC with renewable sources that could avoid the production of GHG in situ and concretize a zero-energy biorefinery, or even a CO₂ sink. There are several challenges, from assuring non-intermittent operations to achieving economic viability. Nonetheless, HTC could benefit from leveraging insights acquired from other biomass thermochemical technologies, such as pyrolysis, hydrothermal liquefaction, and gasification, thereby broadening its scope for potential applications.

To the best of the authors’ knowledge, concentrated sunlight remains the sole investigated renewable energy source in HTC applications apart from biogas or hydrochar combustion [207–209]. Alternative methods, such as coupling with solid oxide fuel cells, have primarily been explored only for hydrothermal gasification [210]. Concentrated solar thermal energy adopts mirrors or lenses to concentrate sunlight from a large area onto a receiver, where the concentrated sunlight is then used to power the HTC process itself. Using solar concentration for sustaining thermochemical processes has experienced substantial development since the mid-2000s (Yadav and Banerjee, 2016), drawing from established concentrated solar power systems employed in electrical production. For instance, in the context of hydrothermal liquefaction (HTL), Pearce et al. [211] proposed a commercial solution integrating a concentrating solar power system with HTL. Moreover, several techno-economic studies have been conducted to analyze the feasibility of solar-HTL integration [212,213].

Generally, the coupling between a hydrothermal system with concentrated solar energy can be achieved via two methods: (1) direct integration, where the reactor becomes also a solar receiver and reactions occur; (2) indirect integration, where solar concentrators heat up a thermal fluid used to transfer heat to a hydrothermal reactor. In this regard, Ayala-Cortés et al. [193] carefully reviewed the details behind these strategies.

In the context of direct coupling for HTC, Ischia et al. [208] developed and tested a hybrid solar HTC apparatus, wherein an HTC reactor directly interfaces with a parabolic dish concentrator (shown in Figure 3). Positioning the HTC reactor, equipped with a highly absorptive coating (copper oxide), at the focal point of the solar concentrator allowed for the efficient absorption of solar energy. This configuration enabled the concentrated sunlight to fulfill the energy requirements of the HTC reactor. However, due to the direct coupling, the reactor was susceptible to fluctuations in sunlight due to weather conditions, making it suitable mainly for small-scale applications or off-grid solutions. Despite the apparent simplicity, this concept can serve as foundational step for further enhancements in developing more complex integrated systems and the provision of off-grid solutions.

In an indirect configuration, Ischia et al. [214] conducted a techno-economic analysis of a conceptual large-scale solar-HTC plant. This design involves heating a stream of molten salts inside solar collectors and subsequently utilizing this heated stream to provide thermal energy to the HTC plant. The results indicate that thermal energy storage facilitates continuous plant operation, potentially leading to a minimum selling price of hydrochar at EUR 34.7/ton, accounting for revenue generated from processing organic wastes.

In another study, Bertolucci et al. [207] introduced an off-grid hydrothermal reactor powered by flat solar absorbers employing vacuum technology developed at CERN. This system utilizes a thermal fluid heated by the absorbers and directed to the hydrothermal reactor. The design is portable and aimed at in situ operation, processing up to 100 L of biomass per day.

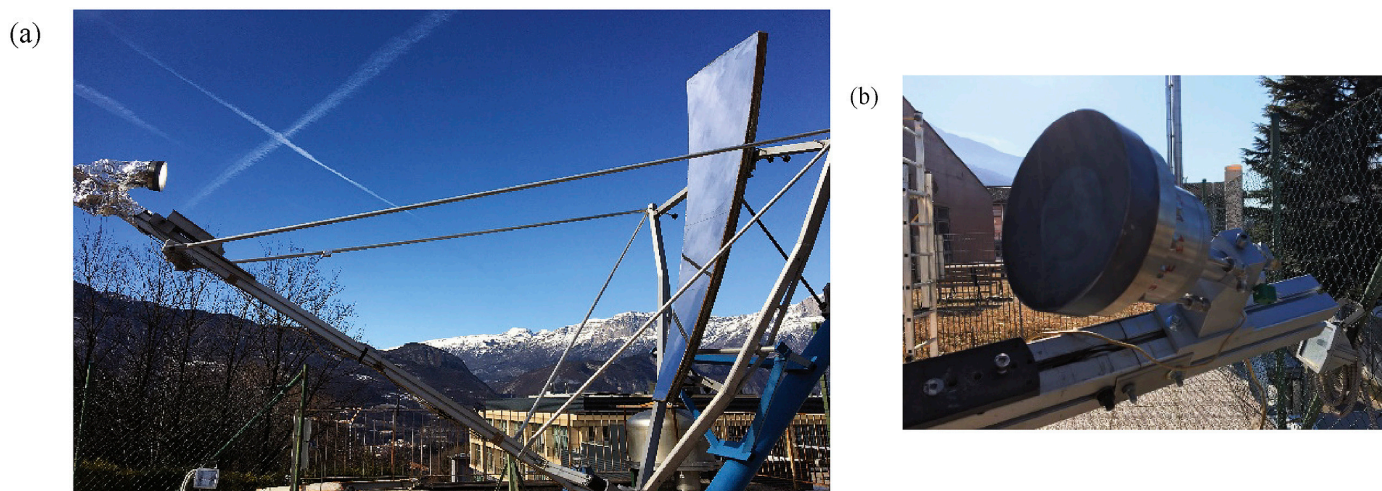


Figure 3. HTC reactor integrated with a solar concentrator apparatus developed by Ischia et al. [208]: (a) HTC reactor placed on the solar apparatus, made up of one parabolic module and a sun tracker; (b) detail of the coated flange (receiver) of the HTC reactor. Reproduced with permission.

HTC-solar integrated plants face numerous challenges, primarily stemming from technical and economic complexities. However, these challenges should not diminish enthusiasm for this integration, as it has the potential to establish a fully sustainable system and potentially facilitate off-grid capabilities, catering to geographical areas in developing countries. In particular:

- Continuous operation of solar HTC: Solar energy, being intermittent and variable, necessitates the integration of thermal storage systems to ensure prolonged operational continuity. However, this integration adds complexity in terms of plant operation and escalates overall costs.
- Direct coupling challenges. Designing an efficient receiver with appropriate absorbing materials is essential. However, this setup faces issues due to gradients caused by uneven concentrated flux distribution; potential operational complications such as plugging in the receiver and its piping due to high solid loads; and intermittent conditions that, combined with hydrothermal effects (e.g., high pressure), can impact the lifespan of the solar receiver.
- Indirect coupling complexities: The primary drawback involves increased costs and additional equipment, with maintenance and operational expenses being major challenges. Moreover, the use of high thermal heat carriers, such as molten salts, poses issues like corrosion, adding to operational complexities and costs.

4. Conclusions

The potential of HTC is well recognized. It is capable of converting biomass into bio-based products, from advanced carbons to chemicals and biofuels, and valorizing unpleasant and unconventional substrates. HTC stands tall as a fully-fledged green route paving the way for a bio-based future. Despite its promise, HTC encounters obstacles in transitioning from academic exploration to industrial implementation. For example, ongoing gaps in understanding complex reaction intricacies impede tailored product optimization, while challenges persist in integrating HTC on a large scale with wastewater treatments, managing HTC process water, and establishing standardized assessment techniques for HTC products. Overcoming these challenges requires a common effort, including scientific research and collaboration across scientific sectors engaged with HTC.

This article offers an overview of the fundamental and technological facets identified as pivotal for HTC's advancements. It delves into fundamental research, exploring the present knowledge of reaction pathways, predictive models, analytical techniques, and frontier concepts like hydrothermal humification and fulvification. Additionally, it examines

HTC's technological applications and challenges, focusing particularly on combined HTC, wastewater integration, resource recovery from HTC process water, and plant energy efficiency. The paper starts from an analysis of the state of the art and provides suggestions to fill knowledge gaps on a scientific and technological level. Despite the challenges, the potential is high, as shown by the numerous virtuous projects, like the continuous Swiss pilot plant, the solar hydrothermal systems, the nutrient recovery studies, the advanced predictive models, and the exploration of co-HTC. With this article, the authors hope to contribute to pushing forward the HTC process to which they have dedicated much of their scientific activity and passion.

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