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Review

Computational Modeling Approaches of Hydrothermal Carbonization: A Critical Review

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Abstract: Hydrothermal carbonization (HTC) continues to gain recognition over other valorization techniques for organic and biomass residue in recent research. The hydrochar product of HTC can be effectively produced from various sustainable resources and has been shown to have impressive potential for a wide range of applications. As industries work to adapt the implementation of HTC over large processes, the need for reliable models that can be referred to for predictions and optimization studies are becoming imperative. Although much of the available research relating to HTC has worked on the modeling area, a large gap remains in developing advanced computational models that can better describe the complex mechanisms, heat transfer, and fluid dynamics that take place in the reactor of the process. This review aims to highlight the importance of expanding the research relating to computational modeling for HTC conversion of biomass. It identifies six research areas that are recommended to be further examined for contributing to necessary advancements that need to be made for large-scale and continuous HTC operations. The six areas that are identified for further investigation are variable feedstock compositions, heat of exothermic reactions, type of reactor and scale-up, consideration of pre-pressurization, consideration of the heat-up period, and porosity of feedstock. Addressing these areas in future HTC modeling efforts will greatly help with commercialization of this promising technology.

Keywords: hydrothermal carbonization; biomass; computational process modeling; heat transfer; hydrochar; research gaps

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1. Introduction

The ability for hydrothermal carbonization (HTC) to incorporate the use of typically undesirable feedstock and wastes with high moisture contents and convert them to higher value products for various applications has generated high amounts of research interests and studies over the years [1,2]. More sustainable methods of producing products from biomass and other waste materials that can be converted and used as biofuels, adsorbents in air or water treatment processes, energy storage for supercapacitors and fuel cells, or catalysts are becoming increasingly imperative in a global transition away from fossil fuels [3]. The capacity to produce these types of products from renewable biomass sources through HTC will help in reducing emissions and waste from agricultural residues, and may be able to reduce the energy consumption under milder reaction conditions when compared to other biomass conversion processes such as pyrolysis or torrefaction, which require substantial energy inputs to dry the feedstock [4,5]. These potential advantages that make this process favorable as a pre-treatment method for second generation biomass has led to its continued development and a more recent shift in research to investigate the optimal conditions and variables that should be used, as well as the challenges that need to be faced to adopt the technology at larger and continuous scales [1,6].

The HTC thermochemical conversion process involves heating the feedstock in the presence of water in the subcritical region generally at temperatures in the range of 180–350 °C, in a

sealed reactor and at autogenous pressures or above the saturation pressure of water [7–9]. The types of feedstock that are commonly studied for HTC are non-food lignocellulosic materials which are mainly composed of lignin (10–25%), cellulose (40–60%), and hemicellulose (15–30%), the amounts of which vary depending on the specific biomass [10]. Through a series of reaction pathways over a certain time (0.5–12 h) [7] that are still not well understood, the feedstock is transformed into a hydrochar solid product and other liquid and gas by-products are produced [8]. Because the method is relatively simple, there are many scientific papers available detailing lab scale batch reactor experiments with different temperatures, residence times, or types of feedstock. An area of research that is lacking for HTC is work on modeling and simulations, which are essential to scale up the process to continuous system designs and larger plant operations [11,12].

Generally, HTC models can be categorized into three different types, kinetic, statistical, and computational. Román et al. [8] differentiated these categories within the embodiment of the mathematical model category, as they typically involve solving a set of governing equations or relationships that are meant to solve kinetic properties taking place during the process. Ischia and Fiori [6] broke down different types of HTC models based on four subsystems of analysis, being the process, reactor, plant, and life cycle assessment; however, they state that kinetic and statistical models are used for process studies and computational models are used to describe the reactor. Despite some overlap and absence of distinct categories, the differences between these three types of models and their utilizations that can be specific for particular studies should be recognized.

1.1. Kinetic Models

Kinetic models envelop the most common form of studies on HTC that are conducted in terms of modeling work and are most frequent in literature publications. Most commonly, these methods are used to find the activation energies and reaction rates of different feedstock under HTC by assuming simplified reaction pathways. The assumption of depicting the process with first-order reactions is usually made to simplify the model, but some studies have been developed to find more specific values for the reaction order [13]. Since the mechanisms involved with HTC are quite complex and still not fully understood, despite their simple implementation and accuracy, these models are limited in their inability to describe the heat transfer phenomena taking place throughout the process and identifying the different types of reactions that are occurring [8]. Their use combined with other methods and experimental data are beneficial and contribute to the understanding of the detailed reaction mechanisms taking place [6].

1.2. Statistical Models

The purpose of statistical models is to optimize operating conditions or key parameters of an HTC process. This can be done using Design of Experiments (DoE) or Response Surface Methodology (RSM) techniques that are able to compare the effects of changing a certain value and its impact on the system, output variables, or other parameters [6,14]. These can also be useful for coming up with relationships for how different types of feedstock behave depending on the severity of the HTC conditions [15]. The shortcomings of statistical models are their limited insight into the understanding of the process taking place, as they do not work to describe reaction mechanisms or the processes taking place and may be specific for certain feedstock or lab-scale environments. They also often require large amounts of data to create significant correlations that can generate accurate predictions, limiting their ability to be used in complex processes.

1.3. Computational Models

Computational models work to simulate the full process taking place in the reactor during HTC to examine both time and space variables which can better investigate the heat transfer phenomena and flow physics [8]. These models are currently the least common in literature but are important to study for the industrialization of HTC because they can

be used to provide a more advanced understanding of what occurs at different points of time inside the reactor. One of the main advantages of computational models is their ability to generate data for the time steps throughout the process. Computational models can also be made to study the Computational Fluid Dynamics (CFD) of a process which can be beneficial for examining the flow behavior of different phases in the reactor. This provides key insights into the effects of operating conditions such as temperature, residence time, the type of feedstock, or the reaction mechanisms and pathways to be analyzed. The frequency of time steps that the governing equations are calculated at during the process is set by the user and is usually limited by computer processing power. The results of these studies provide a means of having visual displays for the response of the system based on the set inputs and allows for easy data processing.

For HTC studies, computational models are commonly used in combination with kinetic models and compared to experimental data for validation. This constitutes the accuracy of the model predictions and is an essential metric to ensure that the process is properly represented. The impact of having reliable models makes it more feasible to understand the energy requirements and economic viability of transitioning the process to a large scale, but due to the complex reaction pathways, variability in feedstock, and change in properties with temperature during HTC, there remains much room for developments in this area [12]. Especially when considering the topics of thermodynamics, such as heat and mass transfer, or the fluid flow taking place during the process, the number of developed computational models is very minimal [8]. The disadvantage of computational models is their complexity, which can demand powerful computers and processers but are necessary to be able to apply to larger commercial adoption of HTC. The limited studies that have been done on these topics of HTC modeling point to multiple research gaps that need to be addressed, and future challenges that will be faced in establishing enhanced models.

For this reason, the purpose of this review is to identify the key aspects that the most recent and up-to-date HTC computational modeling papers have explored, the important questions that the authors of these studies have identified to be conducted in future research, and considerations that are yet to be addressed in literature. The organization of this review is broken down into six research areas that each discuss an area that required more investigation or challenges that should be considered when working on the computational modeling of HTC, as outlined in Figure 1. Each section is significant in that it includes the studies that have investigated the topic as well as suggestions that future researchers could explore.

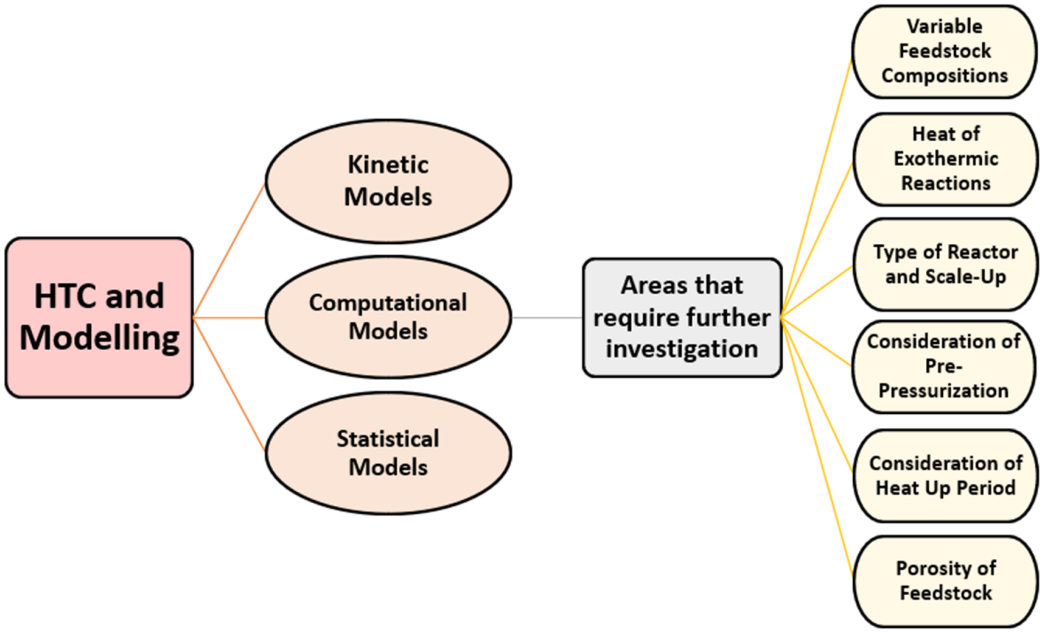

Figure 1. Areas that require further investigation for computational models.

Before exploring these areas of a computational HTC model, a general background of the mass and energy balance and chemical reactions is given, as well as the general approaches and findings from currently available computational models.

2. Chemistry and Mass and Energy Balance in HTC

2.1. Chemistry of HTC

The thermochemical process of HTC yields three main products in different phases. The main phase is a solid hydrochar which is typically the product of interest because it is used as an energy dense carbon material [16]. However, an aqueous liquid phase from degraded biomass polymers in water and gas products are also produced [16]. The use of water as a reactant means that the process is inexpensive and environmentally friendly, and by treating the biomass with hot water retained in the subcritical region under high pressures, the water is more reactive and achieves its maximum ionic product, making it an effective solvent and catalyst [1,17,18]. As already stated, the reaction mechanisms involved in HTC are highly complex at these mild conditions and involve different pathways, such as hydrolysis, dehydration, decarboxylation, aromatization, and condensation reactions [13,19]. The behavior of these reactions will be influenced mainly by the reaction severity, defined by the temperature and residence time [20].

Because hydrolysis has low activation energy, it can be considered the main reaction that governs HTC and is essential for cleaving the bonds of the lignocellulosic components, breaking them down into many smaller groups [16,21]. For lignocellulosic biomass, the decomposition of hemicellulose and cellulose in subcritical water are known to begin at 180 °C and 200 °C, respectively, and lignin decomposes the slowest and over a larger range above 220 °C [1]. The difficulty in understanding the remaining reactions is largely contributed to the unstructured order that they may occur in, as they do not occur in series and are affected by the conditions of the HTC process [1].

Some authors have worked to create depictions of these reaction pathways during the HTC process through flow diagrams to provide a clearer illustration of the chemistry taking place. A flow diagram is outlined in Figure 2 that has been developed for this purpose.

As seen from the schematic, the main components of biomass degrade to form acids, sugars, and other chemical compounds during the reactions. These products are typically formed in the process water and can be valuable by acting as a catalyst during the reaction or by depositing onto the hydrochar and enhancing its morphology [10].

It is common for researchers to perform various techniques to characterize the contents of the liquid process water, such as analyzing the total organic carbon (TOC), organic acids using ion chromatography (IC), and high-performance liquid chromatography (HPLC) for the detection of some other sugars, acids, and various dissolved species [1,22].

The most well-known and basic reaction pathways for the primary components of lignocellulosic biomass are shown in the schematic. In the first stage, the primary decomposition phase begins mostly with hemicellulose degrading by hydrolysis and is broken down into oligomers and monomers such as glucose and fructose and can then further decomposes to form 5-hydroxymethylfurfural and acetic acid during additional decomposition [10,23,24]. Cellulose also undergoes hydrolysis at higher temperatures which can contribute to the formation of acetic, formic, and levulinic acid [10,23]. Lignin remains relatively inert and does not produce acids, but partially hydrolyzes and contributes to the formation of phenolic compounds [10,23,25]. Through a series of remaining reaction pathways, these compounds that have been formed from the decomposition stages either remain in the process water primarily as volatile organic acids (VOCs) or precipitate and add to the formation of the secondary solid layer on the hydrochar [1].

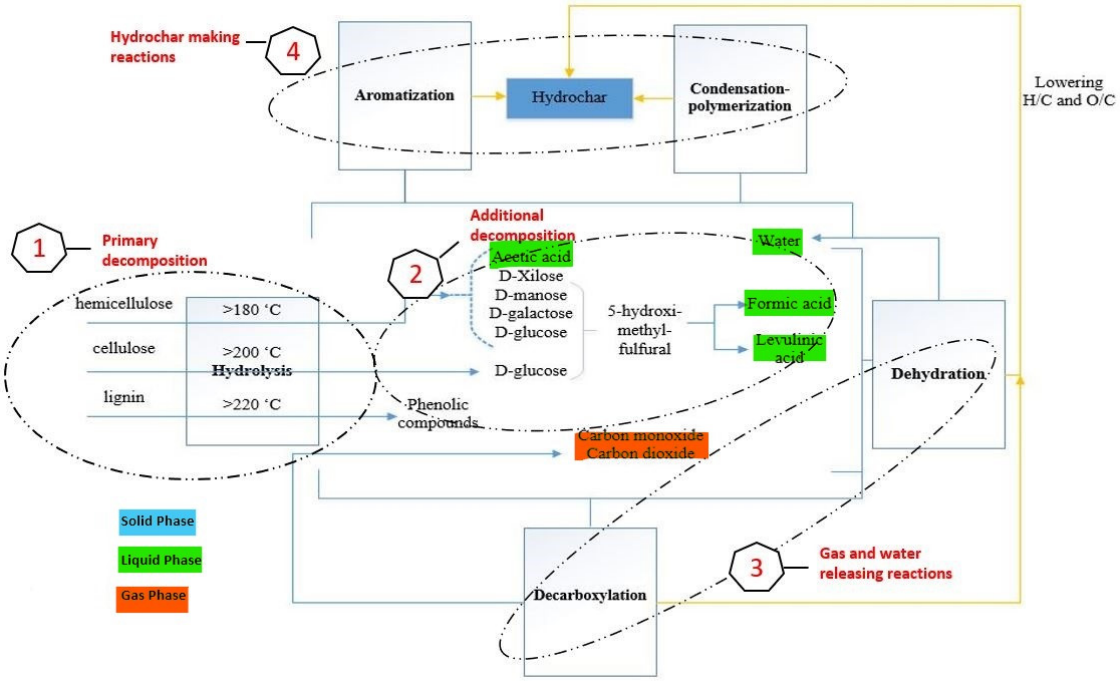

Figure 2. Schematic of the HTC reaction pathway process.

In the third stage, dehydration and decarboxylation reactions are responsible for reducing the hydrogen and oxygen content in the solid phase and increasing the overall carbon content [16,26]. The fourth stage involves reactions that further contribute to the formed hydrochar. Condensation and polymerization reactions add to the formed char as a result of the precipitation of dissolved organic compounds in the process water forming layers of secondary char onto the solid phase, and the behavior of these reactions are usually responsible for the presence of functional groups on the surface [27,28]. The main solid phase (primary char) is a result of the solid-solid conversion of unhydrolyzed lignin and fraction of cellulose due to their higher degradation temperatures than hemicellulose [27]. Aromatization reactions contribute to the degree of carbonization and morphology of the solid product, leading to the development of products with better coal-like properties [1,21]. It should be noted that although there is a reasonable understanding of the types of reactions and their contributions taking place during HTC, their severity, order, and interactions are still not thoroughly known, and the four stages outlined in Figure 2 can occur concurrently [1]. Generally, this summary above serves as a good explanation for the reaction networks that form the products of HTC; however, the feedstock type, temperature, and time will greatly influence the composition of intermediates in the process water [27]. Researchers will often publish studies that describe the degradation of certain feedstock components through kinetic models, which have typically been simplified to first-order reaction models for these reasons. More recent publications have recognized the inaccuracies obtained from these simplifications and have been working to explain the chemistry of reactions with different values of the reaction order [27]. The importance of investigating the reaction pathways occurring during HTC and their variability based on different parameters has become paramount for continuing to improve a more advanced understanding of the process.

2.2. Mass and Energy Balance

The thermodynamic nature of the HTC process is a mix of endothermic and exothermic reactions. Endothermic behavior is largely involved in the initial reactions taking place and relies on the external heating of the reactor [1]. Over time, the procedure shifts from endothermic to exothermic with increased residence time of the feedstock [29]. Mass and energy balances of the overall process can be developed by analyzing the mass percentages and compositions of initial feedstock and comparing to the solid hydrochar yield, aqueous

products, and gas products. Based on literature that agrees upon common characterizations of the products that are formed from HTC, a simple mass balance black box diagram can be constructed, which is shown in Figure 3. This assumes a biomass to water ratio of 1:6.

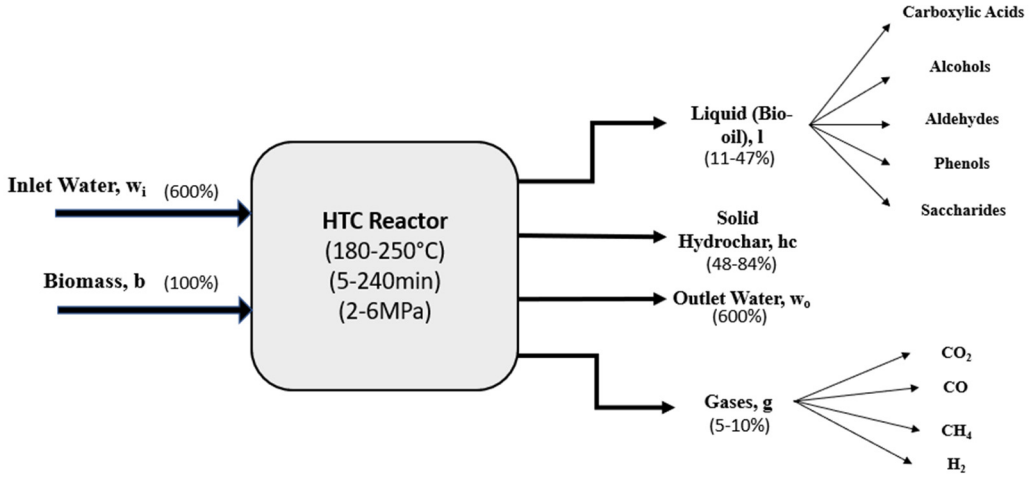

Figure 3. Input and output streams for HTC mass balance.

This figure shows the main input and output streams from an HTC reactor and is adopted from a similar diagram made by Yan et al. [30]. The organic compounds are split into five main categories that each contain many other products as outlined by Cao et al. [31]. The gas products are split into CO, CO2, H2, and CH4, which are the main gases released from decarboxylation reactions as outlined by Pauline and Jospeh [32], although it is known that CO2 has a dominating presence. The mass balance based on these inputs and outputs for an HTC process can be given by Equation (1), where the subscripts of each mass term represent the terms shown in Figure 3:

$$\dot{m_{w_i}} + \dot{m_b} = \dot{m_l} + \dot{m_{hc}} + \dot{m_{w_o}} + \dot{m_g} \quad (1)$$

For the energy balance, the enthalpies of formation of the biomass and products can be determined through combustion in a bomb calorimeter and are usually paired with assumptions to simplify the characterization of the aqueous and gaseous products based on the predominant compound in each. The enthalpy change of the process based on Figure 3 can then be governed by the principles of Hess's law given by Equation (2), as outlined by Pecchi et al., where the enthalpy of formation of the reactants is subtracted by the enthalpy of formation of the products [26]:

$$\Delta H^o{}_{HTC} = \left(\Delta H^o{}_l + \Delta H^o{}_{hc} + \Delta H^o{}_{w_o} + \Delta H^o{}_g\right) - \left(\Delta H^o{}_{w_i} + \Delta H^o{}_b\right) \quad (2)$$

where $\Delta H^o{}_{HTC}$ is the overall enthalpy change of the process usually in the units of energy per mass (J g^{-1}). The rest of the ΔH^o terms are the enthalpy changes of the respective solid, liquid, and gas products and reactants.

The estimations for the solid phase can be predicted accurately if the composition is known by applying Equation (3) for the standard combustion reaction of a feedstock, where x and y are determined from the ultimate analysis [29,30]. The heat of combustion can be used in combination with bomb calorimetry experiments of the biomass to determine the solid enthalpy of formation [1]:

$$CH_xO_y(s) + \left(1 + \frac{x}{4} + \frac{y}{2}\right)O_2(g) \overset{yields}{\rightarrow} CO_2(g) + \left(\frac{x}{2}\right)H_2O(l) \quad (3)$$

However, there are small concentrations of various compounds in the liquid and gas phase, some of which may pose significant contributions to the energy balance [26].

The literature is fairly consistent in assuming CO_2 as the singular gas product, since it accounts for over 90% of the produced gases [29,30]. For the liquid phase, there are many compounds that dissolve in the water, and the number of studies that examine its contents are less prevalent, meaning that some important species may be left out [26].

Overall, studies that aim to calculate the HTC process heat are important to understand the overall reaction behavior. With increasing severity in the HTC process, the overall enthalpy of reactions is known to be more exothermic [7,33], which can create significant differences in how energy intensive the process is.

3. General Approach for Current HTC Computational Models

Depending on the purpose of the model being developed, there are different approaches that could be integrated to generate the desired results. The formulation of a model typically begins with defining and establishing a set of governing equations which will be solved at different points throughout the process, and the equations will be tailored to calculate the parameters that are being investigated. For example, general mathematical models are commonly used to determine the kinetics of reaction pathways of HTC, with the reaction rate being the variable of interest. The reaction rate is usually based on the change in mass over time and is found in simplest terms by describing the reaction mechanism with a first order lumped model where the initial feedstock is converted into the accounted for intermediates and products. This involves the calculation of a constant for the reaction rate and the activation energy—both of which will be specific to the process—and is conventionally defined by the Arrhenius equation:

$$k = AT^n exp^{-\frac{E_a}{RT}} \quad (4)$$

where k is the reaction rate constant (s^{-1} for first order), A is the pre-exponential factor (s^{-1}), E_a is the activation energy (J mol^{-1}), R is the universal gas constant (8.314 $Jmol^{-1}$ K^{-1}), and T is the temperature (K).

However, the importance of developing models that can account for the flow and heat transfer that takes place during HTC is a research area in computational modeling that is rarely considered. To further explain the process, detailed kinetic studies can be compared with computational models that are able to include thermodynamics and transport phenomena of the different phases in the reactor [6,34]. The publications that have contributed to the growth of this form of research and those that have that have made significant conclusions are highlighted in this section.

In terms of accounting for heat transfer, particle transport phenomena, and reaction kinetics, it is difficult to develop a computational model able to describe all three components, evident from the absence of such a model. Instead, models are usually created to target the analysis of one of these components to reduce the complexity and the limitations imposed by computational processing time [35]. These constraints directly limit the degree of intricacy; however, with more emphasis on the simulation of thermochemical conversion processes, computational models are showing their increased potential and importance as a tool for this form of technological development [36]. As these advancements continue to be made, the expectations for what is considered a reasonable model has been raised [36].

One of the first recorded models of HTC that can be credited to computational work—made clear by it being highly cited in the description heat transfer mechanisms—was made by Baratieri et al. [37]. They used a lumped capacitance method to develop a simple first order thermal resistance model. This method assumes that the temperature is constant inside the reactor and only considers the system as one component (i.e., the reactor) which exchanges heat with its surroundings. The equations developed under these assumptions solve the temperature and pressure which are compared to experimental values for the HTC of grape marc from previous experiments conducted by [38]. No simulations or CFD were performed, and the lumped heat transfer model that was depicted using resistance capacitance network is seriously limited by the oversimplifications of constant temperature

and consideration of water as the only phase inside the reactor. However, this work is commonly referenced by other HTC computational models and serves as a good basis for a starting point.

Álvarez-Murillo et al. [39] were one of the first examples that worked to simulate the heat transfer taking place during HTC with a CFD model. They constructed a cylindrical reactor geometry in COMSOL Multiphysics to help solve their kinetic model for the HTC of cellulose, which was made more complex by considering the temperature as a function of time. This work introduced the use of the typical energy conservation equation for heat transfer as shown in Equation (5), where, based on the geometry and properties of the different phases, the temperature can be found at different times throughout the process and used to solve the kinetic parameters:

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_P u \bullet \nabla T = \nabla \bullet k \nabla T + \dot{Q} \quad (5)$$

where ρ, C_p, and k are the density (kg m^{-3}), heat capacity (kJ kg^{-1} K^{-1}), and thermal conductivity (W m^{-1} K^{-1}) of the given material, respectively, u is the velocity vector (m s^{-1}), T is the temperature (K), and $\dot{Q}$ is the amount of energy released as heat by the reactions taking place in the reactor (W m^{-3}), which was actually neglected in their setup after stating that the values would be low enough to ignore.

The configuration used by Alvarez-Murillo et al. [39] to model the heating of the reactor was to represent the stainless-steel autoclave inside a rectangular oven that was heated up to the desired temperature. Conduction, convection, and radiation through the reactor walls were also considered, but the reacting medium was again only treated as water. The results of the theoretical and experimental temperature data over time of the reacting medium were in reasonably good agreement, which was used to find the solid yield results. The model was able to properly predict the solid yield, given by a high R^2 value of 0.9754 for the theoretical and experimental correlation. Therefore, this initial computational model is a fair precedent for providing a simplified representation of an HTC process.

The work by Mendecka et al. [40] was performed to create a CFD model of the HTC of olive pomace and overcome previous simplifications by investigating the heat transfer taking place without assuming the reacting medium as only water. Their model was created in ANSYS Fluent software, and accounted for all three species of air, water, and biomass inside an HTC reactor with their corresponding properties. Additionally, a large portion of the paper is dedicated to the natural convection behavior of the phases. They used a configuration which defined the properties of the three phases in a cylindrical reactor geometry enveloped by a heating band covering two thirds of the reactor's height. Using the ANSYS mixture model to simulate the flow in the reactor, a ratio of the dispersed phase (biomass and water) was defined, and the model was simplified to a two-dimensional axisymmetric problem. The continuity and energy equations were coupled with the momentum equations to solve for the relative velocities of the dispersed biomass phase under the assumption of laminar flow, with conduction and convective heat losses. A comparison in this study was also made to experimental data from [41] to the model results of the temperature over time for four different power inputs of 2.5 kW, 3.0 kW, 4.0 kW, and 5.0 kW. The experimental trend is in reasonably good agreement to the simulation with an input power o 4.0 kW, with a maximum temperature of 34 °C difference during the first 10 min and 23 °C for the rest of the process. The author's report that this work is suitable to be used as an initial reference for better understanding of both the flow and heat transfer processes taking place during HTC.

Heidari et al. [12] took a newer approach by conduction a computational analysis for a mathematical model of HTC by using COMSOL Multiphysics software and including physics for heat transfer in porous media. Biomass materials typically have a high porosity, which is known to have a significant influence on the performance during thermochemical conversion processes. The governing equation used in this case is a modification of

Equation (5), which accounts for the influences from porous properties by considering the density, heat capacity, and thermal conductivity of the solid and fluid phases in the biomass based on the volume fractions.

They constructed a cylindrical reactor geometry and applied a surrounding heat flux to the outside for the heat source but designed a more realistic cap of the reactor and included the biomass phase by arranging 400, 7.5 mm cube particles as a separate geometry inside the water phase in the reactor. However, the main purpose of this work was to use the computational study to solve the mathematical model describing the kinetic parameters, and any particle transport or flow behavior was not considered.

Sangare et al. [35] proposed a computational model also using COMSOL Multiphysics that included a simulation of a stirring component. They solved for both the temperature and velocity fields for the HTC of avocado stone biomass under turbulent flow conditions using the k-ε turbulence flow model. The biomass phase was modeled similarly to the work of Mendecka et al. [40] as a dispersed phase of biomass particles within the water in the reactor. The author's reported that a rotation speed of 550 rpm was needed to achieve homogenous mixing of biomass and water inside the reactor. Given that the maximum rated speed of the magnetic stirrer used in their experimental work was 1500 rpm, a speed of 550 rpm is relatively high and may contribute to increased power consumption but is reasonable as a requirement to achieve homogenous mixing and was the speed that was used for comparison in their experimental study. This mixing speed was validated by comparing the flow velocities experienced during the mixing of the dispersed biomass phase to a hydrodynamic simulation using only water based on the CFD model by Özcan-Taşkin and Wei also using the k-ε model [42]. The comparisons between the models showed the same trends in the curves of the axial and tangential velocity distributions and the authors state that the flow field could generally represent the fluid behavior in the HTC reactor. This approach should likely serve as a foundation for future computational models that wish to incorporate CFD analyses to better understand how the flow of the dispersed biomass phase can influence the thermal behavior of HTC process and reactions taking place.

Most recently, Chater et al. [43] conducted a computational study to analyze the CFD behavior of raw olive pomace during HTC and build on the results obtained from the ANSYS simulation made by Mendecka et al. [40]. They instead use COMSOL to investigate the heat transfer and fluid-dynamics, coupled with a simplified kinetics model and experimental results. The geometry is simplified to a 2D axisymmetric model with the conservation of mass, momentum, and energy governing the continuous fluid phase with laminar flow, and the Eulerian–Lagrangian model (dispersed phase model) is used to account for the motion of the biomass particles. Their main findings include symmetrical temperature and pressure profiles across the horizontal plane of the reactor, but also find a significant temperature difference vertically in the steady state regime, as the biomass particles move to the top of the reactor causing the bottom to be hotter. The work serves as a good contribution to the simulation of HTC processes using modeling software that provides useful insight into the thermodynamic behavior while being able to track the movement of the solid particles in the reactor.

Table 1 summarizes the main computational models that have just been described and points out what each model aimed to study, the type of biomass feedstock or component that was studied, the main contributions of the work, and the gaps that have been identified which could be considered in future models.

Table 1. Summary of available HTC computational models in the literature.

Research Group	Model Type	Software Used	Biomass and Composition	Gaps Identified	Remarks
Baratieri et al. [37]	Thermal Resistance Lumped Capacitance Model	No Software	Grape Marc *Cellulose-10.8%* *Hemicellulose-11.2%* *Lignin-50.9%* [44,45]	• Temperature in reactor was assumed to be constant • System was lumped into one component • Contents of reactor was considered as only water, and other phases were not accounted for	• One of the initial attempts at a heat transfer model • Commonly referenced by other computational studies, although a computational model was not created • Identified importance of coupling kinetic models to studies investigating the heat transfer phenomenon • Established need for using computational software for increasing understanding of HTC
a Alvarez-Murillo et al. [39]	Heat Transfer Model	COMSOL	Cellulose	• Geometry was modeled by the autoclave being heated in an oven, which is not an accurate depiction of common processes • Only water was considered as the reacting medium • No consideration of exothermic heat of reactions	• First identified model that uses computational software for HTC modeling • Considered temperature as a function of time • Identified importance of considering heat-up phase • Model was able to accurately predict yield behavior of process
Mendecka et al. [40]	Thermo-Fluid CFD Model	ANSYS FLUENT	Olive Pomace *Cellulose-30.8%* *Hemicellulose-17.1%* *Lignin-32.6%* [44]	• The mixture model used to represent the dispersed phase does not track the velocities of the particles separately from the water • Collisions or interactions between the particles are not considered • The heat of reactions was not considered. • Simplified to 2D axisymmetric model	• Initial attempt at modeling the flow physics of an HTC process. • Three separate phases of air, water, and biomass were considered • Recognized importance of considering relationships between flow and heat transfer

Table 1. *Cont.*

Research Group	Model Type	Software Used	Biomass and Composition	Gaps Identified	Remarks
Heidari et al. [12]	Heat Transfer Model with Porous Media Equations	COMSOL	Pinewood *Cellulose-39%* *Hemicellulose-34%* *Lignin-12%* [46]	• Geometry of biomass particles were simplified to 7.5 mm cubes stacked on top of each other, and their dynamic behavior was not considered • Deeper analysis on influences of porosity on the heat transfer properties • Transient study on reaction behavior at different times during the process	• Attempt at more realistic representation of biomass particles • More considerations to investigate exothermic heat of reactions were applied • Conclusion that effects of chemical reactions is significant in affecting the power requirements • Results show that effects of porosity are important to consider
Sangare et al. [35]	Thermo-Fluid CFD Model	COMSOL Multiphysics 5.2	Avocado Stones *Cellulose-5.75%* *Hemicellulose-51.34%* *Lignin-28.50%* [47]	• Better representation of dispersed biomass phase in reactor • More focus on how the biomass to water ratio may affect the reactions taking place • Transient study on reaction behavior at different times during the process	• Considering of stirred reactor by incorporating geometry of four bladed impeller • Study of different rotation frequencies for homogeneous mixing
Chater et al. [43]	Thermo-Fluid CFD Model	COMSOL	Olive Pomace *Cellulose-30.8%* *Hemicellulose-17.1%* *Lignin-32.6%* [44]	• Collisions or interactions between the particles are not considered • Gas phase inside reactor was not considered • Simplified to 2D axisymmetric model	• Flow and heat transfer behavior of biomass particles are examined for different heat fluxes • Pressures during the process are tracked

4. Research Areas That Need Additional Consideration

Keeping in mind the general HTC modeling approaches and the information in Table 1, which explains what current numerical models in literature have examined so far, the authors' recommendations for the modeling areas that should be further investigated will now be discussed. Based on the authors' knowledge and review on the topic, six important research areas are presented that could be considered in more detail, improved upon, or included in new studies and numerical models. It should be noted that to best evaluate the impact of considering these research areas into future models, model results should be compared with experimental data to observe the strength of the assumptions and methods that were used.

4.1. Incorporation of Variable Feedstock Compositions

One of the main challenges of HTC is the variety of different feedstock that can be used for the process that require a different set of operating conditions to produce the best products [15,48]. As previously stated, one of the advantages of HTC is the ability to convert second or third-generation biomass feedstock, which would typically go to waste, into valuable products [49]. These types of resources are non-food lignocellulosic materials, which are mainly composed of lignin (10–25%), cellulose (40–60%), and hemicellulose (15–30%) [50], the amounts of which vary depending on the specific biomass. The varying composition and heterogeneity in feedstock is one of the main issues in any biomass conversion process that is used to create value-added products and fuels [51].

In pursuing the main goal of using thermochemical conversion processes to convert lignocellulosic materials to high value energy products, one of the targets is also to reduce the invaluable ash content that the feed contains [15]. HTC presents an advantage over other thermochemical conversion processes of biomass in this regard, as a significant amount of the ash content and alkalinity is dissolved in the process water and removed from the solid hydrochar [52–55].

However, a major problem is presented in developing reliable models and simulations when considering the heterogeneous nature of lignocellulosic biomass. Process variables, such as temperature, time, or water-to-biomass ratio, need to be adjusted for varying feedstock of distinct compositions and have substantial impacts on the products. For this reason, a key aspect that would be beneficial for future HTC models to consider is the ability to generate reliable results using feedstock with different percent compositions of lignin, cellulose, and hemicellulose. The scope of current research in HTC has been largely limited to reaction processes for specific types of biomass or even singular lignocellulosic components [25,56,57]. If computational models were able to adjust and accurately simulate the reaction pathways for varieties of biomass sources, the decrease in specificity would strengthen their reliability for general use. Therefore, developments towards this aspect of computational modeling would assist in achieving significant steps towards commercialization of HTC. However, the more complex understanding of biomass-dependent kinetics during the process that are based on the reaction pathways of the distinct components has proven difficult [1,58].

There has been awareness in recent years in recognizing the need for research in this area and studies have been performed to investigate the behavior of the individual components of lignocellulosic biomass during HTC. The aim of this work is to better understand the kinetics of each and create relationships that can be applied to more generic feedstock. Kang et al. [56] characterized hydrochars based on the HTC of each component and showed that the highest concentration in the hydrochar was lignin followed by cellulose and lastly by hemicellulose. This is because hemicellulose is known to begin degrading at 180 °C during HTC, cellulose at 200 °C, and lignin degrades much slower and over a broader range of around 220–500 °C [45,55].

Borrero-López et al. [25] modeled the HTC of the three components of lignocellulosic biomass at different reaction temperatures and residence times to come up with simple mathematical models for the kinetic behavior as well as the pH, mass yields, and process water characterization.

More recently, Keiller et al. [57] conducted a similar study to that of Kang et al. [56] and came up with kinetic models for each of the three biomass components by subjecting hemp to HTC. Their kinetic model accounted for temperature dependent behavior over the duration of the reaction, recalculating the rate constant every 15 s during the batch reactor's heat-up period to account for any degradation taking place. They also came up with different models for both active and inert lignin, concluding that lignin possesses the most complex reaction pathways of lignocellulosic biomass because only a portion of it is susceptible to HTC, building on their previous study that found 22% of lignin was inert during the HTC of Australian saltbush at 260 °C for 60 min [59].

Mendoza Martinez et al. [3] analyzed the HTC of four different agro-forest based residues to better understand the conditions and biomass types that would be optimal for industrial implementation. Rather than propose a kinetic model for the different biomasses, a plant scale simulation was run using IPSEpro software to examine the larger scale performance of each raw material based on the yield and HHV values found in their lab experiments.

Statistical models are also often used to determine how process conditions affect different feedstock types. Toptas Tag et al. [60] conducted a study with this approach by making a design of experiments model using response surface methodology. The variables analyzed were temperature, residence time, and biomass to water ratio for poultry litter, algal biomass, and sunflower stalk biomasses. They determined that increasing the process temperature had the greatest effect on mass yield and energy densification. Similar models were also made for the specific feedstocks of olive stones [61] and tomato peel [62].

Heidari, Norouzi, et al. [15] used a statistical approach to provide a better understanding of how the three main components of lignocellulosic biomass behave during HTC based on the severity factor—a function of temperature and residence time during HTC—using Equation (6):

$$R_0 = te^{\left[\frac{T-100}{14.75}\right]} \quad (6)$$

where R_0 is the reaction ordinate (min), t is the reaction time (min), and T is the reaction temperature (°C). The severity factor is then represented by taking the logarithm of the reaction ordinate ($\log R_0$) [63]. This expression is the most common method used to describe the factor based on the assumption of first-order reactions and Arrhenius temperature dependence. Their model works to accurately predict values of the products yields, HHV, and carbon content depending on the biomass composition by coming up with equations for these variables after 39 HTC runs of varying compositions. The predicted outputs from the models were in good agreement with experimental data of common biomass samples.

In short, a large gap that remains is the incorporation of these forms of studies that can be used to predict hydrochar characteristics from the HTC of different biomass and their heterogeneous components, into the design of numerical studies. As previously stated, this is difficult to accomplish due to the large variety and different behaviors of different feedstock under HTC conditions. In fact, some studies for HTC continue to contradict the basic trends that are commonly reported and may further slow the progress of developing concrete findings and statistical correlations. A study by B. Zhang et al. [2] found that increasing the process temperature for raw apple and grape pomace during HTC resulted in higher mass yields, contrary to traditional trends in the literature. They did, however, attribute their findings to the higher sugar content of these fruit wastes.

Zhuang et al. [21] compared the HTC of lignocellulosic herbal tea waste to non-lignocellulosic penicillin mycelial waste to establish more knowledge on the reaction pathways of the different biomass types. They created comprehensive diagrams that highlighted the differences in the evolution processes between them during hydrothermal processes. Their study further emphasizes the variability in feedstock that causes difficulties in proposing accurate numerical models, suggesting that a good approach to improve the work on this area could be to create more computational heat transfer models that are designed for many different types of biomass, both lignocellulosic and non-lignocellulosic. The scope of the primary numerical models which were previously discussed are designed for cellulose [39], olive pomace [40,43], pinewood particles [12], and avocado stones [35]. This leaves much room to develop computational models for the HTC of various biomass sources, processing wastes, and agriculture residues.

There are many experimental studies that investigate the HTC of third-generation feedstock or food residues and wastes of different compositions other than hemicellulose, cellulose, and lignin. Toptas Tag et al. [60] subject algal biomass and lignocellulosic biomass to HTC and characterize the hydrochar products to find that the feedstock type undoubtedly had the most significant influence on the mass yield. Some feedstocks, such as citrus peels, also contain more significant amounts of extractives, such as proteins and pectin, that others

only have small amounts of [64]. Because hydrochar properties are impacted so heavily from the feedstock type, models could be made to follow some trends in the literature to incorporate different biomass types such as these that may significantly alter the products. For instance, it is known that the third-generation biomass, i.e., algal biomass is composed of lipids, proteins, and carbohydrates. Prediction of hydrothermal conversion of algae with respect to its components and main operational parameters of the process could be a direction for future research.

4.2. Heat of Exothermic Chemical Reactions

When it comes to the consideration of the enthalpy of reactions for HTC, computational models are noticeably lacking in this respect likely due to the complexity of the processes taking place. As already presented in Section 3, for the types of computational HTC models available in the literature, most of the models created are used as a method to validate and supplement a mathematical or kinetic model, which have been developed from experimental work, and are not used primarily for a detailed heat transfer or thermodynamic analysis. Both review papers by Ischia and Fiori [6] and Román et al. [8] on HTC modeling discuss how to improve upon the credibility and reliability of models to be better implemented for larger scale adoption, and that a better focus on thermodynamic behavior would be one of the effective methods to accomplish this. Given that computational models can be used to analyze the processes taking place at different time steps throughout the thermochemical conversion process, investigating the energy balances and heat transfer data throughout could give valuable insight into the types of reactions occurring and overall behavior under different conditions.

For instance, it is known that hydrolysis is one of the main starting reactions that takes place during HTC and overall is endothermic [2]. It would be valuable to determine the points during the process at which hydrolysis begins or is no longer present, or how much energy it is consuming at different times. Depending on reaction temperatures and residence times the process will shift to predominantly exothermic reactions as more sugars are broken down into smaller molecules accompanied by the release of heat [2,65]. A more detailed description into the chemistry of HTC and the types of reactions taking place can be seen in Section 2.1.

The severity (function of temperature and residence time) of an HTC process is known to influence how soon this turning point occurs, and at low severities, the overall heat of reactions may be found to be endothermic [26]. In fact, many studies that initially attempted to apply Hess's to calculate the overall process enthalpy for HTC found it to be on the endothermic side.

Yan et al. [30] calculated the reaction enthalpy to be slightly endothermic in the range of 0.25–0.56 MJ $kg^{-1}_{feedstock}$ for loblolly pine feedstock with 5 min of residence time. The gas phase was considered as CO_2 and the only volatile acid in the liquid stream that was considered was acetic acid.

More recently, studies have more accurately been able to describe the overall HTC process as exothermic from obtained energy balances. As parameters such as temperature, residence time, and biomass to water ratio are optimized to produce higher energy dense products, and energy balances are made more intricately with detailed analyses and characterizations of the liquid, solid, and gas products, the heat of reaction is better defined [26].

Cuvilas et al. [29] applied a similar experimental design used by Yan et al. but with longer residence times, finding exothermic enthalpy values for runs of 150 and 350 min to be −2.53 and −3. MJ $kg^{-1}_{feedstock}$, respectively.

Other studies that have been continuing to improve upon the uncertainty of heat of reaction evaluations have found exothermic values of −1.06 MJ kg^{-1}, −1.07 MJ kg^{-1}, and −0.76 MJ kg^{-1} for glucose, cellulose, and wood, respectively [66], and −1.0 to −3.9 MJ kg^{-1} and −7.3MJ kg^{-1} for agave pulp and municipal solid waste, respectively [33].

A review by Pecchi et al. [26] concluded that from the collection of literature they looked at, the HTC process enthalpy change falls within the theoretical range of 0 and -1.8 MJ kg^{-1}_{feed}, meaning that it is mildly exothermic.

Some of the available computational models made for HTC do factor in the heat of reactions taking place. One of the first HTC computational models that can be found in literature by Álvarez-Murillo et al. [39] only considers water to be the reacting medium, so there is no consideration of the heat of chemical reactions.

Heidari et al. [12] did compare the power requirements from the heater in scenarios with and without considering the heat of reactions. They concluded that the power requirements will not be as accurate without this consideration. They are able to predict the overall heat released/absorbed from the reactions by finding the difference between the two cases, which they find to be -2.223 MJ/kg for the whole process.

Sangare et al. [35] also took into the account the overall heat of reaction for their computational model of avocado stone HTC by considering the amount of energy required to heat up the different components in the reactor and equating it to the power supplied by the heater. They found the process enthalpy to be -7.25 MJ $kg^{-1}_{feedstock}$, which they stated is in agreement with reported values from Funke et al. [66] and Merzari et al. [33].

From these examples, it is clear that computational modeling can be an effective tool to investigate the change of enthalpies occurring throughout the process. It is suggested that modeling and simulation software is used more comprehensively in future studies by capitalizing on the insight these types of studies could provide. This could include looking into the transient behavior of the reactions, observing the endothermic to exothermic turning point, and helping to explain the reactions that are dominating at different steps during the process and their intensity. With increased information on the understanding of the exothermic behavior in HTC, process conditions can be optimized to possibly enhance the exothermic heat of reactions and overall lessen power requirements, a common barrier that is often considered for industrial HTC plants. Table 2 identifies a summary of some of the potential benefits of how computational models can be used to provide valuable insight into the heat of reactions topic.

Table 2. Potential benefits of using computational models for HTC heat of reactions.

Aspect to Study	Gap that Could be Addressed with Computational Modeling
Transient reaction behavior	• Analysis of endothermicity/exothermicity of reactions at time steps throughout the reaction. • Identification of types of reactions based on enthalpy values • The importance of reactions for contributing to energy released/absorbed • Determining the endothermic to exothermic turning point
Evaluating overall process enthalpy based on reaction conditions	• Simulating the reaction behavior over a range of severities without running time consuming and expensive experiments • Modeling temperatures/residence times that may be difficult to achieve in a lab setup • Ability to essentially evaluate any type of feedstock, biomass, or waste materials
Power requirement measurements	• Measurement of the power requirements over the full length of the process • Evaluating the impact of heat of reactions on supplied power to reactor • Optimizing experimental designs for efficient power use to be applied to larger scales

4.3. Type of Reactor and Scale-Up

The design of the reactor for HTC plays a large role in influencing the heat transfer processes taking place. The environment inside the reactor is the region where the flow of the different phases, heat transfer phenomena, and reaction mechanisms take place [6]. An advantage of developing computational models is the ability to use software to design specific geometries of the reactor. Typically, spherical/cylindrical reactor structures are used for HTC processes because of the high-pressure operation, as the use of these shapes helps to avoid force concentration in specific areas [12]. The material of the reactor and dimensions such as the wall thickness are also aspects of the geometry that can be easily altered using modeling software. This is important to consider because the thermal conductivity of the material and thickness will have influences on the heat transfer properties [67].

Not only can the geometry of the reactor impact these aspects, results can also be highly variable depending on whether the reactor is a stirred reactor, and if a batch or continuous reactor setup is used. These design aspects and how they can be investigated through computational modeling are discussed in this section, as well as the scaling-up of HTC processes.

4.3.1. Stirred Reactor Modeling

It is common for most HTC reactors to be accompanied with a stirrer to allow for the biomass and water mixture in the reactor to be uniformly mixed throughout the process [35]. Along with a rotating impeller that provides the stirring, it is usually recommended that mixed reactors contain baffles to disrupt circular vortex formation and allow for top and bottom mixing [68,69].

Studies that investigate the influences of performing HTC with stirred compared to non-stirred reactors as well as the effect of the stirring speed are uncommon. A study by Jung et al. [70] compared non-stirred and stirred experiments on the HTC of fructose for the formation of carbon spheres. They found that with the stirred HTC experiments, the hydrochar was composed of more agglomerates and experienced distorted morphologies.

Sharma et al. discussed the effects of mixing in a reactor from two HTC studies of yard waste in a non-stirred reactor [71] and a stirred reactor [72]. In their more recent study using the stirred reactor, they explained how a well-grinded sample can naturally mix well without the use of a stirrer, and minimal differences were observed in the fuel quality between the two methods. The evaluation used to compare the quality of the products was based on properties relating to the extent of coalification.

With these indefinite results, these experiments emphasize why the effects of stirring could be important to consider for HTC processes. Many researchers assume that stirred reactors will produce hydrochar with superior quality without much research to reinforce their reasoning. Depending on the intended products and reaction conditions, the stirring affects may create significant differences in the hydrochar properties.

Furthermore, the behavior of the different phases within the reactor can be investigated based on the stirring effects, and computational modeling can be used as a tool for these types of analysis. Although fluid flow and the transport of particles are complex mechanisms to solve numerically and may require high computational costs [40], there are common methods that are used for these types of studies.

In the literature, the only known computational HTC model that incorporates the use of an impeller to represent a stirred reactor is developed by Sangare et al. [35]. Their COMSOL study for the HTC of avocado stones provides results for the flow velocities based on different biomass to water ratios and mixing speeds (100 rpm, 250 rpm, 400 rpm, 550 rpm, and 700 rpm). They concluded from their study that homogenous mixing occurred at a rotational speed of 550 rpm by incorporating the dispersed multiphase flow and transport of diluted species models to approximate the movement of the thousands of individual biomass particles.

It could be valuable to apply similar concepts that were used by Sangare et al. in future computational studies that use more accurate approximations for the dispersed

biomass phase. These types of analysis could also be used to explore how parameters such as the flow velocities, solid yield, or process enthalpies are impacted in both stirred and non-stirred reactors.

4.3.2. Batch and Continuous Reactors

One of the main limitations of commercializing HTC processes is the development of continuous systems that can constantly provide biomass and water into a heated reactor operating at high pressures [73,74]. This feeding process is also difficult due to the long residence times in the reactor, requiring the feed suspension to operate at low flow rates and the use of specialized pumping systems [74,75]. Clogging can commonly occur at such low flow rates, and high pressures are needed to maintain the flow of the biomass suspension [75]. The compositions of the biomass slurries can be highly variable, containing different feedstocks with large ranges of moisture contents [75].

Because of these issues, it is most common for batch reactors to be used in HTC processes, with the main advantages being the increased repeatability and ease of use with minimal problems [75]. The use of batch reactors allows for smaller experiments to occur that are more research focused, as more work is still needed to obtain a better knowledge of the process to progress towards commercialization. In fact, the modeling work that has been discussed thus far have all been developed for batch reactor processes.

Continuous systems are likely a requirement if HTC processes are to be successfully industrialized, as they present many advantages if solutions to the listed challenges are overcome. In summary and as outlined from Heidari et al. [73] and Gómez et al. [76], continuous HTC systems can be beneficial for:

- Producing larger quantities of hydrochar at faster speeds with the elimination of a heat-up and cool-down time;
- Incorporating heat recovery methods using heat exchangers in the system that initially pre heat the biomass slurry, decreasing the energy requirements;
- Integrating with other systems, such as combustion or gasification processes in a biorefinery, since HTC commonly serves as a pre-treatment step.

For these reasons, the progress of developing HTC continuous systems will advance the industrialization of the process, and it is important to understand how these systems may alter the properties and structure of the hydrochar products under different heating rates and conditions [76]. Similar research questions have been investigated on the effects of different heating speeds in slow and rapid pyrolysis [77].

Up until recently, there have not been any computational heat transfer studies for a continuous hydrothermal process. Previous work in this area has been highly theoretical and software has been used for process simulations, but not using computational software [76]. Johannsen et al. have recently formulated a COMSOL model of a continuous-flow hydrothermal liquefaction (HTL) process that was also experimentally performed on a pilot plant scale [78]. Although this study was performed for HTL, the components of the system would be very similar in a hydrothermal carbonization process, and the same fundamental concepts can be applied in an HTC model.

HTL is one of three categories defined in the overall encapsulation of hydrothermal processes, the other two being HTC and Hydrothermal Gasification (HTG) [19,79,80]. HTL operates in higher temperature ranges of 250–375 °C and pressure of 10–25 MPa in the subcritical and supercritical conditions of water to produce organic bio-crude and bio-crude oils as well as solid residue and aqueous liquid and gas products [19,81,82]. Similar to HTC in recent years, the adoption of HTL technology has been advancing in the biofuel industry to produce products with higher HHV and hydrogen content from alternate sources, such as lignocellulosic feedstocks [81].

The study by Johannsen et al. formulates the modeling, simulation, and experimental validation for a pilot-scale HTL plant. The system they design is a continuous plug-flow HTL process. This requires the use of a high-pressure reciprocating pump (HPRP) to control the flow rates and to pump the biomass feed mixture. The mixture is pumped through a

heat exchanger and trim heater to initially preheat the slurry to the reactor temperature before entering the reactor where the HTL reactions start. An oscillatory flow system is also used to maintain proper flow and increase the heat recovery. A schematic of the HTL system they developed is shown in Figure 4.

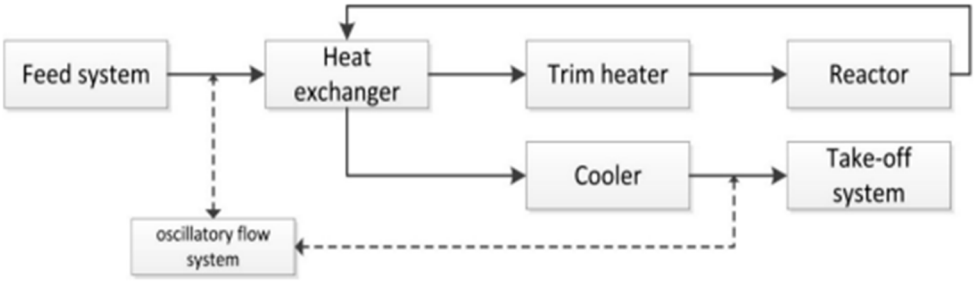

Figure 4. Schematic of the HTL system developed by Johannsen et al. [78].

For the modeling work, a macroscale model for the fluid flow and heat transfer on the pipe domain and a microscale model for one heat exchanger unit were numerically solved in COMSOL. The two-scale model was creatively used to help overcome computational limitations. The simulated results fit moderately well to the experimental data, but there were faults in the macroscale model in observing the differences of the altering temperature distributions induced by the oscillations.

The components of this HTL continuous system would essentially be the same for an HTC process. In general, both hydrothermal processes convert high moisture containing feedstock into upgraded products in pressurized reactors using high temperature water as the reacting medium [19]. Both processes also typically operate in the liquid phase and below the critical point of water (373 °C, 22.1 MPa); however, at the elevated HTL temperatures, the water properties are substantially changed due to the decreased dielectric constant [18]. The change in the dielectric constant allows more non-polar substances to be dissolved, explaining why the main products from HTL are in the liquid phase [19,78]. Therefore, if a continuous HTC computational model were to be made, the main process components from this study as shown in Figure 4 could be resembled to build the model. However, considerations based on the differences of the reaction kinetics and behavior due to the different process conditions need to be made to accurately simulate the formulation of the product.

Overall, this work serves as a strong lead in computational modeling for thermochemical conversion processes by identifying new ideas and strategies for functional continuous systems which are essential to study the commercialization of hydrothermal technology.

4.3.3. Scale-Up of HTC

Along with the development of continuous systems to move towards industrialization of hydrothermal processes, another factor to consider is the scale-up of the reactor to accommodate larger quantities of feedstock and produce more hydrochar. Increasing the size of the reactor can cause differences in the rate of heat production and removal because the surface area-to-volume ratio is changed but the geometry is kept the same [67]. Heating the reactor and evenly distributing the heat across all sections of the reactor also becomes more difficult in this situation, because the conventional method that is used in smaller reactors of heating from the outside is not as practical [75,83]. Internal heating by steam injection or other methods are often required to achieve uniform heating [75,83].

Theoretical scaling correlations assume that large systems will behave similarly to the smaller systems that they have been scaled up from, but in reality, this is not typically the case [75]. Proper methods need be considered when attempting to scale up from small setups used in research to ensure a safe and efficient process is used and to reduce associated risks [67]. Some equations are developed for this purpose. For example, Equation (7)

presented by Kruse, Baris, et al. [75] describes the necessary wall thickness required based on characteristics of the reactor:

$$s = \frac{D_a p}{23\frac{K}{S} - p} \quad (7)$$

where s is the necessary wall thickness, Da is the external diameter, p is the internal pressure, K is the strength of the material, and S is the safety factor.

Computational modeling can also be used as an effective tool for scaling-up purposes. The use of modeling software allows for easy alterations of the geometry to be implemented, meaning different reactor sizes can be easily tested for evaluating differences in the heat transfer properties and temperature distributions over different volumes. This could also be useful for monitoring the pressure in larger volume reactors for local areas where it may be concentrated, which could be potential safety hazards.

The HTC computational studies that are emphasized in this review in Table 1 are all made for laboratory-scale reactor sizes which fall within a range of internal diameters from 5.6–9 cm. They also all incorporate the use of external heating. As pointed out, for the commercialization of HTC processes, it is important that heat transfer mechanisms and flow behavior are modeled in pilot scale and larger scale reactors of similar sizes that would be used in industrial processes. A potential future computational model could be developed to investigate an HTC process at such a scale, and different heating methods could be examined to observe the alterations in the heat transfer phenomena that using them could induce.

Modeling work on the temperature distribution and heat transfer properties of different reactor sizes is uncommon in literature for any type of study, especially for HTC processes. Dickerson et al. [67] conducted a general COMSOL study on different flask sizes of 100 mL^{-1} L to find the differences in the overall heat transfer coefficient with the ambient environment during cooling. The results displayed that the overall heat transfer coefficient decreased with the larger flask sizes. Studies of this kind could be adopted for HTC processes with more complex considerations of reaction kinetics and flow phenomena, to be considered for scaling up purposes. It is also important to note that for scaled-up processes, a focus on continuous systems would be beneficial.

4.4. Consideration of Pre-Pressurization

The selection of the pressure value is not often discussed for HTC, since the process takes place at autogenous pressures, meaning the high pressures are generated on their own from the reactions occurring in the sealed reactor. These pressures usually fall within the range of 2–6 MPa [16]. In this range, the water in the reactor remains below its saturation point and in the subcritical region at the elevated temperatures that are reached. As previously discussed, the water that remains as a liquid at these high temperature ranges is highly reactive and promotes the occurrence of the reactions.

Saturation pressure curves of water can be used to find the pressure needed to keep the water entering the supercritical region. This prevents the formation of vapor, which maintains an optimal ionic product and dielectric constant for the water, allowing higher rates of ionic-reactions and the solvation of polar compounds [19]. For example, the critical point of water is 373 °C and 22.1 MPa—much higher than the top end range of HTC—and above these conditions water enters the supercritical region [19,84].

To prevent the pressure from being too low, it is common for reactors to be pre-pressurized to keep water in the subcritical state. A study by MacDermid-Watts et al. on the HTC of corn bio-ethanol by-products is an example of a paper that mentions a pre-pressurization step in their procedure, as they initially pre-pressurize the autoclave in their experiment with nitrogen to 135 psi (~0.93 MPa) [85]. However, researchers do not always use a pre-pressurization step, or report the value that they pre-pressurize to.

A question presents itself for if the initial pressurization may have an effect on the overall properties of the hydrochar, and to what extent if it does [16]. It is apparent that increases in the initial pressure will result in overall higher pressures throughout the process,

which will prevent vapor from forming, but also require higher energy demands [16]. On the contrary, a decrease in heating time may be experienced for HTC operations at higher pressures, as less energy is forfeited to latent heat of vaporization when water remains in the liquid state [9].

There are limited studies that investigate the effect of increased pressure for HTC process. Minaret and Dutta [9] conducted a comparison between liquid and vapor HTC, where water is kept in the liquid state and a mixture of water in both liquid and vapor phase is used, respectively. Their results showed only slight differences in the HHV of the products, with the liquid HTC being slightly higher but also displaying more favorable coal-like properties and requiring less energy.

Funke et al. [86] performed a similar study and found that the solid content on the hydrochar from liquid HTC had a higher carbon content compared to vapor HTC.

Although these limited examples suggest that the pressure conditions during HTC do not influence on the resulting hydrochar properties as substantially as temperature and pressure, they do indicate that operating at very high pressures could promote changes to the HHV properties of the hydrochar and the degree of graphitization [19]. These affects can be attributed to the decreasing presence of dehydration and decarboxylation reactions but increasing occurrence of polymerization and condensation reactions at the higher pressures [19,32,87]. Any determined benefits from pre-pressurization and operating at higher pressures needs to be weighed against associated costs through an economic assessment [16].

There is a large opportunity for computational models to be used to investigate this topic. Pressure is a commonly defined parameter as an initial condition in modeling software, and comparisons can be made between simulations with runs at different initial pressure values. This can be used in combination with an analysis on the transient reaction behavior and paired with kinetic models to better understand the reaction rates in the different pressure conditions. In this respect, numerical studies that include this aspect would be quite easy to incorporate, but some thought would have to be put into the explicit conclusions that can be made from the pressurization effect.

4.5. Consideration of a Heat-Up Period

It is well known that following temperature, the residence time is the process parameter which has one of largest influences on the hydrochar properties, such as the degree of carbonization, O/C and H/C ratios, solid yield, and other fuel properties [15,87]. However, the consideration of the point at which the reaction time is measured from is not always consistent in the literature. Because of variabilities in heating rates between different reactors and debate on the temperature at which any reactions begin to take place during HTC, some researchers measure the reaction time from the point at which heating begins [88], while others take different reference points, such as the target heating temperature [62].

For example, in the numerical simulation performed by Mendecka et al. [40], they determine the reaction rate using the Arrhenius equation only when the temperature has reached a threshold of 170 °C. Below this temperature, they state that no reactions occur and k = 0, and above this temperature hydrolysis will start to beginning with the degradation of hemicellulose. They cite this value as being chosen from the information provided the review by Funke and Ziegler [89]. Most researchers support this claim with the fact that hemicellulose (which is the first lignocellulosic component to degrade) does not begin hydrolysis until 180 °C [89,90], and similar to the introduction of this review, most papers state that the reaction temperature range of HTC falls within 180–250 °C. It is commonly accepted that these temperatures are needed for significant changes to occur. However, some research has concluded that considering the heat-up period is important in the conversion process of HTC and should not be neglected.

The COMSOL model developed by Álvarez-Murillo et al. [39] aimed to highlight the importance of the heating time by considering the heating up process in their first-order kinetic model of the HTC for cellulose. They stated that during the heating phase,

significant amounts of cellulose can be converted into hydrochar, and concluded in their results that reactions begin to occur at approximately 140 °C and that it is in fact important to consider the initial heat-up time. They further state that the reactions accelerate at 170 °C.

The results of the study by Mendecka et al. [40], which aimed to analyze the flow characteristics in an HTC reactor using ANSYS, showed non-uniformities in the temperature fields at different times during the start of the process until the mixing of the flow reached equilibrium. They state how these non-uniformities cause local regions of higher temperatures, which could be important to consider how the reaction mechanisms are being affected before the threshold of 170 °C that they consider.

In terms of the particle transport behavior of the solid biomass phase during the heat-up phase, the COMSOL model developed by Chater et al. [43] demonstrated that the solid phase was randomly dispersed throughout the reactor during this phase (600 s). After this, the particles gravitated to the top of the reactor due to their low bulk density, where they experienced much lower velocities. This behavior can affect the temperature distribution in the reactor, causing the bottom of the reactor to be hotter due to the higher thermal conductivity of the water contained there.

From the results of these studies, it can be established that the heating phase during HTC can have a significant role in the behavior of the reactions taking place, and that computational modeling work can serve as a useful method to better understand how different reactor configurations and heating rates may be causing these changes. Not only can computational studies be useful to help with more accurate depictions of the feedstock conversion during the heating phase, but it can also be beneficial to quantify and evaluate the power requirements that are typically at their highest during the initial heating of the reactor.

The model created by Heidari et al. [12] also tracked the heat-up phase in their COMSOL model of the HTC of pinewood particles. They displayed their results for the power usage that was predicted numerically verses the experimental power usage. Figure 5 shows the results of their power data, where, during the heat-up time, the power is at its highest at 640 W for the 35 min that it takes to reach the target temperature of 220 °C, and then remains lower than the heater while only needing to be switched on and off for short periods of time to keep the temperature constant. The model accurately matches the experimental results and the maximum temperature difference with the experimental data was only 3.39 °C.

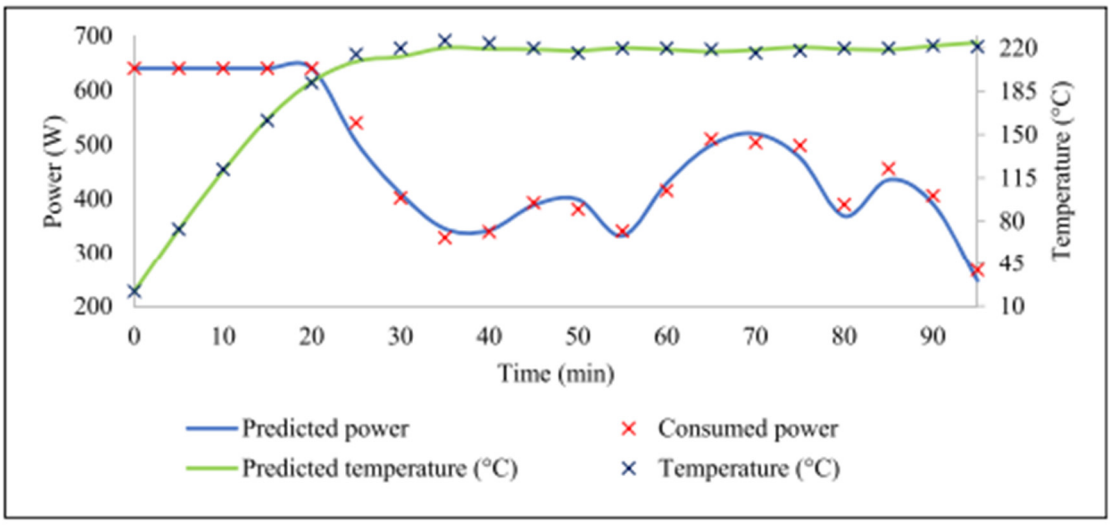

Figure 5. Predicted and actual consumed power from computational and experimental model by Heidari et al. [12].

With models like these that can accurately mimic the power requirements of actual processes, the developed methods can be scaled up to industrial processes to optimize and track power consumption based on operating parameters and cost–benefit analyses. These results show the value in using computational modeling for power analysis in HTC processes, and why the heat-up period should be considered.

4.6. Porosity of Feedstock

One of the most important properties that is often omitted in computational models that have been developed for HTC is the consideration of the porosity of feedstock materials, which are commonly lignocellulosic biomass types [91]. More often than not in any type of thermochemical conversion model, biomass particles are modeled as a solid, and the porous nature that biomass particles possess is left out [92]. The porosity of lignocellulosic biomass materials in particular is known to be important in affecting the yields of biomass undergoing pre-treatment [91,93]. Research has shown relationships between the level of enzymatic hydrolysis and porosity of the biomass, and feedstocks with smaller pores are known to impede enzymatic hydrolysis while larger pores enhance it [91,93,94].

Because HTC is largely governed by hydrolysis reactions to initially degrade the feedstock into smaller monomers, it may be important to consider the porosity of the feedstock to properly design the operating conditions in a given process. The heat and mass transfer properties will also be influenced by the porosity of the feedstock, which will cause differences in the conversion efficiency, reaction rates, and porous properties of the products [95–97].

Although different levels of porosity create significant changes in the conversion process, there remain many challenges in incorporating porosity into the development of accurate modeling and simulation methods [98]. This is largely due to the complexity of dealing with different length scales (micro-, meso-, microporous) and the variability of porosity in different lignocellulosic materials that dictates their physical properties [5,92,98].

A recent review by Fatehi et al. [92], which discusses emerging developments in numerical modeling for biomass conversion processes, pointed out the modeling of biomass porous medium and the different methods that have been used. Some approaches that are listed are pore-scale modeling, volume average modeling, and single particle models. They highlighted that it is important for the mesh being used to properly represent the length scale that is being investigated to accurately achieve the larger macroscopic or smaller microscopic properties of the particles. The extent of how many elements the mesh is broken up into will have an impact on the computational costs involved.

Out of the HTC computational models listed in Table 1, only one has considered the porosity of feedstocks for HTC processes. For models that investigate heat and mass transfer during HTC, the heat transfer in porous media physics can be coupled with heat transfer in solids and liquids, which uses the modification of Equation (5) shown in Section 3. As described in that section, Hediari et al. [12] incorporated porous media physics in their model of pinewood particles, which they measured to have a porosity of 0.54. They then supported the accuracy of their energy consumption results by comparing the data in the case when porosity was not considered and found that the consumption was considerably lower. From these results, the question remains of how accurately the pore scale was represented by the meshing to best simulate the heat transfer taking place in the porous structure. It does, however, show how failing to consider the porosity of biomass will negatively affect the reliability of results.

The model created by Regmi et al. [99] was made for a torrefaction process of poplar woody biomass. Although it was developed for a different thermochemical conversion process, it serves as a good example of a 2D axisymmetric model with heat transfer in porous media physics. They investigated the heat transfer properties at different L/D ratios of the particle, and compared their numerical results to the experimental work performed by [100]. The good agreement between the numerical and experimental work supports the significance of considering the porosity of the biomass.

Work in this area should be a continued focus to incorporate into future HTC models to improve upon the accuracy in how pore structures of biomass are accounted for. As computational power is increased and newer methods are developed to depict different length scale requirements more accurately for different components in an HTC system, the porosity can be better represented. A review by Xiong et al. [101] on computational simulations for pyrolysis processes pointed out how major challenges remain in describing the effects of porosity both numerically and experimentally in porous media modeling approaches. These challenges have created a large literature gap due to the limited number of studies that assume accurate heterogeneous structures for biomass in thermochemical conversion processes and has much potential to be incorporated in future HTC models.

5. Summary of the Identified Gaps and Main Contributions from Research Areas

This detailed review of existing HTC computational models with supporting information from a variety of other studies surrounding HTC has formed a thorough discussion on six research areas that would be beneficial for future models to investigate based on underlying research gaps that have been identified. By building off of Figure 1, which initially presented these six areas, an overall summary of the main gaps that were discussed for each aspect has been developed and is presented in Figure 6.

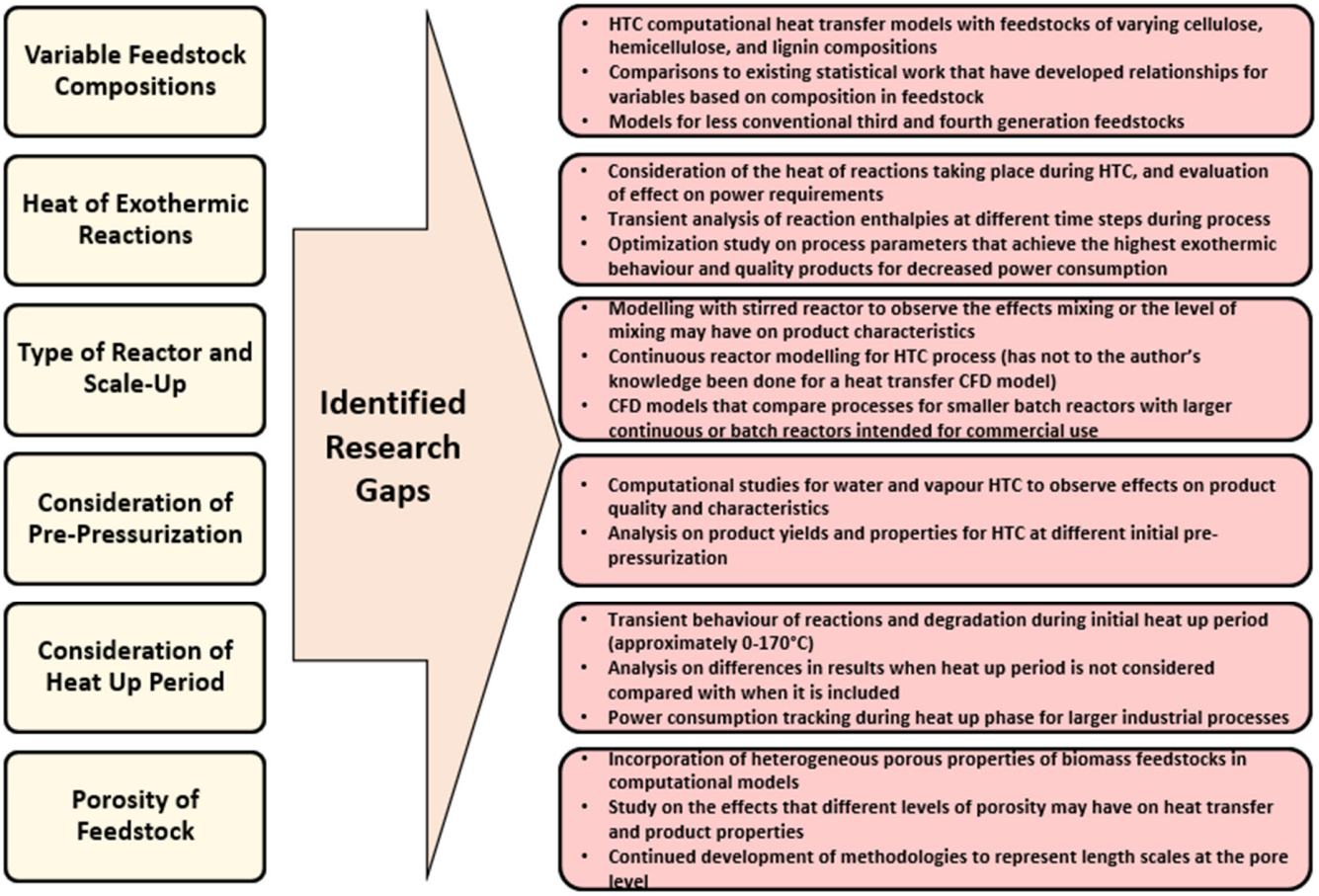

Figure 6. Summary of identified research gaps for six discussed areas of computational HTC models that require further investigation.

Overall, the main intention of this review has been to identify the research gaps that exist based on the scope of what current studies have been able to evaluate. For this reason, an evaluation of the influence that investigating some of these topics may have on contributing to the development of accurate model results is not largely discussed. Outside of why the research areas may be interesting and important to include based on

the analysis of up-to-date modeling publications, the main determinations of their potential improvements to the accuracy of HTC models are left to future studies.

For a general evaluation of the most important research areas, when discussing the contribution to the greater goal of HTC commercialization, it was commonly found that the development toward continuous reactor systems are needed to make the process economically viable. There are many challenges that need to be overcome for continuous systems to be successfully industrialized. A main requirement is a suitable feeding system that can be used to constantly transport the solid biomass to the heated and pressurized reactor. For these reasons, the type of reactor and variable feedstock composition can be identified as the leading research areas in computational modeling that could have the greatest impact for helping industrialize HTC processes. An HTC computational model based on a continuous system is yet to be made, and it is important to ensure there is a well-defined understanding of how the type of feedstock used in continuous processes will behave to reduce complications. As a result, it is suggested that these research areas be prioritized.

6. Conclusions

The conversion of raw biomass materials using HTC into hydrochar with upgraded quality is proven to be a cleaner and less energy intensive thermochemical method for feedstocks and waste materials, especially those with high moisture contents. As HTC continues to expand in the research community and focuses are shifted to discovering the best methods to transition to industrial processes, it is apparent that there are still many barriers that need to be addressed. Computational modeling has proven to be a valuable tool to conduct analyses on HTC and has the potential to look into some of the remaining questions that are yet to be thoroughly understood. There are few computational models to date that are available in the literature, leaving room for future models to be developed further and to investigate a variety of different topics.

The contents of this review provided six areas that could be further considered for future computational modeling work, identified from the most recent and up-to-date papers that have been published. The six areas of variable feedstock compositions, heat of exothermic reactions, type of reactor and scale-up, consideration of pre-pressurization, consideration of heat-up period, and porosity of feedstock that have been suggested as major topics have been discussed and underlying gaps within each have also been identified. The hope from this review is for researchers to take these research gaps into consideration to approach future work that aims at modeling HTC processes with computational and simulation software.

From the ideas that have been reviewed, it can also be concluded that in general the type of models that are lacking are those that investigate heat and mass transport as well as flow physics of the feedstock particles in the reactor. Especially with particle transport, the extent to which these phenomena are explored is largely limited to computational power. However, the coupling of distributed kinetic models with these kinds of computational simulations can be favorable for optimizing product yields and reaction rates while forming better understandings of the reaction mechanisms taking place and the power requirements involved, to move towards the commercialization of HTC.

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