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Theoretical framework for estimating design reactor pressure for water-based hydrothermal carbonization (HTC) systems

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ABSTRACT

Hydrothermal carbonization (HTC) has been shown to be a valuable system component in sustainable management strategies for wet organic residues from agriculture, industries and municipalities. While the reaction temperatures in HTC are much lower than those in alternative thermochemical processes, the pressures reached in HTC are much higher, rising with temperature as the autogenic pressure of water rises, and as reaction gas is produced from hydrothermal reactions. An important basis for designing cost-effective equipment for the HTC systems is understanding the safety aspects and costs associated with the reactor pressure. This paper presents a theoretical framework to predict the expected HTC reactor pressure for hydrothermal reactions with biomass that produce CO_2. A model was developed that uses the thermodynamic properties of CO_2-water mixtures at HTC reaction conditions and was validated using well-defined experiments with CO_2-H_2O. Comparison of the pressures predicted by the theoretical model to actual pressures in HTC reactions with real biomass (bark mulch, sugar beet pulp) showed relative errors ranging from −18.5% to 7.3%. A simple design procedure was suggested to predict HTC reactor pressure and demonstrated on a further case. The results of a sensitivity analysis showed that the pressure estimation is most affected by the parameters related to the amount of CO_2 formed during the HTC reaction. The easy-to-follow methodology developed in this study will help researchers, design engineers, and manufacturers to estimate the pressure reached in the HTC reactor based on desired design goals and promote the widespread use of HTC for converting wet wastes into value added hydrochar which can improve soil health and reduce environmental pollution.

Introduction

The worldwide drive to develop a circular bioeconomy must include sustainable management strategies for wet organic residues from agriculture, industries and municipalities. Cascade strategies that promote the sequential and consecutive use of the carbon and nutrients from such residues can create added-value in a circular economy [1], while reducing greenhouse gas emissions and minimizing environmental pollution risks. Hydrothermal processes such as carbonization (HTC) have been shown to be valuable system components in such strategies. Since they use water as the reaction media to thermochemically convert organic residues to carbon-rich solids or liquids at temperatures ranging from 180 to 280 °C, they have been used to valorize wet organic residues and wastes from numerous sources to liquid products (fatty acids, oils, aromatics) or to a solid product (hydrochar). Applications range from converting livestock wastes to hydrochar to be used as a fossil coal alternative [2] or soil amendment [3,4], simultaneously removing antibiotic resistance genes [5], to valorizing biowastes to produce platform chemicals, liquid biofuels [6,7], or carbon materials that can be used as adsorbents to remove pollutants from water or gases [8] or for other applications such as batteries [9]. The ability of HTC to reduce the time to transform or stabilize organic residues to hours or minutes [10] compared to months or days (e.g. biological treatment) makes them interesting for integration into large-scale applications such as sewage sludge treatment [11], and biogas plants [12]. In addition, HTC has become an accepted means of upgrading fresh lignocellulosic biomass for carbon–neutral electricity generation [13].

Research to improve the economic viability of HTC applications continues to grow, focusing on how the operating mode (batch, semi-continuous, continuous) [13,14], and the initial phase of the water

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contacting the solid (liquid water-based HTC vs. vapor-based VTC) [15] influence product formation and characteristics (solid and liquid). However, an important basis for designing cost-effective equipment for hydrothermal systems is to understand the safety aspects and costs associated with the reactor pressure, which results from hydrothermal reactions. While the reaction temperatures in HTC are much lower than those in alternative thermochemical processes for biomass such as pyrolysis, gasification or combustion usually operating at atmospheric pressures, the pressures reached in HTC are much higher (10–65 bar), rising with temperature as the autogenic pressure of water rises, in addition to the pressure increase due to reaction gas production. A major drawback of hydrothermal equipment, therefore, is the cost to construct equipment that can withstand the high pressures. These high pressure conditions determine important design parameters, such as material type and thickness, and manufacturing techniques used for the reactor system. Thus, it is very important to predict what HTC reactor pressure will be reached, before we design a reactor system to hydrothermally carbonize biomass. Reactor pressure will depend on many variables such as type and amount of biomass, initial biomass/water ratios, design HTC reaction temperature, HTC reaction time (impacting the extent of reaction – directly affecting gas production), etc. In a previous paper, we explored safety aspects and process changes that must be taken into consideration as the process temperature rises, such as the expansion of liquid water and the rise in reactor pressure due to water vapor, however, we did not consider pressure increases due to the production of gas from HTC reactions [15]. Up until now, we have not found a systematic method to predict the HTC reactor pressure for biomass systems reported in the literature.

The objectives of this study are to 1) develop the theoretical framework and model for predicting the HTC reactor pressure for hydrothermal reactions with biomass that produce CO_2, 2) validate the developed model with well-defined experiments involving H_2O and CO_2 only, 3) compare the accuracy of the theoretical model with actual HTC reaction systems containing biomass, 4) suggest a simple design procedure to predict HTC reactor pressure, and 5) assess the sensitivity of the model to various design parameters affecting the HTC reactor pressure.

Theoretical background for hydrothermal reactor design

Hydrothermal reactions and pressure change

In hydrothermal reactions with biomass as feedstock, the organic matter in the biomass can be converted to carbon-rich solids (hydrochar), soluble organic compounds (acids, sugars, aromatics), and gases (CO_2, CH_4, CO, H_2S, trace organics). In general, most of the carbon remains in the solid product, typically 50–80%, while 5–20% dissolves into the process water and 2–10% is transformed into gaseous products [16,17] (Fig. 1). Solid yields of hydrochar are often inversely dependent on the reaction temperatures and times [18]. Although the amount of carbon that transfers to the gas phase is relatively small, it can still cause a large increase in the reactor pressure above the saturation pressure of the water P_{sat}. The majority of the gas is made up of CO_2, which is only partially soluble in water. Therefore, when planning hydrothermal reaction systems, the prediction of the pressure increase due to gas production may be possible based on knowledge about the behavior of the CO_2-water system at the hydrothermal reaction conditions.

Hydrothermal reactor design

Two important parameters for designing a hydrothermal system are 1) the reactor volume V_R needed to handle the mass of biomass and liquid to be processed and 2) the maximum pressure P_{Max} to be expected from the hydrothermal reactions. V_R must be chosen to avoid the conditions at which the reactor system enters the subcooled compression liquid region due to expansion of liquid volume at high temperature, which poses the danger of explosion. Furthermore, the design V_R and fill volume will determine how the water initially contacts the feedstock, i.e. whether the feedstock is immersed in bulk liquid water (HTC) or is in direct contact with steam only (vapothermal carbonization VTC). This was discussed in detail in [15], in which we theoretically developed models to analyze water-only systems for safety and process considerations. With the model to predict the change in the volume fraction of liquid water VF_w, we showed that when the available reactor volume is less than half full with water (i.e. initial volume fraction of water $VF_o \leq 0.5$), VF_w increases very slowly below 300 °C, and does not enter the dangerous subcooled compressible region below the supercritical temperature. Another model was developed to predict the water distribution between the gas and liquid phases as a function of temperature, so that the amount of water in contact with the feedstock can be analyzed. In addition, a model was developed to predict reactor pressure in water systems with an added non-soluble and inert gas [15]. However, in HTC reactor systems with biomass, the reactor pressure depends not only on the pressure of the water vapor and any added non-soluble inert gas at the design temperature, but also on the amount of soluble gases such as CO_2 produced by hydrothermal reactions. Therefore, for systems with biomass and water, the previous models need to be expanded to evaluate the conditions as a function of the biomass characteristics and expected gas production, in addition to the temperature. The model development presented in the paper is for batch hydrothermal reactors.

The reactor volumes must be adjusted to account for the volume displaced by the feedstock V_{FS} when estimating the expected volume expansion of water at the desired operating temperatures. In our previous study [15], we looked at the changes in VF_w due to changes in the physical properties of water as the reactor temperature increased and discussed the importance of avoiding the overfilling of the reactor with water, so that the reactor system does not enter the subcooled compression liquid region, with its danger of blowing the safety release

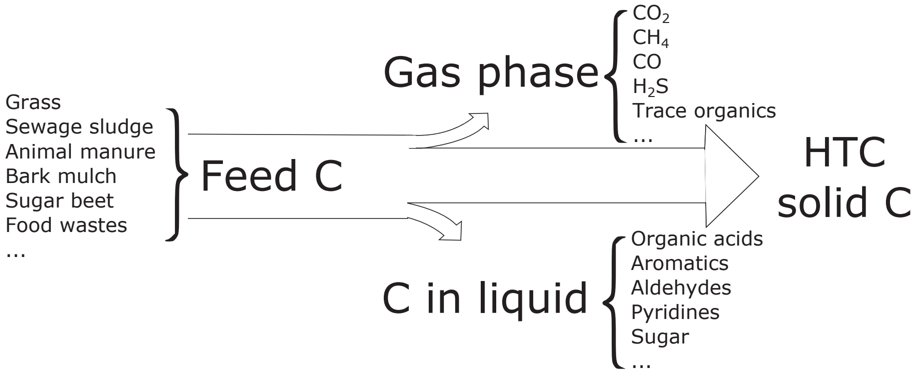

Fig. 1. Distribution of carbon between the three phases in hydrothermal reactions.

valve, or worse, exploding the reactor. The addition of biomass feedstock in the reactor system can change headspace volume V_g due to water displacement, so that available reactor volume must be adjusted when calculating VF_w. This is included in the model developed here. As the hydrothermal reactions proceed, some biomass solids are transformed in the water to liquid and gaseous products, potentially changing the biomass density and volume it displaces. However, these changes in the headspace conditions over time are assumed to be negligible in the model development.

The total system pressure *P(T)* at the reaction temperature T_R can be calculated following Dalton's law from the sum of the partial pressures of: (1) the saturated water vapor pressure P_{sat}, (2) any inert gases such as nitrogen P_{N2} added to pre-pressurize the system and (3) gases that are produced by the hydrothermal reactions with the biomass (i.e. mainly CO_2 [16]). The minimum pressure will always be the value for P_{sat} as long as water is present as a liquid in the system for the relatively low ionic strength aqueous solutions normally used. The procedure to estimate (1) and (2) were described in [15]. For (3), in order to determine the effect of gases produced on the reactor pressure, knowledge about the volume of the gas phase, amount of gases produced and their distribution between the liquid/gas phases at hydrothermal conditions is required. In most hydrothermal reactions, *P(T)* often increases well above $P_{sat} + P_{N2}$ due to gases released from the liquid phase. Because the main gaseous product CO_2 is partially water-soluble, only some of it is transferred to the gas phase at T_R, and calculation of the effect of its production on reactor pressure is not straightforward. In the following sections, a model to estimate the reactor pressure for a specified amount of CO_2 is developed. The model is then experimentally validated for the CO_2-H_2O system and used to simulate experimental results from HTC runs.

Estimation of pressure change in HTC reaction system

In this section, an algorithm that allows the estimation of the pressure in a HTC-reactor is developed based on a given number of moles of CO_2 N_{CO2} and H_2O N_{H2O} in the reactor. For water, N_{H2O} is generally known from the mass or moles of water introduced into the reactor as a liquid or in the feedstock (M_{H2O} or n^L_{H2O}) and the water molecules initially present in the headspace air as humidity are neglected ($i.e. n^g_{H2O} = 0$) (Eqn (1)). As the reactor temperature increases, the distribution of water between the liquid and gas phase can be calculated from models developed in [15]. The pressure due to water vapor P_{sat} is governed by thermodynamics and is not influenced by the presence of other gases or liquids for dilute aqueous solutions. However, CO_2, which is normally produced in the liquid phase and escapes to the gas phase, is soluble in water, so that the total moles of CO_2 in the reactor N_{CO2} are distributed between the gas and water phases depending on the reaction conditions (Eqn (2)). At low pressures and temperatures, the partitioning between water and gas can be calculated using an equation for Henry's Law and the ideal gas law (Eqns (13), (14)). However, to describe the thermodynamic properties of CO_2-water mixtures at HTC reaction conditions, accurate values are needed for wide temperature and pressure ranges near the critical region. Such values can be obtained from a commercially available computer program, NIST Reference Fluid Thermodynamic and Transport Properties (REFPROP) for a wide range of temperatures and pressures [19]. REFPROP (v. 10.0) uses the EOS–CG model, a Helmholtz energy mixture model, to determine the properties of CO_2/H_2O water systems at equilibrium. The model combines property models for the pure components with a mixture model approach, fitted to the most accurate experimental mixture data [20]. Using the NIST REFPROP program, values for the equilibrium mole fractions of H_2O and CO_2 in the liquid and gas phases ($y^L_{CO2}, y^L_{H2O}, y^g_{CO2}, y^g_{H2O}$) and molar densities of both liquid and gas phases (ρ_L, ρ_g) can be obtained for the reaction conditions. Combining these values with known values of N_{H2O} and N_{CO2}, we developed a model to predict the pressure for a reaction system at T_R.

For the validation of our model without involving actual biomass HTC reactions, we carried out experiments with pure CO_2 and H_2O to show that it is possible to predict the reactor pressure at a given temperature and CO_2 and H_2O amount in the reactor. In a second validation step, the model was applied to actual hydrothermal experiments with feedstock (bark and sugar beet pulp) and gas production. Based on these two validation cases, the efficacy of the model to predict maximum operating pressures in order to design reactor systems for specific temperatures and biomass/water loadings was evaluated.

Theoretical development of equations and algorithm

The equations for the mole balances and partial volumes required for the procedure (or algorithm) to predict the HTC pressure are developed in the following paragraphs. The theoretical formulations were developed for a HTC reactor system containing a H_2O-CO_2 mixture.

Mole balances. Total moles of water and CO_2 in the reactor written in terms of mole fractions in liquid and gas phases are:

$$N_{H2O} = n^L_{H2O} + n^g_{H2O} = y^L_{H2O}N^L + y^g_{H2O}N^g \tag{1}$$

$$N_{CO2} = n^L_{CO2} + n^g_{CO2} = y^L_{CO2}N^L + y^g_{CO2}N^g \tag{2}$$

Where

N_{H2O} = total moles of H_2O in the reactor (mol),
N_{CO2} = total moles of CO_2 in the reactor (mol),
N^L = total moles in the liquid phase (mol),
N^g = total moles in the gas phase (mol),
y^L_{H2O} = mole fraction of H_2O in the liquid phase (-)
y^L_{CO2} = mole fraction of CO_2 in the liquid phase (-)
y^g_{H2O} = mole fraction of water in the gas phase (-)
y^g_{CO2} = mole fraction of CO_2 in the gas phase (-)

The equations for the total moles in each phase (liquid and gas) are:

$$N^L = n^L_{H2O} + n^L_{CO2} \tag{3}$$

$$N^g = n^g_{H2O} + n^g_{CO2} \tag{4}$$

Where

n^L_{H2O} = mole of H_2O in the liquid phase (mol),
n^L_{CO2} = mole of CO_2 in the liquid phase (mol).
n^g_{H2O} = mole of H_2O in the gas phase (mol),
n^g_{CO2} = mole of CO_2 in the gas phase (mol).

Equations 1–2 can be combined to give the total mole fraction for each component:

$$Y_{CO2} = \frac{N_{CO2}}{N_{CO2} + N_{H2O}} \tag{5}$$

$$Y_{H2O} = \frac{N_{H2O}}{N_{CO2} + N_{H2O}} \tag{6}$$

$$Y_{CO2} + Y_{H2O} = 1 \tag{7}$$

Where

Y_{CO2} = total mole fraction of CO_2 in the reactor (-)
Y_{H2O} = total mole fraction of H_2O in the reactor (-)

The distribution of water between the phases can also be calculated based on Equations 1–4. This information is important for understanding water–feedstock interactions (i.e. where the hydrothermal reactions are likely to take place) and for determining changes in the biomass concentration in the liquid phase at the reaction temperature *%S(T)*. This was discussed in depth in [15], which evaluated the distribution of water between the liquid and gas phases on a mass fraction basis $x_{v,H2O}$. When looking only at the distribution of one compound between the two phases, use of mole and mass fractions gives the same value. Therefore, Equations 1–4 can be combined to give the following equation:

$$x_{v,H2O} = \frac{n^g_{H2O}}{N_{H2O}} = \frac{y^g_{H2O}N^g}{N_{H2O}} \tag{8}$$

Where

$x_{v,H2O}$ = fraction (mass and/or mole) of total H_2O as vapor in the gas phase

Partial volumes. The reactor volume consists of the liquid volume, volume of the feedstock and gas volume or headspace at the initial conditions.

$$V_R = V_{L,i} + V_{g,i} + V_{FS} = V_{L,i} + V_{g,i} + \frac{M_{FS}}{\rho_{FS}} \tag{9}$$

Where

V_R = reactor volume (L),
$V_{L,i}$ = liquid volume in the reactor at T_i (L),
$V_{g,i}$ = headspace in the reactor at T_i (L),
V_{FS} = volume of feedstock in the reactor at T_i (L),
M_{FS} = mass of feedstock in the reactor (gDM),
ρ_{FS} = bulk density of submerged feedstock (gDM/L).

The volume displaced by the submerged feedstock V_{FS} must be included in the safety calculations to determine that there is enough headspace to accommodate the water expansion at the design reaction temperature T_R. The value of V_{FS} can be calculated using the mass of the initial feedstock added and the measured bulk density of the submerged feedstock ρ_{FS} (Eqn (9)). This value is used throughout the calculations, even though it probably overestimates the volume occupied by hydrochar at $T_{R,}$ since solid mass is lost through the hydrothermal reactions.

In the algorithm to predict the reactor pressure, the liquid and gas volumes and the volume of the solids in the reactor at T_R and guessed reactor pressure P_{Max} are combined to estimate reactor volume $V_{R,est}$ and compared to the actual reactor volume. The liquid and gas volumes can be written in terms of moles and molar density of the two phases, so that $V_{R,est}$ can be calculated by the following equation:

$$V_{R,est} = V_L + V_g + V_{FS} = \frac{N^L}{\rho_L} + \frac{N^g}{\rho_g} + V_{FS} \tag{10}$$

Where

$V_{R,est}$ = reactor volume (L),
V_{FS} = volume of submerged feedstock in the reactor at T_R (L),
V_L = liquid volume in the reactor at T_R (L),
V_g = headspace in the reactor at T_R (L),
ρ_L = liquid density at T_R (mol/L),
ρ_g = gas density at T_R (mol/L).

In a subsequent step, the combined volume fraction of the liquid water and feedstock ($VF_{w,FS}$) at T_R should be calculated to ensure that it remains below 1.

$$VF_{w,FS} = \frac{V_L + V_{FS}}{V_R} \tag{11}$$

Calculation of the total moles of H_2O and CO_2 in the system. The HTC pressure prediction algorithm requires values for N_{H2O}, N_{CO2} , and the corresponding total mole fractions Y_{H2O}, Y_{CO2} as inputs. The value for the total moles of H_2O in the reactor N_{H2O} is calculated from the mass of water M_{H2O} or volume of water $V_{L,i}$ introduced into the reactor, including the water content in the feedstock. The total moles of CO_2 in the reactor N_{CO2} were estimated for two cases in this paper: (1) from the amount of pure CO_2 injected into the reactor for the first validation experiment, and (2) from biomass decomposition during the hydrothermal reactions for the second validation experiment and the design example:

Case 1. *Validation with CO_2. To estimate the total amount of pure CO_2 introduced into the system N_{CO2}, the following procedure based on the ideal gas law and Henry's Law was used.*

The value of n^g_{CO2} can be calculated using the ideal gas law for the equilibrated initial pressure before heating P_i, using the assumption that the gas volume $V_{g,i}$ is filled only with CO_2.

$$n^g_{CO2} = \frac{(P_i + P_{atm}) \times V_{g,i}}{R \times (T_i + 273.15)} \tag{12}$$

Where,

P_i = equilibrated initial pressure of reactor just before heating (bar_g),
$V_{g,i}$ = initial gas volume of reactor (L),
T_i = initial temperature of reactor before heating (°C).

For n^L_{CO2}, a value for the Henry's coefficient at the initial equilibrated reactor temperature must first be calculated using the equation [21]:

$$H(T) = H_o exp\left(\frac{1}{T} - \frac{1}{T_o}\right) \tag{13}$$

Where

H(T) = Henry's coefficient at temperature *T* (mol/m^3-Pa),
H_o = Henry's coefficient at reference T_o of 298.15 K (3.4 × 10^{-4} mol/m^3-Pa for CO_2),
T = reactor temperature (K),
T_o = reference temperature (298.15 K)

Once *H(T)* is calculated, n^L_{CO2}, the moles of CO_2 in the liquid volume $V_{L,i}$ can then be estimated from:

$$n^L_{CO2} = H(T) \times P_i \times V_{L,i} \tag{14}$$

Case 2. *HTC reactor systems with biomass. In hydrothermal reactions, CO_2 is normally produced in the liquid phase as the carbon in the feedstock is transformed. In this case, the difference between the mass of C in the raw feedstock and the hydrochar is assumed to be converted to CO_2. This assumption will overestimate the carbon in the gas phase. A further assumption is that the CO_2 is distributed between the gas and liquid phases at equilibrium for the reaction conditions, the majority escaping to the gas phase. Values for N_{CO2} can be calculated based on the measured or predicted carbon yields for the process conditions.*

$$N_{CO2} = \frac{\left[\left(M_{FS} \times \frac{\%C_{FS}}{100}\right) - \left(M_{HC} \times \frac{\%C_{HC}}{100}\right)\right]}{12} = \frac{\left(M_{FS} \times \frac{SY}{100} \times \frac{\%C_{HC}}{100}\right)}{12} \tag{15}$$

Where

M_{HC} = mass of hydrochar (gDM),
$\%C_{FS}$ = carbon content in the feedstock (%),
$\%C_{HC}$ = carbon content in the hydrochar (%),
SY = solid yield of hydrochar, M_{HC}/M_{FS} (%)

With these values for N_{H2O} and N_{CO2}, the total mole fractions of H_2O and CO_2 (Y_{H2O}, Y_{CO2}) can be calculated from Equations (5) and (6) and used in the algorithm for estimating pressure described below.

HTC pressure prediction algorithm

The maximum pressure in the reactor *P(T)* under hydrothermal conditions with biomass can be estimated following the steps of the algorithm described below and illustrated in Fig. 2. The algorithm is based on the assumptions that i. CO_2 is the only gas produced by the hydrothermal reactions, ii. no other highly reactive compounds are present, iii. there is a clear distinction between the liquid and gas phases, iv. the distribution of H_2O and CO_2 between the gas and liquid phases is at equilibrium, and v. the amount of H_2O and CO_2 in the reactor is known.

Step 1. Define the CO_2-H_2O reactor system – V_R, T_R, Y_{H2O}, Y_{CO2}

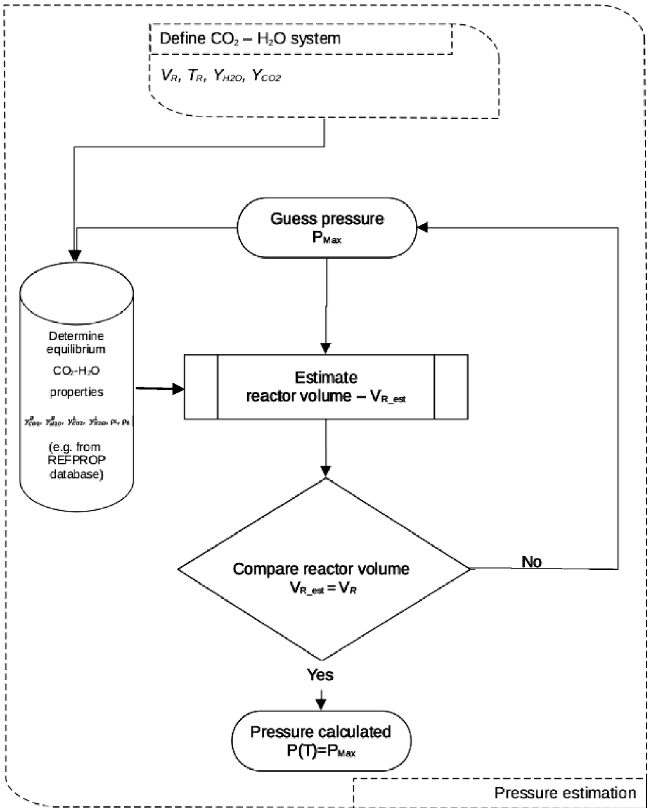

Fig. 2. Flow diagram of the algorithm to estimate pressure in the reactor using the CO_2-H_2O properties under HTC conditions.

a. Set values for the reactor system (volume V_R, desired HTC reaction temperature T_R) and mass of inputs into the system. In addition to the amount of water in system M_{H2O}, values are required that allow the calculation of the mass of CO_2 in the system. For cases with biomass, the amount and composition of feedstock (M_{FS}, $\%C_{FS}$), and expected outputs (SY, $\%C_{HC}$) must be defined. For the CO_2 validation case, the initial pressure, temperature and volume fractions were defined.
b. Calculate the total moles of water in the reactor N_{H2O} from the mass of liquid water in system M_{H2O}, which includes mass of water added and in feedstock.
c. Calculate the total moles of CO_2 in the reactor N_{CO2} from expected biomass decomposition (Eqn (15)). For the CO_2 validation case, the amount of pure CO_2 injected was estimated using Eqns (12), (13) and (14).
d. Estimate the total mole fractions of CO_2, H_2O in the reactor Y_{CO2}, Y_{H2O} from N_{CO2}, N_{H2O} using Eqns. (5) and (6).

Step 2. Guess a value for the maximum reactor pressure P_{Max} to be expected at T_R. This is the beginning of the iterative loop.

a. For the first iteration, choose a reasonable value for P_{Max} based on the saturated vapor pressure P_{sat} at T_R, or previous experience. It is important to avoid solutions that converge mathematically but are not realistic physical conditions. Continue to Step 3a.
b. Further iterations with an adjusted value for P_{Max} may be necessary to reach the cut-off criteria, $V_{R,est} = V_R$. Choose a new P_{Max}, and continue to Step 3b.

Step 3. Determine the equilibrium distribution of CO_2 and H_2O molecules between the liquid and gas phases for the guessed P_{Max}.

a. Use input values for REFPROP database calculated in Step 1. Two state variables of the H_2O/CO_2 system at equilibrium must be defined to determine the other properties of the system. In this case, the reactor temperature T_R and overall composition Y_{CO2}, Y_{H2O} in the reactor are used.
b. Retrieve values for y^g_{CO2}, y^g_{H2O}, y^L_{CO2}, y^L_{H2O}, ρ_L, ρ_g from the REFPROP database for P_{Max}. The database offers a table of density and mole fractions for the gas and liquid phases at T_R for various pressures values.

Step 4. Estimate the reactor volume $V_{R,est}$ using the REFPROP database outputs and Equations (1), (2) and (10).

a. First, determine values for the total moles in the liquid and gas phases $\left(N^L, N^g\right)$ by solving Equations (1) and (2) simultaneously, using values from the database for the mole fractions of the two components in the liquid and gas (y^L_{H2O}, y^L_{CO2}, y^g_{H2O}, y^g_{CO2}) at the guessed P_{Max} and the total moles of water N_{H2O} and CO_2 N_{CO2} in the system.
b. Then calculate the liquid and gas volumes using the total moles in liquid phase and gas phase $\left(N^L, N^g\right)$ and the density values (ρ_g,ρ_L) in Eqn (10). The sum of the volumes including the feedstock volume is $V_{R,est}$.

Step 5. Compare the estimated reactor volume $V_{R,est}$ with the real reactor volume V_R

a. Check if the real reactor volume (V_R) and the calculated one ($V_{R,est}$) match within a reasonable relative error % (e.g. $< 1\%$). If the error is too large, go back to Step 2 and guess another P_{Max}, and continue the loop.
b. Stop when the error in the volume comparison becomes close to null ($<1\%$). Then the guessed pressure is the predicted maximum pressure *P(T)* and the sought-after value is found.

Step 6. In a last step for the validation cases, the guessed P_{Max} was compared to the experimentally observed *P(T)* and the relative error between the two values was determined.

This procedure was validated at first using only CO_2 gas without any biomass feedstock in distilled water at common HTC conditions (T_R from 180 to 250 °C). The second validation was made using HTC process data with two solid biomasses (T_R from 200 to 250 °C) with experiments up to about 70 bar_g. This algorithm to estimate the HTC reactor pressure is theoretically valid as long as the system is not in the super-critical range where gas and liquid phases are not clearly separated. The results of the two validation cases and a further design case to demonstrate how the method can be used for designing purposes are presented in Section 4. The iterative process in Fig. 2 is the basis for all three cases. The significant difference between the three cases is the method used to determine the amount of CO_2 in the reactor.

Materials and methods

Validation HTC experiments with H_2O and CO_2 only

Experimental set-up

The above equations and algorithm were validated by predicting the reactor pressure for a system containing a known amount of water and carbon dioxide. The measured pressure at two reactor temperatures *P(T)* was compared to the pressure predicted by the model P_{Max} for a given number of moles of water N_{H2O} and CO_2 N_{CO2} introduced into reactor. In a 18.64-L stainless steel reactor (Model 4557, Parr Instrument Company, Moline, IL), 932 or 9320 g of deionized (DI) water was loaded to give the initial volume fractions of water (VF_o) of 0.05 or 0.50, respectively. The reactor was then flushed with CO_2 for approximately 20 min at 5 L/min to replace residual air with CO_2. After flushing, the reactor was pressurized with pure CO_2 (Praxair, Danbury, CT) to an initial pressure of 15 bar. The reactor was then sealed with all gas valves closed and was left to equilibrate overnight. Equilibrium was achieved when headspace pressure did not change with time, approximately 8 h. The method for calculating the amount of CO_2 introduced is described in 3.1.2. A constant stirring rate of 100 revolutions per minute (rpm) was applied to the reactor content during the entire experiment. After the CO_2-H_2O mixture was equilibrated overnight, the reactor was heated to either 180° or 250° and held until reactor pressure remained constant for an hour, usually for 2 or 4 h to simulate HTC reactions. The reactor was allowed to passively cool overnight. The temperature and pressure of the reactor were continuously monitored for the entire duration of the experiments.

Calculation of N_{H2O} and N_{CO2} for H_2O and CO_2 only

The HTC pressure prediction algorithm described above requires values for N_{H2O}, N_{CO2}, and the corresponding total mole fractions Y_{H2O}, Y_{CO2} as inputs. The value for N_{H2O} was calculated from the mass of water M_{H2O} or volume of water $V_{L,i}$ introduced into the reactor. However, quantifying the amount of CO_2 introduced as a gas into the system could only be made indirectly, since the flow of CO_2 to the reactor system was not metered and CO_2 can partition into the water during the period of headspace flushing, before the reactor is pressurized. More will dissolve during equilibration following Henry's Law. Therefore, the procedure described in Section 2.2 for estimating the total amount of CO_2 introduced into the system N_{CO2} was used. The moles of CO_2 in the gas phase n^g_{CO2} were determined by the ideal gas law (Eqn (14)) for the equilibrated initial pressure before heating P_i, using the assumption that the gas volume $V_{g,i}$ is filled only with CO_2. Henry's Law was used to calculate the CO_2 dissolved in the liquid phase n^L_{CO2} according to Equations (13)–(14). With these values for N_{H2O} and N_{CO2} (Table 1), the total mole fractions of H_2O and CO_2 were calculated and used in the algorithm for estimating pressure described above.

Validation HTC experiments for actual hydrothermal system with feedstocks

Experimental set-up

A 1-L high pressure and temperature reactor made of Alloy C276 with valves and fittings made of T316 Stainless Steel (Model 4680 HT, Parr Instrument Co., Moline, IL, USA) was used with two dried and ground feedstocks (bark mulch and sugar beet pulp; <2 mm) added to distilled water to obtain an initial solid concentration of 20% (wt). A 1500-watts heater surrounding the outside reactor wall along with a programmable temperature controller was used to heat the reactants to the desired temperature (200 or 250 °C) with a heating rate of about 7 °C/min. The reactor temperature was maintained for reaction times of 3 or 20 h with no stirring. This reactor system was modified to improve control and data logging capability. Afterward, the reactor was cooled to room temperature before the reaction products were filtered and dried at 100 °C. The reactor conditions are summarized in Table 2 for all six runs.

Measurement of bulk density of submerged biomass

The bulk density of submerged biomass was determined using water displacement. Dry biomass with a known mass was placed in a 500-mL graduated cylinder, and water was added covering the entire volume of biomass until the total mixture volume reached 500 ml. It was lightly stirred and allowed to stand for 30 min. The weight of water added to the graduate cylinder and the appropriate water density was used to calculate the volume of water added. This water volume was subtracted from the total mixture volume to determine the volume of the biomass. This was combined with the weight of the biomass sample to obtain the bulk density of the submerged biomass.

Table 1

Values used for the validation experiment for CO_2-H_2O system: $H(T)$, N_{H2O} and N_{CO2}.

T_R	VF_o	$P_{i,CO2}$	T_i	$H(T_i)$	N_{H2O}	N_{CO2}
(°C)	(-)	(bar, gauge)	(°C)	(mol/m^3-Pa)	(mol)	(mol)
180	0.05	14.3	16.0	0.00034	51.8	11.75
180	0.05	14.7	17.0	0.00034	51.8	12.02
180	0.5	9.8	15.0	0.00034	517.8	7.62
180	0.5	10.2	18.0	0.00034	517.8	7.86
250	0.05	14.5	19.0	0.00034	51.8	11.87
250	0.5	10.1	18.0	0.00034	517.8	7.79

Results and discussion

Validation of the theoretical model with a pure CO_2-H_2O system

In order to ensure that the underlying model based on the equilibrium partitioning of CO_2 between the liquid water and gas phase at the reaction temperatures and pressures is valid, several experiments with only CO_2 and water were carried out. The advantage of this path was the precision in knowing the initial amount of CO_2 in the reactor and the availability of equilibrium data for CO_2-H_2O systems. Once the reactor was filled with water (with VF_o at 0.05 or 0.5) and CO_2 to an initial pressure $P_{i,CO2}$, it was heated and maintained at conditions similar to common hydrothermal reaction conditions (T_R at 180 or 250 °C). The experimental pressure conditions were logged, and the maximum pressure obtained was compared with the calculated one in order to validate the equations and procedure followed. A comparison of the observed reactor pressures $P(T)$ for the six experimental runs to the pressures estimated by the algorithm P_{Max} is shown in Fig. 3. The good agreement between the predicted pressures and experimental values at the two temperatures and two initial liquid volume fractions (less than ± 2% difference) demonstrates that procedure is valid. It is possible to predict the reactor pressure at a given temperature for known amounts of CO_2 and H_2O in the reactor.

Validation of the theoretical model in actual experiments with a feedstock-water system

In the above validation experiment, it was shown that the HTC pressure prediction algorithm can be used for a pure CO_2-H_2O system at a given reaction temperature. However, in an actual hydrothermal system with feedstock reacting to hydrochar, the partitioning behavior of CO_2 between the liquid and gas phases may be influenced by organic and inorganic compounds dissolving into the liquid water, as well the production of solids and additional gases. Therefore, the application of the above procedure for predicting the maximum reactor pressure was further evaluated by comparing the predicted reactor pressure to the actual reactor pressure data from the hydrothermal carbonization of bark mulch and sugar beet pulp [22].

In these HTC-experiments, dried bark mulch and sugar beet pulp were carbonized in a 1-L reactor at various process conditions (T_R 200 to 250 °C; t 3 to 20 h; M_{FS} 25.1 to 54.1 gDM; $VF_{o,FS}$ 0.19 to 0.31). The parameters that define the reaction system are found in Table 2. The results of the algorithm to estimate the maximum reactor pressure for each of the six experimental runs are listed in Table 3. Values for N_{CO2} were calculated for each run based on the measured carbon yields in the experiments. The difference between the mass of C in the raw feedstock and the hydrochar was assumed to be converted to CO_2. Values for N_{H2O} were calculated based on the mass of initial water added and/or contained in the biomass M_{H2O}. The total mole fractions Y_{CO2}, Y_{H2O} in the reactor were then calculated. The initial guess for P_{Max} was based on the experimentally measured pressure. The REFPROP software was used to determine the equilibrium distribution of H_2O and CO_2 between the liquid and gas phases for Y_{CO2}, Y_{H2O}, T_R and the guessed P_{Max}. The output from REFPROP contains the molar fractions of H_2O and CO_2 in the liquid and gas phases, along with gas and liquid densities. These were used in Eqn (1), 2 and 10 to estimate the reactor volume $V_{R,est}$ and

Table 2
Values used in the validation experiment for actual hydrothermal system with the feedstocks bark and sugar beet.

	Experiment		1	2	3	4	5	6
	Biomass Feedstock	Units	bark	bark	bark	beet	beet	beet
process conditions	V_R	(L)	1	1	1	1	1	1
	T_R	(°C)	199	239	241	203	243	253
	t	(h)	3	20	3	3	20	3
	$\%So$	(%)	20	20	20	20	20	20
inputs and experimental conditions	M_{FS}	(gDM)	25.22	40.00	25.08	40.43	54.05	39.97
	$\%C_{FS}$	(%)	59.8	59.8	59.8	51.1	51.1	51.1
	ρ_{FS}	(g/L)	272	272	272	625	625	625
	V_{FS}	(L)	0.09	0.15	0.09	0.06	0.09	0.06
	Solid/Water ratio	(w/w, %)	25.27	24.78	24.99	25.25	24.94	24.98
	M_{H2O}	(g)	99.80	161.42	100.36	160.12	216.72	160.01
	N_{H2O}	(mol)	5.54	8.97	5.58	8.90	12.04	8.89
	V_{Li}	(L)	0.10	0.16	0.10	0.16	0.22	0.16
	VFo	(-)	0.10	0.16	0.10	0.16	0.22	0.16
	$VF_{o,FS}$	(-)	0.19	0.31	0.19	0.22	0.30	0.22
	V_{gi}	(L)	0.81	0.69	0.81	0.78	0.70	0.78
	$P(T)$	(bar_g)	17.1	39.3	36.8	22.1	47.9	61.3
CO_2 produced	SY	(%, db)	77.4	56.1	62.7	57.7	43.9	45.4
	M_{HC}	(gDM)	19.52	22.44	15.73	23.33	23.73	18.15
	$\%C_{HC}$	(%)	64.4	72.2	70.8	61.3	72.2	71.1
	M_{CO2}	(g)	2.51	7.72	3.86	6.36	10.49	7.52
	N_{CO2}	(mol)	0.06	0.18	0.09	0.14	0.24	0.17
	Y_{CO2}	(-)	0.010	0.019	0.016	0.016	0.019	0.019
	Y_{H2O}	(-)	0.990	0.981	0.984	0.984	0.981	0.981

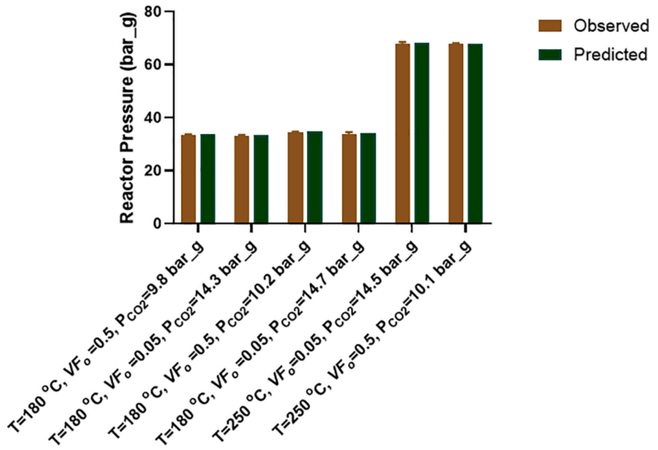

Fig. 3. Comparison of observed vs. predicted pressure for the six runs with the CO_2-H_2O system.

compared to the actual reactor volume V_R. This was repeated with a new guess for P_{Max} until the difference between calculated and actual reactor volume became small. The relative error in the volume estimation was very small, below 0.4% in all the cases (Table 3).

The resulting P_{Max} was compared to the experimentally measured pressure and both are shown in Fig. 4. The relative errors in predicting reactor pressure ranged from −18.5% to 7.3%. These are larger than those found for the CO_2-H_2O only system and might be due to the assumptions used such as all carbon not in the hydrochar is converted to CO_2 and the use of the raw feedstock volume for that of the hydrochar. The sensitivity of the predicted values to the various inputs is explored later in Section 4.4.

In addition, the values from the prediction algorithm were further analyzed to determine whether the feedstock was immersed in bulk liquid water (HTC) or was in direct contact with steam only (vapothermal carbonization VTC) [15]. With the help of Eqn (8), $\%S(T)$, the amount of liquid water in physical contact with feedstock and x_V, the fraction of water in the vapor phase, were calculated. Evaluation of the six experimental runs shows that all can be classified as HTC (Table 4). Even for a low initial volume fraction of water and high temperature (run 3, $VF_o = 0.1$, 241 °C), only 13.7% of the water was vaporized, raising the solid content from 20 to 22.5%. At process conditions and with feedstock occupying some of the reactor volume, the model (Eqn (11)) predicted that the dangerous region of subcooled compression liquid was avoided in all runs with $VF_{w,FS} \leq 0.34$ (Table 4).

Application of theoretical model to estimate reactor pressure at design temperature

In this section, the procedure to estimate the maximum expected design pressure with real biomass is described following the algorithm in Fig. 2. The values used in each step are listed in Table 5. In the first step, the reaction system was defined (V_R, M_{H2O}, M_{FS}, VF_o, $\%S_o$), the process conditions (T_R, t), the biomass and hydrochar properties (ρ_{FS}, $\%C_{FS}$, $\%C_{HC}$), and the expected conversion SY at those conditions were estimated. The expected conversion was based on previous results, alternatively it can be calculated using correlations available in the literature. In Step 2, N_{CO2}, N_{H2O}, and Y_{CO2}, Y_{H2O} were calculated from those values. P_{Max} was guessed based on the P_{sat} at T_R (Step 3), and the REFPROP software was used to determine the equilibrium distribution of CO_2 and water between the liquid and gas phases (y^{g}_{CO2}, y^{g}_{H2O}, y^{L}_{CO2}, y^{L}_{H2O}, ρ_L, ρ_g) for P_{Max} (Step 4). When the calculated $V_{R,est}$ (Step 5) equaled the real V_R within a reasonable error (Step 6), the value for the predicted maximum pressure $P(T)$ was obtained. Otherwise, a further iteration was made from Step 3 with a new guess for P_{Max}.

The final iteration resulted in an estimated pressure of 53.23 bar for this design case at 250 °C (Table 5). The check on the expected distribution of water between the phases and volume expansion shows that only 4% of the water is expected to vaporize and volume fraction filled by water and solids should only reach 0.42 which is well below 1.

In the procedure to predict the maximum pressure in hydrothermal reactions with biomass, a number of assumptions are required, as noted previously in Section 2.3.2. For instance, in both the design case and the validation with biomass, the mass of carbon lost from the feedstock was assumed to be converted wholly into CO_2. However, the liquid phase can also retain carbon, especially in the case of the hydrothermal liquefaction process, which would decrease the amount of CO_2 produced. On other hand, the intermediate reactions during hydrothermal process can produce other carbon-based compounds, such as methane, carbon monoxide or other gases with lower solubilities and, thus, differing

Table 3

Results for the validation of the algorithm to predict pressure in actual HTC experiments with two feedstock-water systems: bark mulch and sugar beet pulp.

Experiment		1	2	3	4	5	6
Step 1. Define the CO_2-H_2O system ($V_R = 1$ L)							
Biomass + H_2O	Units	bark	bark	bark	beet	beet	beet
T_R	(°C)	199	239	241	203	243	253
N_{CO2}	(mol)	0.06	0.18	0.09	0.14	0.24	0.17
N_{H2O}	(mol)	5.54	8.97	5.58	8.90	12.04	8.89
Y_{CO2}	(-)	0.010	0.019	0.016	0.016	0.019	0.019
Y_{H2O}	(-)	0.990	0.981	0.984	0.984	0.981	0.981
Step 2. Guess P_{Max}	(bar_g)	16.82	42.16	37.54	22.90	47.80	49.96
Step 3. Determine the CO_2-H_2O equilibrium distribution for the guessed P_{Max} with REFPROP							
y^L_{CO2}	(-)	0.000	0.002	0.001	0.001	0.003	0.002
y^L_{H2O}	(-)	1.000	0.998	0.998	0.999	0.997	0.998
y^g_{CO2}	(-)	0.139	0.199	0.098	0.266	0.223	0.146
y^g_{H2O}	(-)	0.861	0.801	0.902	0.734	0.767	0.854
ρ_L	(mol/L)	48.03	45.07	45.00	47.70	44.69	43.94
ρ_g	(mol/L)	0.50	1.18	1.06	0.66	1.32	1.39
Step 4. Estimate the reactor volume $V_{R,est}$							
• solve Eqns (1)&(2) simultaneously for N^L and N^g							
N^L	(mol)	5.20	8.36	4.81	8.54	11.40	8.00
N^g	(mol)	0.40	0.17	0.85	0.50	0.87	1.05
• calculate V_{FS} , V_L and V_g from Eqn (10)							
V_L	(L)	0.11	0.19	0.11	0.18	0.25	0.18
V_g	(L)	0.80	0.67	0.80	0.76	0.66	0.76
V_{FS}	(L)	0.09	0.15	0.09	0.06	0.09	0.06
$V_{R,est} = V_L + V_g + V_{FS}$	(L)	1.00	1.00	1.00	0.999	1.00	1.00
Step 5. Compare $V_{R,est}$ to V_R							
Relative error in $V = (V_{R\text{-}est}\text{-}V_R)/(V_R)$	(%)	<0.01%	<0.01%	<0.01%	−0.04%	<0.01%	<0.01%
Step 6. Compare P_{Max} to observed $P(T)$							
Observed $P(T)$	(bar_g)	17.0 ± 0.7	39.1 ± 0.9	36.6 ± 2.6	22.0 ± 0.9	47.7 ± 1.5	61.1 ± 8.4
Relative error in $P = (P_{Max}\text{-}P(T))/\ P(T)$	(%)	−1.6%	7.3%	2.0%	3.6%	−0.2%	−18.5%

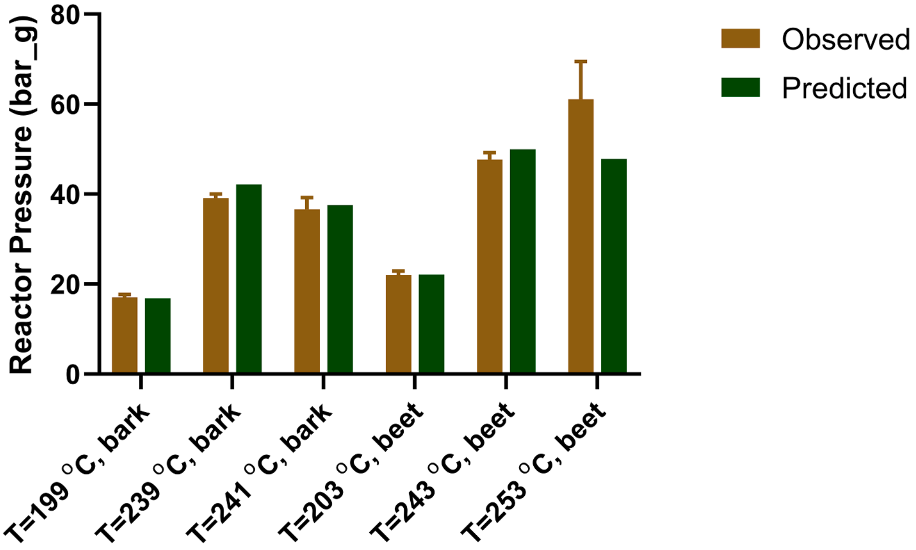

Fig. 4. Comparison of observed reactor pressure $P(T)$ vs. predicted reactor pressure P_{Max} at T_R with two feedstock-water systems: bark mulch and sugar beet pulp.

Table 4

Check expected reactor conditions in system at T_R for validation and design cases: expansion of liquid water ($VF_{w,FS} < 1$) and the distribution of water between the phases.

	Experiment	1	2	3	4	5	6
Parameter	Units						
T_R	(°C)	199	239	241	203	243	253
v_R	(m^3/kg)	0.010	0.006	0.010	0.006	0.005	0.006
$VF_{w,FS}$	(-)	0.20	0.34	0.20	0.24	0.34	0.24
$x_{v,H2O}$	(-)	0.062	0.015	0.137	0.041	0.055	0.101
$x_{L,H2O}$	(-)	0.938	0.985	0.863	0.959	0.945	0.899
$\%S(T)$	(%)	21.2	20.1	22.5	20.8	20.9	21.7

Table 5
Steps to determine the predicted pressure for a design case with a feedstock-water system using the algorithm. (Note: same values were also used for the sensitivity analysis in Section 4.4).

Reaction system: Feedstock + water	Units	Values
Step 1. Define the CO_2-H_2O system		
a. Set values for the reactor system		
V_R	(L)	1
T_R	(°C)	250
t	(h)	2
$\%S_o$	(%)	20
M_{FS}	(gDM)	50
$\%C_{FS}$	(%)	60
ρ_{FS}	(gDM/L)	272
V_{FS}	(L)	0.18
Solid/Water ratio	(w/w, %)	25
M_{H2O}	(g)	200
VF_o	(-)	0.2
$VF_{o,FS}$	(-)	0.38
SY	(%)	56.1
$\%C_{HC}$	(%)	72.1
b-d. Estimate the total mole fractions of CO_2, H_2O in the reactor		
N_{CO2}	(mol),	0.222
N_{H2O}	(mol)	11.11
Y_{CO2}	(-)	0.020
Y_{H2O}	(-)	0.980
Step 2. Guess P_{Max}		
P_{Max}	(bar_g)	53.23
Step 3. Determine the CO_2-H_2O equilibrium distribution for the guessed P_{Max} with REFPROP		
y^L_{CO2}	(-)	0.003
y^L_{H2O}	(-)	0.997
y^g_{CO2}	(-)	0.218
y^g_{H2O}	(-)	0.782
ρ_L	(mol/L)	44.11
ρ_g	(mol/L)	1.48
Step 4. Estimate the reactor volume $V_{R,est}$ (Eqns. (1), (2) and (10))		
N^L	(mol)	10.47
N^g	(mol)	0.85
V_L	(L)	0.24
V_g	(L)	0.58
V_{FS}	(L)	0.18
$V_{R,est} = V_L + V_g + V_{FS}$	(L)	1
Step 5. Compare $V_{R,est}$ to V_R		
Relative error in $V\ (\%) = (V_{R,est}-V_R)/(V_R)$	(%)	0.00
Predicted pressure $P(T) = P_{Max}$	(bar)	53.23

partial pressures, requiring an adapted methodology. We also assumed the raw biomass feedstock volume was maintained throughout the HTC reaction. This might not be true as the raw biomass feedstock underwent hydrolysis and other HTC reactions. Exact HTC reaction mechanisms for beet and bark decomposition and hydrochar formation along with the combined volume of hydrochar and the remaining biomass feedstock are not known. All these factors probably contribute to the error in predicting reactor pressure. Despite all these effects, our methods still yielded the relatively small errors in the range of −18.5 to 7.3% for beet and bark HTC experiments. The low error demonstrates that the simplification through the CO_2 path and the use of the raw biomass feedstock volume to approximate the final volume of the solids after the HTC reaction seem to be useful and flexible enough for the main purpose of the pressure estimations. Based on the error range observed, it also makes a sense to employ a safety factor of at least 1.185 when designing reactor pressure using the procedure presented here.

Sensitivity of the predicted maximum reactor pressure to changes in the HTC process conditions

In order to estimate how the assumptions and procedure affect the accuracy of the pressure estimations, a sensitivity analysis was carried out. The results in Section 4.2 for the validation case with biomass feedstock already showed that the procedure can slightly overestimate the expected pressure (7.3%) as well as underestimate it by 18.5%. The factors influencing the predicted pressure are the values of the process parameters chosen, the properties database consulted, and the volume error allowed in the iteration process, along with the simplifications discussed above. In the sensitivity analysis, changes in process parameters that determine the amount and composition of the CO_2-H_2O system, i.e. $\%S_o$, ratio of solid/water (M_{H2O} varied), $\%C_{FS}$, SY, $\%C_{HC}$, were systematically evaluated by varying them individually (+10%). The initial values of the parameters are those of the design case and can be found in Table 5.

The results in Fig. 5 show that the parameters that affect the amount of CO_2 gas produced from the biomass cause the largest change in the estimated pressure. Variation in the solid yield or carbon content in the hydrochar has an inverse effect on the predicted maximum pressure. For example, using values for the SY or $\%C_{HC}$ that are too high by 10%, reduces the predicted total amount of CO_2 produced N_{CO2}, causing a decrease in the estimated pressure by −8%. In contrast, using 10% higher values for the feedstock carbon content $\%C_{FS}$ or $\%S_o$ will increase the predicted maximum pressure, 8% and 4%, respectively. The effect of changing the volume of the water (through the solid/water ratio) or the volume occupied by the solid V_{FS} on the pressure was negligible to small (<5%). This is notable since the change in the solid properties as the feedstock is transformed to hydrochar is a major source of uncertainty in the hydrothermal system. Further calculations showed that disregarding the volume occupied by the solids for small values of V_{FS} had little effect on the pressure predictions; the pressure was only underestimated by 6% for using $V_{FS} = 0$ instead of 0.18. From these results, it can be seen that for uncertainty or errors of approximately + -10%, a similar magnitude of error will be found the pressure predictions.

Conclusions

The methodology developed and presented here will help researchers, design engineers, and manufacturers to estimate the maximum pressure reached in the reactor based on desired design goals and the extent of HTC reaction for specific biomass feedstock. The methodology was validated with a CO_2-H_2O only system, in addition to being validated against actual HTC reaction pressures with biomass feedstock. The predicted P ranged from −18.5 to 7.3% of the observed P of actual HTC reactions. The causes of the error might be due to assuming negligible gas production other than CO_2. This finding suggests that it would be safe to use a safety factor of at least 1.2 using this procedure. From a sensitivity analysis, we identified that the pressure estimation is most affected by the parameters related to the amount of CO_2 formed during the HTC reaction, e.g. C contents in biomass feedstock and hydrochar and the solid yield.

A further design question for hydrothermal reactor systems can also be answered using the values obtained in the pressure estimation procedure. Based on the equilibrium values, the distribution of water between the phases in the reactor can be predicted in order to decide

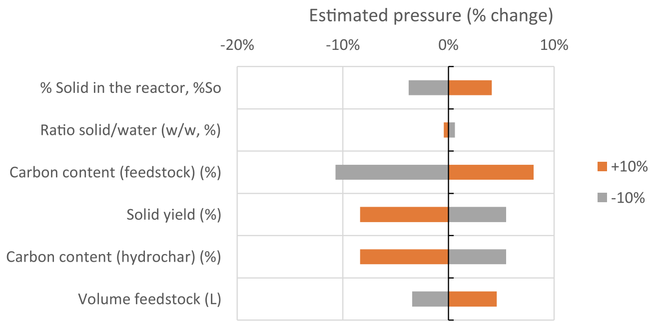

Fig. 5. Estimated change in reactor pressure due to changes in the process parameters that determine the amount and composition of the CO_2-H_2O system.

whether the feedstock will be immersed in bulk liquid water (HTC) or will be in direct contact with steam only (vapothermal carbonization VTC) [15]. The expected solid content *%S(T)* and expansion of the liquid water volume at the reaction temperature can then be calculated.

The easy-to-follow design method can be used not only to assist in predicting maximum HTC reactor pressure, but it can also be used to systematically analyze HTC reaction kinetics based on observed reactor pressure with respect to time. This is an important step in order to gain more knowledge about the reactions taking place in high-pressure systems that are difficult to observe or sample. Furthermore, since the expected pressure conditions determine cost and safety-relevant construction parameters, such as wall thickness, materials and manufacturing techniques for a hydrothermal reactor system, this systematic method for estimating pressure in hydrothermal biomass systems can help promote the widespread use of HTC for converting wet wastes into value added hydrochar which can improve soil health and reduce environmental pollution.

Glossary

Symbol	Definition	Units
$H(T)$	Henry's coefficient at temperature T	(mol/m^3-Pa)
H_o	Henry's coefficient at reference T of 298.15 K (3.4×10^{-4})	(mol/m^3-Pa)
M_{FS}	mass of feedstock in the reactor as dry mass (DM)	(gDM)
M_{H2O}	mass of water in the reactor	(g)
N_{CO2}	total moles of CO2 in the reactor	(mol)
N_{H2O}	total moles of H_2O in the reactor	(mol)
N^g	total moles in the gas phase	(mol)
N^L	total moles in the liquid phase	(mol)
n^L_{CO2}	moles of CO_2 in the liquid phase	(mol)
n^g_{CO2}	moles of CO_2 in the gas phase	(mol)
n^L_{H2O}	moles of H_2O in the liquid phase	(mol)
n^g_{H2O}	moles of H_2O in the gas phase	(mol)
$P(T)$	pressure at target reactor temperature (gauge)	(bar_g)
P_i	equilibrated pressure of reactor just before heating	(bar_g)
P_{Max}	predicted maximum pressure of reactor at target temperature (gauge)	(bar_g)
REFPROP	Reference Fluid Thermodynamic and Transport Properties	
$\%S_o$	nominal solid content at the start of the run—ratio of mass of feedstock in DM to total mass in reactor. ($M_{FS}/(M_{H2O} + M_{FS})$)	(%)
$\%S(T)$	actual solid content based on mass of liquid water in contact with feedstock ($M_{FS}/[(x_{L,H2O} \times M_{H2O}) + M_{FS}]$)	(%)
SY	solid yield of hydrochar relative to feedstock (M_{HC}/M_{FS})	(%)
T	reactor temperature for $H(T)$ in K	(K)
T_o	reference temperature for $H(T)$ (298.15 K)	(K)
T_i	initial temperature of reactor before heating	(°C)
T_R	reaction temperature or target reactor temperature	(°C)
t	reaction time	(h)
V_{FS}	volume of feedstock in the reactor at T_i	(L),
V_g	volume of gas in the reactor at temperature T_R	(L)
V_{gi}	initial gas volume of reactor before heating	(L)
V_L	liquid volume in the reactor at temperature T_R	(L)
V_{Li}	initial liquid volume in the reactor before heating	(L)
V_R	reactor volume	(L)
$V_{R,est}$	reactor volume estimated	(L)
v_R	overall specific volume of reactor liquid water and steam mixture V_R/M_{H2O}	(m^3/kg)
VF_o	volume fraction of liquid water in the reactor at initial temperature T_i	(-)
$VF_{o,FS}$	volume fraction of liquid water and feedstock in the reactor at initial temperature T_i	(-)
VF_w	volume fraction of liquid water in the reactor at temperature T_R	(-)
$VF_{w,FS}$	volume fraction of liquid water and feedstock in the reactor at temperature T_R	(-)
$x_{L,H2O}$	mass fraction of total water present as liquid (also mole fraction)	(-)
x_{vH2O}	mass fraction of total water as vapor in the gas phase (also mole fraction)	(-)
Y_{CO2}	total mole fraction of CO_2 in the liquid phase	(-)
Y_{H2O}	total mole fraction of water in liquid phase	(-)
y^g_{CO2}	mole fraction of CO_2 in the gas phase	(-)
y^L_{CO2}	mole fraction of CO_2 in the liquid phase	(-)
y^g_{H2O}	mole fraction of water in the gas phase	(-)
y^L_{H2O}	mole fraction of H_2O in the liquid phase	(-)
ρ_{FS}	bulk density of submerged feedstock	(gDM/L)
ρ_g	bulk molar gas density	(mol/L)
ρ_L	bulk molar liquid density	(mol/L)

(*continued on next column*)

(*continued*)

CRediT authorship contribution statement

Andrés Alvarez-Murillo: Theory development, data processing, draft and final writing. **Judy A. Libra:** Conceptualization, experimentation, draft and final writing. **Kyoung S. Ro:** Conceptualization, theory development, experimentation, draft preparation.

Declaration of Competing Interest

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

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