Challenges and Opportunities of Hydrothermal Carbonization of Biomass

by

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ABSTRACT

CHALLENGES AND OPPORTUNITIES OF HYDROTHERMAL CARBONIZATION OF BIOMASS

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Hydrothermal Carbonization (HTC) is one of the most promising methods for biomass treatment. Research on the HTC in the lab-scale has progressed recently. However, due to complex reaction mechanisms and operating conditions (e.g., high temperature and pressure), more improvements are required in order to account it as a commercial technology. This thesis is an effort to find solutions for some of the impediments and gaps towards commercialization of HTC including research on the effects of recycling water and biomass particle size on the HTC, finding a generic model to predict the main products from HTC, developing a reliable heat and mass transfer model that considers the complexities such as the heat of the reactions and the porous nature of the biomass, development of a continuous reactor and characterization of its products, and the integration of HTC with other processes. The results indicate that in order to move towards an industrial set-up, the recovery of water and heat to the process not only decreases the energy and water consumption but also improves the quality of the products. In addition, a proper kinetic and heat and mass transfer model is a necessary step for design of an industrial HTC reactor. By knowing the time and the amount of energy released by the exothermic reactions during the HTC process, there are opportunities for consuming less energy. Moreover, the results of performing HTC in a novel continuous reactor designed and developed in this research revealed that continuous HTC at temperatures above 240 °C, reaches higher degrees of carbonization and delivers products with higher porosities and thermal stabilities. The research also succeeded in finding generic equations for prediction of HTC with regards to the biomass composition (cellulose, hemicellulose, and lignin), and process intensity (temperature and time). Finally, by applying the knowledge obtained from the previous parts, an integrated HTC and anaerobic digestion (AD) system was proposed and it was shown that using HTC for conversion of biomass with high moisture content to energy is promising.
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**Symbols**

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$A_i$</td>
<td>Pre-exponential factor (1/s)</td>
</tr>
<tr>
<td>$C_{ap}$</td>
<td>Capacity</td>
</tr>
<tr>
<td>$C%$</td>
<td>Carbon content (%)</td>
</tr>
<tr>
<td>$\frac{dw}{dt}$</td>
<td>Rate of weight (% per min)</td>
</tr>
<tr>
<td>$E_{a,i}$</td>
<td>Activation energy (kJ/mol)</td>
</tr>
<tr>
<td>$h$</td>
<td>Heat transfer coefficient (W/m.K)</td>
</tr>
<tr>
<td>$h_{reac}$</td>
<td>Heat of reaction (kJ/kg)</td>
</tr>
<tr>
<td>$H/C$</td>
<td>Atomic ratio of hydrogen to carbon</td>
</tr>
<tr>
<td>$I$</td>
<td>Investment cost (USD)</td>
</tr>
<tr>
<td>$K$</td>
<td>Thermal conductivity (W/m.K)</td>
</tr>
<tr>
<td>$K_i$</td>
<td>Reaction rate coefficient (1/s)</td>
</tr>
<tr>
<td>$L$</td>
<td>Length of the cylinder (m)</td>
</tr>
<tr>
<td>$O/C$</td>
<td>Atomic ratio of oxygen to carbon</td>
</tr>
<tr>
<td>$\dot{Q}$</td>
<td>Rate of heat transfer (W)</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant (8.314 J/mol.K)</td>
</tr>
<tr>
<td>$R_{tot}$</td>
<td>Total thermal resistance (K/W)</td>
</tr>
<tr>
<td>$R_0$</td>
<td>Reaction ordinate (min)</td>
</tr>
<tr>
<td>$R^2$</td>
<td>Coefficient of determination (%)</td>
</tr>
<tr>
<td>$r$</td>
<td>Radius (m)</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>$T_h$</td>
<td>Burnout temperature (K)</td>
</tr>
<tr>
<td>$T_i$</td>
<td>Ignition temperature (K)</td>
</tr>
<tr>
<td>$T(t)$</td>
<td>Temperature (K) at time t</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$V$</td>
<td>Volatile matter stream</td>
</tr>
<tr>
<td>$Wt%$</td>
<td>Weight percent</td>
</tr>
<tr>
<td>$\Delta G^o$</td>
<td>Gibbs free energy of the reaction (kJ)</td>
</tr>
<tr>
<td>$\Delta H_{ec}$</td>
<td>The heat of combustion (kJ/g)</td>
</tr>
</tbody>
</table>
\( \Delta H_f \) Enthalpy of formation (kJ/mol)

\( \Delta H_{\text{reaction}} \) Enthalpy of reaction (kJ/mol)

\( \Delta H^o \) Enthalpy change of the reaction (kJ/mol.°K)

\( \Delta S^o \) Entropy change of the reaction (J/mol.°K)

\( \frac{\partial M}{\partial t} \) Changes in mass with time

**Abbreviations**

AD Anaerobic digestion

ANOVA Analysis of variance

ASTM American Society for Testing and Materials

BET Brunauer–Emmett–Teller

C Cellulose

CCF Combustion characteristic factor

DA Diode array

DOE Design of experiments

EES Engineering equation solver

EMC Equilibrium moisture content

ERF Energetic recovery efficiency

FC Fixed carbon

FTIR Fourier transform infrared spectroscopy

GC Gas chromatograph

GHG Greenhouse gases

H Hemicellulose

HC Hydrochar

HHV Higher heating value (MJ/kg)

HPLC High performance liquid chromatography

HTC Hydrothermal carbonization

HTC-xxx HTC at xxx °C temperature

HTC-xxx-xx min HTC at xxx °C temperature for xx min

HTG Hydrothermal gasification

HTL Hydrothermal liquefaction

IC Ion Chromatography

L Lignin

LCA Life cycle assessment
MY  Mass yield (%)  
PW  Process water  
rec  Recycle  
RH  Relative humidity  
RI  Refractive Index  
RSM  Response surface methodology  
SCWG  Supercritical water gasification  
SEM  Scanning electron microscope  
SF  Severity factor  
TGA  Thermo-gravimetric analysis  
TOC  Total organic carbon  
TSE  Twin-screw extruder  
UV  Ultraviolet  
VM  Volatile matter  
VOCs  Volatile fatty acids  
WC  Water content  
5-HMF  5-(Hydroxymethyl)furfural
Chapter 1. Introduction

This chapter presents the motivation, research statement, objectives and approaches, scopes and limitations, and outline of this Ph.D. thesis on hydrothermal carbonization of biomass.

1.1. Motivation

Research on developing sustainable energy systems based on renewable biomass feedstock is a global attempt to tackle problems associated with climate change. Biomass is any material, excluding fossil fuel, which was a living organism that can be used as a fuel either directly or after a conversion process [1]. As the raw biomass quality may not be economically and technically suitable to use, thermochemical conversion processes are pathways to produce biofuels or other value-added products from raw biomass. Except hydrothermal carbonization (HTC), all other thermochemical conversion processes require a primary stage of drying. HTC is performed at a temperature range of 180–350 °C during which the biomass is submerged in water and heated in a closed system under pressure (2–6 MPa) for 5–240 minutes [2]. HTC is performed in the presence of water. Therefore, there is no need for pre-drying in this process which enables it to treat biomass that contains high moisture content. Moreover, HTC can remove a portion of the incombustible material which is participating in ash formation during combustion [3]. The main product of HTC is a solid named hydrochar which can be used as biofuel or in many other applications (e.g., soil amendment, water treatment [4]). In addition to producing hydrochar, HTC will also produce a liquid (aqueous soluble) and gas (mainly CO₂) [5].

Although HTC has shown a great potential for industrial production of sustainable materials, there are a number of impediments that hinder its expansion. Firstly, the kinetics and reaction pathways of HTC have not yet been fully discovered. Due to synergies and interactions of the reaction pathways with the quality of the products and the energy consumption during the process, simulation of this process is complex. Hence there is also a lack of understanding of the heat and mass transfer of the process. Secondly, as the biomass composition varies from one to another, the results obtained from experiments on one biomass cannot extend to others. Therefore, a model that can simulate the effects of HTC on the raw biomass based on its composition is also required [6]. In addition, there is a lack of effort in assessment and fabrication of the systems that can be used in larger scales in industries. Most of the research is performed in a lab-scale batch reactor and
does not consider the operational difficulties of the process on a larger scale. The main issue for this type of research is the high pressure required in the HTC process that makes the continuous feeding of the biomass into the reactor difficult. In an industrial continuous system, it is also important to know, how the water and energy requirements can be audited. This can be achieved by investigating the effects of water recirculation, biomass size, and the integration of continuous HTC with other processes.

1.2. Problem statement
As it was mentioned above, many aspects of HTC have not been yet discovered. Although the main goal of this research is the design of a continuous reactor, some of the initial studies in this direction can be carried out in batch reactors. For instance, the modeling of energy consumption of the process can be validated with experiments in the batch reactor. Other than that, the effects of water recirculation or biomass size as well as finding a model for the effects of HTC based on the biomass composition can be achieved by batch experiments. As there is a research gap in the aforementioned areas, obtaining enough knowledge is necessary before developing an industrial design. The results obtained from this Ph.D. thesis entitled “Challenges and opportunities of hydrothermal carbonization of biomass” are expected to pave the way for commercialization of HTC and consequently provide new opportunities for conversion of biomass (especially the ones with high moisture contents) to valuable products.

1.3. Objectives and approaches
This study explores different aspects of HTC that is required before stepping towards the commercialization of HTC. The main objectives of this research can be categorized as follows:

- A comprehensive literature review study around HTC that can show the gaps in the research.

**Approach:** After determining the subdivisions of this review work, Google Scholar and Scopus were used to find the documents based on the keywords. For management purposes and to keep track of the papers, a reference management software called Mendeley was used. Based on the subdivisions, several folders were created and in each of them, the related papers were collected. A total number of 256 documents were found by this searching approach. The first step for screening the papers was reading the abstract. Hence, some of the unrelated papers were identified and removed. Taking notes during the reading of any paper was necessary to
avoid keeping papers with the same information. The screening in this stage reduced the number of papers to 163. Finally, the notes from different subdivisions were gathered and written as constitutive parts of the whole manuscript with a logical structure and the suggestions were presented accordingly.

- Investigating the effect of water recycling and the size of biomass feedstock on the products of HTC.

**Approach:** For the first part of this study (process water recycling effect), the HTC experiments were performed in three different set temperatures and three different residence times. After each HTC test, the process water was separated by a filter paper and reused in the next round. This recirculation was repeated for three times. The products of each experiment were characterized using different techniques to track the changes in the quantity and quality of the hydrochar. Regarding the second part (effects of particle size), Three smaller reactors containing feeds with different particle sizes were placed in a larger reactor to ensure that the process conditions for all particles remained the same. The changes were again explained using several techniques.

- Development of a mathematical model for the prediction of HTC based on the process severity factor and the composition of lignocellulosic biomass.

**Approach:** Knowing that the main components of lignocellulosic biomass are hemicellulose, cellulose, and lignin, the pure type of these materials were purchased from Sigma-Aldrich Canada Co. as the model components of the biomass. These materials were then mixed or used solely in several HTC experiments. The HTC experiments were set as 180, 220 and 250 °C and the residence time was 30 min for all experiments. Several characterization techniques were used on the obtained hydrochars. Response surface methodology was used to find the optimal number of experiments as well as the best fitting equations that relate the variables including the cellulose content, hemicellulose content, lignin content, and severity factor (a combination of process temperature and residence time), with the responses including mass yield, heating value, carbon content, and energy recovery factor.
• Development of a mathematical model to address the heat and mass transfer of HTC considering the heat of reactions and porous nature of the biomass.

**Approach:** HTC experiments were conducted at different temperatures and times. An energy meter and a temperature logger were connected to the heat supplier and the reactor’s outer surface respectively to monitor the changes and the feedstock and the obtained hydrochar were characterized. The whole HTC process was modeled using COMSOL Multiphysics by connecting modules of the software including heat transfer in solids, heat transfer in liquids, heat transfer in porous media, mass transfer in diluted species and chemistry. The required data of the simulation were found by performing experiments, from the literature, and from the software’s data bank. Finally, the obtained results from the experiments and the simulation were compared and it was shown that the model can be an acceptable implication of the HTC process.

• Design and development of a continuous system to perform continuous HTC on the biomass and comparison with a batch operation.

**Approach:** A novel continuous HTC system was designed and built. The novelty of this system is in designing the pumping system where the hydraulic force helps the pressure of the new feed (upstream of the reactor) overcome the pressure of the feed inside the reactor. Hence, when the valve at the top of the reactor opens, the new feed can enter the reactor and biomass encounters the high temperature and pressure immediately rather than a slow increase from room condition. The obtained hydrochars from this method were compared with the ones from batch experiments using characterization techniques.

• Development of a numerical energy model for integrated HTC and anaerobic digestion systems with power cycles.

**Approach:** Engineering Equation Solver (EES), was used to develop two integrated scenarios for power generation from biomass. In the first scenario, HTC and anaerobic digestion were used to produce solid and gaseous fuels and Rankine and Brayton cycles were coupled to utilize these fuels. Whereas, in the first scenario, direct combustion of the biomass was used in a Rankine cycle. The governing thermodynamic equations of the systems were developed by EES and then the sensitivity analysis was performed to assess the performance of the systems under changes of the main parameters.
1.4. Scope and limitations

One of the major challenges of the current century is the increasing need for energy and consequently global warming. There is a crucial need to diversify the energy systems that can contribute to production of alternative fuels and materials and reduce waste. Lignocellulosic biomass is one of the most abundant sources that can produce sustainable energy and materials. One of the main impediments of many types of biomass is the high moisture content that makes their treatment through usual thermochemical conversion methods highly energy-intensive. HTC is a thermochemical process that can address this issue because it uses water as a reaction medium. Hence, the moisture content of the biomass is in favor of the process. The current research addresses the technical barriers to utilize this method on an industrial scale. By utilizing this method, it is expected to find opportunity for conversion a wide range of biomass. Hence this research opens a new scope to reduce waste, promote energy systems diversity, and mitigate climate change. The intended audience is decision-makers of energy policies. Biomass is a great renewable source and the research is trying to make the technologies of biomass treating commercial and large scale. Giving the superiorities of the methods will help policymakers, investors and stakeholders to select the best technology for their specific requirements.

The research presented in this thesis faced some limitations. The common limitation throughout different studies of this thesis was the upper temperatures of HTC. In order to fully investigate the effects of hydrothermal reactions on the biomass, the ideal approach was to consider the temperature from 180 °C-350 °C. However, the reactors used in this research could not go above 270 °C due to safety issues that arise with higher pressures associated with higher temperatures. The other limitation was that most of the studies required a continuous HTC system for authentic results extendable to industrial HTC. However, due to plenty of time required for design and development of continuous HTC, some of the studies like heat and mass transfer modeling, and HTC prediction with regards to biomass composition and severity factors were validated by experiments in the batch reactors. The other notable limitation was that the biomass used in this research was often gone through preparation stages such as chopping, grinding and pulverization and this was not addressed in feasibility studies of this research. Moreover, as it was stated, although HTC is able to convert different kinds of biomass to value-added products, in this research the main focus was on the second-generation biomass and the performance of the designed HTC was not assessed using another kind of biomass such as third-generation (algae).
Finally, for some parts of the energy model and integration of different processes (such as anaerobic digestion, and power cycles), data obtained from literature (secondary data) or data from calculations were used as performance of the experiments on those were not the focus of this study.

1.5. Structure of the thesis

This thesis is divided into eight different chapters. The chapters present different information, but the main objective framework remains same. Chapter 1 is reporting the basic introduction to the research and explains the necessity and methods of this research by problem statement, objective and approaches, and scope and limitation. Chapter 2 provides a thorough literature review on the subject and explains what the main research gaps towards commercialization of HTC are. The next chapters deal with the research gaps found in chapter 2. As in a commercial scale, the process water is supposed to return to the reactor and the biomass feedstock is also important, Chapter 3, assesses these two issues. Chapter 4 is an effort to find a generic model for studying the behavior of biomass under hydrothermal process by studying the composition of biomass (cellulose, hemicellulose, and lignin) and the severity of the process (temperature and time). Chapter 5 is about the development of a heat and mass transfer model for HTC considering the effects reactions and porosity of the biomass. Chapter 6 discusses the design, development and product evaluation of a continuous HTC system. Chapter 7 is an investigation to show the possibilities of process integration of HTC with other processes like anaerobic digestion and power generation cycles. Finally, chapter 8 presents the overall conclusion and explains the direction for future works.

1.6. Contribution of the thesis

The major contributions of this research are summarized in Table 1.1. Most of these contributions have been published in scientific articles as listed in the next section. Apart from the advisor and co-advisor, some individuals contributed intellectually to the findings reported in the papers. Dr. Shohel Mahmud contributed to the methods of the literature review. Dr. Syeda Tanim helped with the numerical modeling of HTC. Shakirudeen Salaudeen, and Omid Norouzi analyzed and interpreted data, and helped in designing and performing the experiments. Precious Arku critically revised the numerical modelling work for chemical equations and analysis. Kevin MacDermid-Watts helped with the design and performance of semi-continuous experiments.
Table 1.1. Major contributions of this research

<table>
<thead>
<tr>
<th>Contribution</th>
<th>Major findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Effects of process water recycling and biomass feedstock sizes on the</td>
<td>• Both issues can greatly affect the technical and economic feasibility of industrial HTC systems.</td>
</tr>
<tr>
<td>hydrochars obtained from HTC</td>
<td>• The mass yield was increased by recycling the process water which is due to the increase in the acidity of the recycled water. However, after two cycles the reactions reached equilibrium.</td>
</tr>
<tr>
<td></td>
<td>• HHV and energy recovery efficiency enhances with recycling. While the energy recovery efficiency without any recycling was 66.17%, it increased to 80.17% and 82% after the first and the second recycles respectively.</td>
</tr>
<tr>
<td></td>
<td>• The TGA and BET indicated that the combustion behavior of the hydrochars obtained with recycled water is different which is due to the addition of materials with less reactivity than the usual hydrochar.</td>
</tr>
<tr>
<td></td>
<td>• In HTC, Smaller particle sizes undergo higher conversion due to an increase in the surface area for heat and mass transfer resulting in hydrochars with higher amounts of carbon.</td>
</tr>
<tr>
<td>2. Proposing mathematical equations for the prediction of HTC based on the</td>
<td>• Final equations were proposed to find MY, HHV, C%, and ERF from an HTC experiment with respect to the severity factors and the abundance of the main components of lignocellulosic biomass (cellulose, hemicellulose, and lignin). Errors of less than 1% for all of the responses showed that the models fit perfectly with the experimental data.</td>
</tr>
<tr>
<td>process severity factor and the composition of the biomass.</td>
<td>• The proposed equations were tested with experimental data of HTC on 10 different real...</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
biomass and it was shown that the model is reliable especially at low ash and water extractives contents.

- The equations can reveal important information for design and feedstock selection of an HTC plant. For instance, it was found that the higher the lignin and the lower the cellulose contents in the raw biomass, the higher the energy content of the hydrochar. Moreover, it was observed that by selecting the suitable biomass feedstock with as low SF as 4.5, MY of around 67%, and HHVs of around 25 MJ/kg can be obtained.

3. Simulation of heat and mass transfer of HTC considering the heat of reactions and porous nature of the biomass.

- For the first time the porosity of the biomass and the heat released due to the exothermic reactions during the HTC were considered in a mathematical model of HTC. The temperature, power, and mass profiles of the model were validated with those of the experiment and showed a good agreement.

- While the overall process consumed an average of 465 W for 95 min, it was shown that without considering the heat released by the reactions and porosity, the estimated power will be far from reality.

- In order to address the concerns of high energy intensity of this process, a well insulated, sealed, and continuous reactor was considered in the model, and it was shown that for each 100 g of the biomass, a total amount of 303.53 kJ energy can be used to convert it to the 55 g hydrochar with a heating content of 1326.60 kJ.
4. Design and development of a continuous system to perform continuous HTC

- As the main challenge to operate HTC in a continuous mode is feeding the biomass against high pressure of the reactor, a stacked dual-piston-cylinder with common shaft was designed and utilized with a hydraulic pump. The development of different sections of the continuous HTC system was explained. Then, the procedure for comparison of the hydrochars obtained in the batch and continuous modes from this system was defined.

- Hydrochars obtained from continuous operation at temperatures below 240 °C were only slightly less carbonized, but above 240 °C they even showed higher degrees of carbonization. These results were particularly interesting at 270 °C, where the continuous operation was partially similar to hydrothermal liquefaction and significantly more carbonized than the batch operation at the same temperature.

- TOC, XRD, FTIR, BET, and TGA experiments suggested that the changes are possibly due to the suppression of the secondary polymerization and instead enhanced primary carbonization. The promising conclusion of these results is that by introducing continuous systems in HTC, not only will the time and energy consumption of the process decrease, but also higher qualities of hydrochar are achievable.

5. Development of a numerical energy model for integrated HTC and AD system with direct combustion of biomass

- The numerical comparison of an integrated HTC-AD system with direct combustion of biomass revealed by increase in the moisture of the biomass
AD systems with power cycles

- the advantages of HTC-AD system are more pronounced.
  - It was also found that the performance of the bioenergy systems improves if the composition of the PW contains more HMF or levulinic acid.
  - Effects of PW temperature and water to biomass ratio were also investigated.

### 1.7. Journal Publications of the Thesis

Versions of this thesis have been published in different peer-reviewed journals and two of these chapters are under reviewing process. Publications so far made during the period of this study (2016 to 2020) are listed as follows:


• Mohammad Heidari, Shakirudeen Salaudeen, O. Norouzi, B. Acharya, A. Dutta
  “Numerical Comparison of a Combined Hydrothermal Carbonization and Anaerobic
  Digestion System with Direct Combustion of Biomass for Power Production,” Processes,
  vol. 8, no. 43, 2020.
Chapter 2. Literature Review

The aim of this chapter is to provide a better understanding of HTC and discuss the recent research progress, gaps and new ideas for future work.


2.1. Introduction

Hydrothermal carbonization (HTC) is a thermochemical process for the pre-treatment of high moisture content biomass to make it viable in several applications. HTC is performed in a temperature range of 180–350 °C during which the biomass is submerged in water and heated under pressure (2–6 MPa) for 5–240 min [2]. The main product of HTC is a solid named hydrochar. It also produces liquid (aqueous soluble) and gas (mainly CO₂) by-products [5].

HTC is a promising method for utilizing the potential of biomass for cleaner production. More research on the chemistry of the HTC, its kinetics and heat transfer, the effect of operational parameters and catalysts, energy and heat recovery, combinations with other technologies, and technical and economic aspects are required. The key component of a potential industrial HTC plant is the reactor. Most of the reactors used in the literature are the batch type, however, for an industrial plant, a continuous reactor that can work at a high temperature and pressure is required. This chapter is aimed at providing a better understanding of HTC and discussing the recent research progress, gaps and the directions for improvement of this process. Figure 2.1. indicates the main structure of this chapter.
Biomass is organic material from plants and animals that has stored sunlight in the form of chemical energy. Biomass can be categorized as non-lignocellulosic and cellulosic. Non-lignocellulosic biomass is usually sewage sludge and animal manure and mostly contains fatty acids, protein and small amounts of hemicellulose, cellulose, and lignin [7]. On the other hand, the main components of lignocellulosic biomass are hemicellulose, cellulose, and lignin. It also contains some amounts of water extractives and ash. Agricultural farms, forests and municipal biological solid wastes are the main sources of lignocellulosic biomass [8]. While the composition of biomass depends heavily on the type, maturity, and climate conditions, it can be said that it contains 20-40% hemicellulose, 40-60% cellulose and 10-25% lignin [9]. The structure and cell wall of typical lignocellulosic biomass are shown in Figure 2.2.
The thermal treatment of biomass decomposes the hemicellulose, cellulose, and lignin. Hemicellulose usually decomposes at around 160 °C in subcritical water and around 200-300 °C in ambient conditions, while cellulose and lignin start decomposing at 180-200 °C and above 220 °C in subcritical water, and 300-400 °C and above 600 °C in ambient conditions respectively [10]. HTC is a method for fast coalification by subjecting a mixture of biomass and water to high temperature and pressure conditions. HTC simulates the million-year natural process of converting biomass to coal in only a few hours. By the beginning of the 21st century, HTC was considered a promising method for tackling climate change and greenhouse gas emissions problems [11]. HTC can treat biomass with high moisture content as it uses water as a reaction media, eliminating the need to initially dry the biomass like other conversion processes (i.e., torrefaction, gasification [12], [13]). Moreover, HTC is compatible enough to be combined with other processes, thus allowing products with certain characteristics in terms of morphology, porosity, chemistry and electronic properties [14] to be produced for specific applications such as power generation [15], nanoparticles (for making composites) [16], water purification [17], carbon capture [18], and soil amendment [19].

2.3. General knowledge of HTC

2.3.1. Brief chemistry
The aqueous medium used for the HTC process is kept under its critical point. Ionic or polar reactions take place to form the liquid phase at lower temperatures while free radical reactions
occur to form the gas state at higher temperatures. Also, molecular reactions mostly occur when the condition is closer to the critical region of the water [20].

Many reactions take place during the process and the detailed nature of the reaction pathways is not fully understood yet. However, as hydrolysis has a lower activation energy than most of the other reactions, it can be stated that HTC is governed by hydrolysis. During the hydrolysis, the ester and ether bonds of the hemicellulose (at T>180 °C), cellulose (at T>200 °C), and lignin (at T>220 °C) break down into many fragments [21], [22]. The next two important reactions are dehydration and decarboxylation which are responsible for reducing H/C and O/C ratios [23]. Dehydration also releases more water in the reaction medium. As an example, the dehydration of glucose is as Equation 2.1. [24].

\[
C_6H_{12}O_6 \rightarrow C_6H_4O_2 + 4H_2O
\]  

(2.1)

By decarboxylation, carboxyl and carbonyl groups degrade and release CO₂ and CO. The next important reaction is condensation polymerization, during which some of the highly reactive fragments of the previous reactions participate. Two molecules combine, resulting in the simultaneous formation of a larger molecule and the release of a small molecule (usually water). Moreover, aromatization reactions will result in aromatic polymer structures which are stable under hydrothermal conditions and are considered as the building blocks of the hydrochar [25]. It is important to note that the main problem in understanding the chemistry of the HTC is that the reactions do not occur in series and their order, severity, and interactions are not discovered yet [26], [27].

### 2.3.2. Products specification

The main product of HTC which retains most of the carbon content of the initial feed is the solid product named hydrochar. In addition to the hydrochar, the liquid by-product (process water) and gas by-product are obtained. The distribution of these products depends on the type of feedstock used and the process conditions. Table 2.1 shows the yield of each phase obtained by HTC on several feedstocks in the literature.
Table 2.1. Yield of solid, liquid and gas for different HTC experiments

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Temp.</th>
<th>Time</th>
<th>Solid yield (%)</th>
<th>Liq. Yield (%)</th>
<th>Gas yield (%)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Different wastes</td>
<td>180-250</td>
<td>1 h -12 h</td>
<td>50-80</td>
<td>5-20</td>
<td>2-5</td>
<td>[3]</td>
</tr>
<tr>
<td>Different wastes</td>
<td>180-250</td>
<td>3 h -18 h</td>
<td>75-80</td>
<td>15-20</td>
<td>5</td>
<td>[28]</td>
</tr>
<tr>
<td>Jeffery Pine and White Fir</td>
<td>215-295</td>
<td>30 min</td>
<td>50-69</td>
<td>12-14</td>
<td>5-12</td>
<td>[29]</td>
</tr>
<tr>
<td>Loblolly Pine</td>
<td>220</td>
<td>5 min</td>
<td>63-83</td>
<td>8-17</td>
<td>9-20</td>
<td>[30]</td>
</tr>
<tr>
<td>Sugarcane Bagasse</td>
<td>215</td>
<td>30 min</td>
<td>64</td>
<td>20</td>
<td>4</td>
<td>[31]</td>
</tr>
<tr>
<td>Tahoe mix</td>
<td>235</td>
<td>30 min</td>
<td>63.68</td>
<td>17.66</td>
<td>7.86</td>
<td>[31]</td>
</tr>
<tr>
<td>Pinyon/juniper</td>
<td>235</td>
<td>30 min</td>
<td>62.73</td>
<td>30.37</td>
<td>6.13</td>
<td>[31]</td>
</tr>
<tr>
<td>Corn stove</td>
<td>235</td>
<td>30 min</td>
<td>56.41</td>
<td>32.41</td>
<td>7.79</td>
<td>[31]</td>
</tr>
<tr>
<td>Rice hulls</td>
<td>235</td>
<td>30 min</td>
<td>64.33</td>
<td>25.37</td>
<td>5.23</td>
<td>[31]</td>
</tr>
</tbody>
</table>

**Solid**

Almost all studies on HTC present information about solid mass yield and characterization of hydrochar. Proximate and ultimate analysis, HHV, mass, and energy density, compression strength, durability, hydrophobicity, and water-resistance are some of the ways of characterizing hydrochar [32].

The proximate analysis, which is performed per ASTM standards, measures moisture (ASTM-E871), ash (ASTM-E1755), volatile matter (ASTM-E857) and fixed carbon content of the sample [33]. Moreover, with ultimate analysis or CHNSO, the amount of carbon, hydrogen, nitrogen, sulfur, and oxygen in the hydrochar can be found using elemental analyzers. The concentration of these elements determines the calorific value of the hydrochar and can be used to find an empirical formula for the hydrochar. Also, the calorific value is usually found using bomb calorimeters by combusting a small amount of the sample and measuring the temperature rise of a certain amount of water [34].

For storage and transportation purposes, hydrochar can be densified into a pellet using a mechanical press with a cylindrical die and controlling the temperature [35]. The compressive
strength of the pellet can be determined by placing it in an Instron machine and recording the maximum force before the first crack. Also, its durability can be found by the amount of dust (fine particles) produced after subjecting the pellets to mechanical or pneumatic agitation [32].

To measure the hydrophobicity, the EMC of the sample should be determined by placing the samples in a controlled environment (i.e., RH = 48-52% at 22 °C). To test the hydrophobicity of a hydrochar sample, it is first weighed, dried at 100 °C and reweighed to find the weight change due to the loss of moisture. Moreover, water-resistance of the samples can be found by immersing the samples in water, drying, and measuring the weight [36]. Measuring the swelling and standard durability of the hydrochar pellets which both require the immersion of the samples in water may also be of use. Hoekman et al. [37] showed that pellets made from hydrochars produced under HTC temperatures as low as 200-275 °C exhibit good durability. Better durability was obtained using higher temperatures within this range. At temperatures below 200 °C, the obtained pellets were considerably less durable and had significant swelling upon water immersion, whereas temperatures above 275°C lead to pellets that were more brittle. More information about palletization of hydrochar can be found in references [38], [39]. Table 2.2. reports some of the mechanical properties of the pellets from raw biomass and hydrochars in literature.

Table 2.2. Effects of HTC on some of the mechanical properties of biomass

<table>
<thead>
<tr>
<th>Feed</th>
<th>HTC condition</th>
<th>Hydrophobicity</th>
<th>Durability (%)</th>
<th>Mass density (kg/m³)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tahoe Mix</td>
<td>No treatment</td>
<td>98.69</td>
<td>99.22</td>
<td>1220</td>
<td>[37]</td>
</tr>
<tr>
<td>Tahoe Mix</td>
<td>225 °C, 30 min</td>
<td></td>
<td></td>
<td>1300</td>
<td>[37]</td>
</tr>
<tr>
<td>Loblolly pine</td>
<td>No treatment</td>
<td>-</td>
<td>97.5</td>
<td>1080</td>
<td>[38]</td>
</tr>
<tr>
<td>Loblolly pine</td>
<td>260 °C, 5 min</td>
<td>-</td>
<td>99.8</td>
<td>1478</td>
<td>[38]</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>No treatment</td>
<td>11</td>
<td>92.2</td>
<td>834</td>
<td>[32], [40]</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>190 °C, 5 min</td>
<td>7.5</td>
<td>93</td>
<td>887</td>
<td>[32], [40]</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>225 °C, 5 min</td>
<td>6.2</td>
<td>94</td>
<td>959</td>
<td>[32], [40]</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>260 °C, 5 min</td>
<td>3.6</td>
<td>88.8</td>
<td>1035</td>
<td>[32], [40]</td>
</tr>
</tbody>
</table>
It should be noted that for a more accurate comparison, the differences in the palettization and durability tests should be considered. The Van Krevelen diagram indicates the O/C and H/C ratio of fuel on the X and Y axis, respectively. HTC process results in an increase in the weight percentage of carbon, and a decrease in both H/C and O/C ratios due to dehydration and decarboxylation respectively, thus making the hydrochar’s characteristics closer to that of coal [41]. The elimination of hydroxyl and carboxyl groups also increases the hydrophobicity. Table 2.3 indicates the characteristics of some of the hydrochars studied before. It should be noted that usually raw lignocellulosic biomass has an HHV between 17-19 MJ/kg, the carbon content of 35-45%, H/C of 1.7-1.9, and O/C of 0.7-0.9.

Table 2.3. Effect of HTC on several feedstock

<table>
<thead>
<tr>
<th>Feed</th>
<th>Temp. (°C)</th>
<th>Time (min)</th>
<th>Solid mass yield (%)</th>
<th>Carbon content (%)</th>
<th>Ash content (%)</th>
<th>HHV (MJ/Kg)</th>
<th>H/C ratio</th>
<th>O/C ratio</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lawn grass</td>
<td>200</td>
<td>180</td>
<td>48</td>
<td>45</td>
<td>-</td>
<td>19</td>
<td>1.5</td>
<td>0.45</td>
<td>[42]</td>
</tr>
<tr>
<td>Lawn grass</td>
<td>240</td>
<td>180</td>
<td>32</td>
<td>55</td>
<td>-</td>
<td>20.8</td>
<td>1.2</td>
<td>0.4</td>
<td>[42]</td>
</tr>
<tr>
<td>Corn husk</td>
<td>260</td>
<td>15</td>
<td>33.2</td>
<td>63.41</td>
<td>3.74</td>
<td>27.66</td>
<td>1.1</td>
<td>0.3</td>
<td>[4]</td>
</tr>
<tr>
<td>Bambu</td>
<td>190</td>
<td>20</td>
<td>48</td>
<td>56.5</td>
<td>-</td>
<td>21</td>
<td>1.27</td>
<td>0.6</td>
<td>[43]</td>
</tr>
<tr>
<td>Cellulose</td>
<td>220</td>
<td>30</td>
<td>58.4</td>
<td>63.5</td>
<td>1.4</td>
<td>26.5</td>
<td>0.9</td>
<td>0.36</td>
<td>[44]</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>260</td>
<td>360</td>
<td>35.7</td>
<td>64.2</td>
<td>10.8</td>
<td>26.2</td>
<td>1.02</td>
<td>0.22</td>
<td>[45]</td>
</tr>
<tr>
<td>Grape pomace</td>
<td>275</td>
<td>30</td>
<td>48</td>
<td>68.32</td>
<td>2.7</td>
<td>28.31</td>
<td>1.01</td>
<td>0.25</td>
<td>[46]</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>180</td>
<td>240</td>
<td>80</td>
<td>53.5</td>
<td>1.75</td>
<td>21.2</td>
<td>1.33</td>
<td>0.55</td>
<td>[47]</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>200</td>
<td>240</td>
<td>65</td>
<td>56.6</td>
<td>0.88</td>
<td>21.4</td>
<td>1.25</td>
<td>0.48</td>
<td>[47]</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>220</td>
<td>240</td>
<td>58</td>
<td>63</td>
<td>1.05</td>
<td>23.9</td>
<td>1.1</td>
<td>0.36</td>
<td>[47]</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>200</td>
<td>120</td>
<td>65</td>
<td>54.9</td>
<td>1.75</td>
<td>21.1</td>
<td>1.29</td>
<td>0.51</td>
<td>[47]</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>200</td>
<td>720</td>
<td>65</td>
<td>58.7</td>
<td>0.83</td>
<td>23.4</td>
<td>1.24</td>
<td>0.25</td>
<td>[47]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>200</td>
<td>360</td>
<td>65</td>
<td>40.81</td>
<td>24.54</td>
<td>15.7</td>
<td>1.3</td>
<td>0.39</td>
<td>[48]</td>
</tr>
<tr>
<td>Saw dust</td>
<td>240</td>
<td>30</td>
<td>49.45</td>
<td>-</td>
<td>0.84</td>
<td>24.5</td>
<td>-</td>
<td>-</td>
<td>[49]</td>
</tr>
<tr>
<td>Loblolly pine</td>
<td>230</td>
<td>120</td>
<td>63.65</td>
<td>-</td>
<td>0.5</td>
<td>22.7</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>Sugarcane Bagasse</td>
<td>175</td>
<td>30</td>
<td>69.6</td>
<td>48.3</td>
<td>-</td>
<td>18</td>
<td>1.41</td>
<td>0.72</td>
<td>[51]</td>
</tr>
<tr>
<td>Sugarcane Bagasse</td>
<td>215</td>
<td>30</td>
<td>67.7</td>
<td>48.4</td>
<td>-</td>
<td>19.7</td>
<td>1.19</td>
<td>0.56</td>
<td>[51]</td>
</tr>
<tr>
<td>Loblolly pine</td>
<td>175</td>
<td>30</td>
<td>77.7</td>
<td>52.2</td>
<td>-</td>
<td>21</td>
<td>1.38</td>
<td>0.58</td>
<td>[51]</td>
</tr>
<tr>
<td>Loblolly pine</td>
<td>215</td>
<td>30</td>
<td>72.4</td>
<td>54.8</td>
<td>-</td>
<td>22.1</td>
<td>1.55</td>
<td>0.54</td>
<td>[51]</td>
</tr>
</tbody>
</table>
The thermochemical decomposition behavior of the hydrochars can be found by TGA. TGA is usually performed by placing a sample of hydrochar in a crucible and heating it from room temperature to around 1000 °C to find percent weight loss as a function of temperature in an inert atmosphere. The reaction zones and activation energies for the decomposition of the hydrochar can be found by TGA data [52].

BET analysis is used to find the specific surface area (m$^2$/g) of the hydrochar based on the amount of adsorption of a standard gas (usually Nitrogen) molecule in the pores of the hydrochar [53]. Additionally, for visualizing the changes in the surface morphology and microstructure of untreated and treated biomass, SEM analysis is used. By varying resolutions of the SEM machine in different conditions, informative visual information can be obtained. For example, it may be seen that the raw material is unstructured and flaky. When the temperature reaches 150 °C, the transformation of the surface morphology of hydrochar appears, and when it reaches around 200 °C, the microspheres formed during carbonization can be visible [54].

**Liquid**

For characterizing the liquid phase product or the process water (PW), the HPLC method is used. This method is based on the difference in absorbance of the PW and a mobile phase by a stationary phase [55]. By introducing standard samples of the possible compounds to the system, they can be identified if they exist in the PW. Table 2.4 indicates the results of HPLC analysis for different kinds of feedstock. Using HPLC analysis, different sugars and related organic compounds of the PW can be distinguished, but some of the compounds may remain undetected. For analysis of small organic acids, IC is more common. Depending on the goals of the study, either of these methods or one of them may be used. For example, Hoekman et al. [31] used IC to analyze organic acids including lactic, acetic, formic, methane sulfonic, glutaric, succinic, malonic, maleic, and oxalic acids and HPLC to quantify selected sugars, furfural, and 5-HMF in the PW of HTC. It should be also noted that TOC analysis and pH tests are typically the primary and most common methods to characterize the PW. TOC analysis is a fast and simple analytical method and allows for detection of all organic and carbon-containing species and regardless of the classification of the compounds, it will report a single total organic carbon value.

In general, it could be concluded that the organic compounds dissolved in the process water mainly include volatile fatty acids (VOCs), specifically formic acid and acetic acid. Moreover, phenols,
furfurals, and their derivatives can be present in lower concentrations [56]. The presence of these compounds is strongly related to the type of feedstock and process conditions.

Table 2.4. HPLC analysis of liquid products for different feeds

<table>
<thead>
<tr>
<th>Feed(s)</th>
<th>Detector</th>
<th>Mobile phase</th>
<th>Identified compounds</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest biomass</td>
<td>UV/RI</td>
<td>Sulphuric acid</td>
<td>Formic acid, Acetic acid, glycolaldehyde, Levoglucosan, Acetol, Glyoxal</td>
<td>[14]</td>
</tr>
<tr>
<td>Wheat straw, poplar wood, pinewood</td>
<td>DA</td>
<td>Water/acetonitrile</td>
<td>Acetic acid, Propionic acid, Furfural, Hydroxy-methyl-furfural, 2-Methoxyphenol, 2-Methylbenzofuran</td>
<td>[57]</td>
</tr>
<tr>
<td>Sugarcane Bagasse, Loblolly pine</td>
<td>RI</td>
<td>Water</td>
<td>5-HMF, furfural, Eluted sugars (sucrose/trehalose, galactose/xylose/mannose/fructose)</td>
<td>[51]</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>RI</td>
<td>Sulphuric Acid</td>
<td>Formic acid, Lactic acid, Furfural, Phenol, Guaiacol, Catechol, Cresol, Fructose, Sucrose, Glucose</td>
<td>[45]</td>
</tr>
<tr>
<td>Loblolly pine</td>
<td>RI</td>
<td>Water/sulphuric acid</td>
<td>acetic acid, formic acid, lactic acid</td>
<td>[58]</td>
</tr>
</tbody>
</table>

Gas

Increasing the process temperature will result in more gaseous products. Decarboxylation is the main reaction responsible for the formation of the gas during the HTC process. In addition to CO$_2$ which usually has a concentration in the range of 70-90%, other gases such as CH$_4$, CO and H$_2$ can be found [28].

As was mentioned in section 2.3.1, after the initial hydrolysis of biomass in subcritical water, many intermediate products such as formic acid and acetic acid will be formed. These compounds then will undergo a decarboxylation process. Considering formic and acetic acid, the decarboxylation reactions are as equations (2.2) and (2.3) respectively.

$$\text{CH}_2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2$$  \hspace{1cm} (2.2)
$$\text{CH}_3\text{COOH} \rightarrow \text{CO}_2 + \text{CH}_4$$  \hspace{1cm} (2.3)
Using standard-state enthalpy of formation and absolute entropy data and considering the reaction temperature as 200 °C, the Gibbs free energy of the reaction ($\Delta G^\circ$) can be found from equation (2.4):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$  \hspace{1cm} (2.4)

Where $T$ (°K) is the temperature at which the reaction occurs and $\Delta H^\circ$ (kJ/mol.°K) and $\Delta S^\circ$ (J/mol.°K) are enthalpy and entropy change of the reaction and can be found by Equations (2.5) and (2.6):

$$\Delta H^\circ = \sum H_f (\text{products}) - \sum H_f (\text{reactants})$$  \hspace{1cm} (2.5)

$$\Delta S^\circ = \sum S^o (\text{products}) - \sum S^o (\text{reactants})$$  \hspace{1cm} (2.6)

Where $H_f$ (kJ/mol.°K) and $S^o$ (J/mol.°K) are the enthalpy of formation and standard entropy.

Using the data available for the standard entropy and enthalpy of formation of the compounds of Equations (2.2) and (2.3), the Gibbs free energies of the reaction are found as -70.43 kJ/mol and -26.22 kJ/mol respectively. These values for $\Delta G^\circ$ shows that the decarboxylation reactions can happen spontaneously and increase carbon dioxide yield during the process.

### 2.3.3. Effect of parameters

#### Temperature

Temperature is the main factor that controls the reactions in HTC and improves biomass conversion efficiency by providing more energy for breaking the intermolecular bonds in the biomass [59], [60]. Considering Tables 2.1 and 2.3, by increasing the temperature, the solid yield will decrease, but gaseous and liquid yields will increase. Yan et al. [61] performed HTC experiments on loblolly pine at 200 and 230 °C and found that the mass yield of hydrochar at 230 °C was approximately 10% lower than that at 200 °C for the same retention time. The reason is that at higher temperatures, a larger portion of biomass (cellulose and lignin) will participate in the reaction while at low temperatures it is mostly hemicellulose that is degraded. For the same reason, the HHV of the hydrochar obtained by HTC at higher temperatures is higher than that obtained at lower temperatures. Knowing that HHV of hemicellulose, cellulose, and lignin are 14.7-18.2, 16.1-19 and 22.3-26.6 MJ/Kg respectively [62], HTC at higher temperatures will remove more cellulose and hemicellulose and result in higher fractions of lignin. It should be noted that the maximum
temperature for HTC is about 350 °C. At higher temperature ranges than HTC, the process is called HTL in which the liquid yield is more considerable than the solid and gas yields. If the temperature increases more (supercritical state), due to the enhancement of radical reactions, the gas yield will be dominant. This process is called HTG or SCWG [63].

**Pressure**

The pressure of the HTC reaction is a variable which depends on the temperature. The liquid state of water has better transport characteristics and can be a good solvent for polar compounds and a catalyst for organic ones. Hence, if most of the water remains in the liquid state, the more efficient hydrothermal conversion is accepted [5]. Minaret and Dutta [4] selected three different pressures above the saturation pressure of water in 260 °C (4692 kPa) to investigate the effect of pressure for HTC of corn residuals. The results indicated that increasing the pressure had little effect on the physical structure of the obtained hydrochar. Little to no effect was observed by SEM images and BET analysis at higher pressure. It was found that at higher pressures, smaller and more distributed particles will exist in the hydrochar which is in line with other research works [64]. Moreover, the pore volume and radius of the hydrochar at higher pressure were increased and decreased respectively. They also showed that higher pressures increased hydrogen content and reduced oxygen content by a small margin. HHV also experienced a slight increase due to an increase in pressure. It is worthy to note that, although the effect of pressure on the products is not considerable at pressures below 30 MPa, if the reactors were able to withstand higher pressures, the impacts could be detected more clearly. Moving to extremely high pressures such as 100 MPa, can enhance graphitization of the hydrochar and increase the HHV significantly.

In many of the lab-scale HTC experiments, the reactor is pressurized prior to the experiment to ensure no vapor is formed. However, an autogenous pressure will also keep most of the water in the liquid state. As on a commercial scale, the small benefits mentioned hereof over-pressurization may be offset by the higher costs of operation, and thus it is expected a commercial HTC reactor would perform under autogenous pressure.

**Time**

Reaction time not only affects the product’s specification but also influences energy consumption. Several retention times can be found in literature, and they range from a few minutes to several hours. It has been reported that higher conversion rates can be achieved at higher retention times
This increment can be seen by an increase in PW production or gaseous products. Moreover, by increasing residence time, better physical properties such as porosity, pore-volume, and surface area can be achieved. Considering the HHV, Zhang et al. performed HTC of corn cob at 250 °C and increased the residence time from 0.5 to 6 hours in small increments. They discovered that the HHV of the hydrochar increased from 24.3 MJ/kg for 0.5 hr to 24.9 MJ/kg for 5 hours. Hence, in comparison to temperature, increasing the residence time does not have a significant effect on the HHV of the hydrochar. To indicate the impacts of reaction time and temperature together, reaction severity (SF) given by Equations (2.7) and (2.8) is defined based on Arrhenius equation [70]:

\[
R_0 = t \cdot e^{(T-100)/14.75} \tag{2.7}
\]

\[
SF = \log R_0 \tag{2.8}
\]

where \( R_0 \) is the reaction ordinate (min), \( t \) is reaction time (min) and \( T \) is the reaction temperature (°C). The severity factor then can be found as the logarithm of the reaction ordinate (\( \log R_0 \)).

This equation assumes a first-order reaction with an Arrhenius temperature dependence. A reference temperature of 100 °C is used. The equation is proposed by Abatzoglou et al. [71]. The concept of severity was first developed by Genlesse and Reuter to find the effect of time and temperature for cracking of the oils. In their study, they showed that a temperature increase of 17 °C halves the time necessary to produce the same results.

\[
SI = 2^{t \cdot e^{[(T-480)/17}}} \tag{2.9}
\]

Where SI is the time-temperature index, \( T \) is the temperature and \( t \) is the time.

Similarly, in hydrothermal carbonization, 14.75 °C is the temperature increase which has an exponential relation with reaction order to produce the same changes in the hydrochar [70].

It is clear from Equation 2.7 that temperature has a higher impact on increasing the reaction severity. As an example, using the equations above, HTC-220 °C-40 min has an SF of 5.14. While increasing the time of this process by 40 min (HTC-220 °C-80 min) will increase the SF to 5.44, increasing the temperature by 40 °C (HTC-260 °C-40 min) increases the SF to 6.31.

As expected, the hydrochar mass yield reduces with an increase in SF, however, the carbon content and HHV increase. Hoekman et al. performed HTC with different times and temperatures on Loblolly pine and indicated that no energy densification occurs at SF values below 4, slight energy
densification occurs at SF values of 4-5, much stronger energy densification occurs at SF values of 5-6, with little additional change at SF above 6. This is in line with the findings of Kim et al. [73] who determined that at severity factors above 4.5, nearly all hemicellulose and some lignin components of the biomass are removed.

**Water: biomass ratio**

The amount of water used in the HTC reaction should be enough to ensure complete dispersion of biomass in the reaction medium, which results in more efficient hydrothermal reactions. However, it should be noted that the water consumption and the required energy for the heating increase with high water to biomass ratios. Sermyagina et al. [74] assessed the effect of a higher amount of water for HTC of coniferous biomass and noted that hydrolysis reactions would intensify and result in higher carbonization rates when more water is used. Also, other studies have indicated that adding more water will have a positive effect on physical characteristics such as surface area and pore volume [75]. On the other hand, lower water: biomass ratio can result in lower residence times, earlier polymerization and higher hydrochar yield [76].

It can be concluded that the amount of water in HTC should be such that it ensures the occurrence of hydrothermal reactions for the whole biomass sample as well as sufficient heat and mass transfer. These factors can also be highly affected by the density, structure, and hydrophobicity of the biomass as well as the design of the reactor such as incorporating a stirrer. The higher the density of the biomass, the higher amount of water is required to ensure sufficient heat and mass transfer. Similarly, if the structure of the biomass is more porous, water can penetrate easier to the pores and less water would be required. More hydrophobic feedstocks require a higher amount of water for hydrothermal reactions. Finally, if the design of the reactor is such that it can ensure the uniform and efficient heat transfer to the whole volume of the reactor, less water would be required. This can be done by incorporating a stirrer in the reactor.

**Catalyst**

The use of catalysts in HTC initially changes the characteristics of the water biomass mixture and results in the desired changes to the process and products. As a result, the selection of the catalyst depends on the final purpose of the user. For example, the formation of hydrochar can be increased by using acid catalysts which facilitate hydrolysis. Conversely, the hydrochar formation can be decreased by applying basic catalysts to enhance the formation of liquid products [68].
Furthermore, catalysts can be used for controlling emissions such as NOx, formed as a result of combustion of biomass or hydrochar. NOx is not only formed due to high-temperature thermal fixation of nitrogen in the combustion air with excess oxygen but also due to the conversion of nitrogen which is chemically bound in the fuel. Therefore, one of the factors that affect the amount of NOx produced, is the fuel N content. The pre-combustion control of NOx is related to the N behavior during the HTC treatment and it has been shown that replacing the pure water with more acidic and basic aqueous solution by using catalysts, can increases the removal of N [77].

Mumme et al. [78] studied the impacts of natural Zeolite in HTC of an agricultural digestate and cellulose. Zeolite increased the energy and carbon content of the obtained hydrochar from the digestate considerably and from cellulose slightly. Moreover, the surface area and pore volume of the products from catalytic HTC were higher. The differences of the obtained results for digestate and zeolite are mainly due to the physical and chemical shielding by the formation of a zeolite layer on organic compounds like cellulose. This is verified by observing that zeolite preserved the cellulose fraction of the digestate. Abd Hamid et al. [79] found that using Lewis acid catalysts (FeCl₂ and FeCl₃) in HTC can lead to complete carbonization at temperatures as low as 200 °C. The effect of catalysts such as KOH, KCl, Na₂CO₃, NH₄Cl and acetic acid on the hydrochar of HTC has been addressed before [58], [80], [81]. Research in this area is not limited to hydrochar. Takeuchi et al. [82] found that by using different acid catalysts and varying their concentrations, the production of desired liquid products including HMF and levulinic acid from glucose can be controlled.

**PW recycling**

In order to decrease water and energy demand, recycling the PW seems necessary. Moreover, the existence of volatile organic compounds in the obtained PW makes its filtration and usage for other processes or discharging to the environment difficult [83]. Reza et al. [84] used a wet air oxidation approach for treating PW from HTC of dairy manure and wastewater. They found that with different oxygen loadings, the treated PW will have lower amounts of total organic carbons and be composed mostly of short-chain organic acids which are not recognized as dangerous compounds for the environment. There are few studies in the literature that deals with PW recycling in a batch reactor. Stemman and Ziegler [85] investigated the characteristics of hydrochar after 19 times of PW recycling for poplar wood and found a higher HHV and
hydrophobicity. However, they did not address the variation of other parameters such as mass yield. Uddin et al. [86] found that by recycling, the mass yield increases by 5-10% but HHV does not change considerably. In another study, Weiner et al. [87] reused the PW of HTC of paper at 200 °C for 16 h, four times. The mass yield increased significantly for the first time and slightly for the next three times. One of the most recent investigations about PW recycling has been performed by Kambo et al. [88]. Firstly, they characterized the PW after HTC and found a high content of organic acids, HMF and total organic carbon in it. Also, it was shown that the acidity of the PW increased with increasing temperature. While the pH of the deionized water was 4.4, it decreased to 3.3, 2.8 and 2.6 after performing HTC at 190, 225 and 260 °C respectively. Then, they reported a 5-10% and 15% increase in mass and energy yield of the obtained hydrochars respectively by recirculation of the PW. They attributed this increment in mass yield to the increased acidity of the PW as acidic HTC has shown to go through different chemical pathways and produce different products [89], [90]. It has been shown in the literature that the repolymerization of the biomass components occurs due to the acidity during the processes. The carbonium ion intermediate, which is formed from structures such as benzyl alcohol in the lignin, originates the polymerization reaction [91]. Hence, by the increased acidity resulting from PW recycling and the presence of the carbonium ion, the polymerization enhances by recycling and increases the production of the hydrochar. Hence, after the first recycle, as the pH does not decrease significantly and the reaction mechanism reaches an equilibrium gradually during recirculation, the hydrochar’s yield and properties do not change considerably.

**Particle Size**

There are few papers in the literature about the effect of biomass particle sizes on other thermochemical processes such as gasification [92], [93] and pyrolysis [94]. Regarding the effect of the feed’s size on HTC, recently a paper was published [95]. As it is expected that lower size particles undergo higher conversions resulting in lower mass yields but with higher calorific values. Reducing the size of the biomass can help the water to penetrate in the feedstock easier, can provide a greater surface area resulting in an increase in the rate of heat and mass transfer and enhance the reaction kinetics, resulting in disintegration and separation of the lignocellulosic matrix. As a result, a greater proportion of the biomass will be converted, thus resulting in lower mass yields. However, due to an increase in decarboxylation and dehydration reactions, the carbon
content of the hydrochars obtained from lower particle sizes would increase resulting in a higher HHV. Regarding the biomass components, it is known that the lignin part of the biomass combines with and reinforces cellulose fibers via physical and chemical bonds in the cell wall as a filling and binding agent. Between hemicellulose, cellulose, and lignin, hemicellulose is the easiest to degrade and lignin is the most difficult one. It has been shown that the lignin portion of the biomass would experience an increase in degradation when the particle sizes decreases [96]. Size reduction can also have the potential for reducing the crystalline characteristic of cellulose [97]. Reduction in crystallinity improves the mass transfer characteristics and facilitates the hydrolysis as the first hydrothermal reaction. Knowing that lignocellulosic biomass like sawdust can have about 50% cellulose and 30% lignin [49], the lignin and cellulose would experience a more effective conversion when the particle size is smaller.

It should be noted that the size reduction increases energy costs. Depending on the feedstock and the extent of potential positive effects of the particle size reduction, the expenses of reducing the sizes may outweigh the benefits. Hence an optimum size should be chosen. Knowing that the particle size reduction increases the HHV and decreases the mass yield, considering the energetic recovery efficiency rather than HHV or mass yield alone may be beneficial. Energetic recovery efficiency is defined by Equation (2.10):

\[
\text{Energetic recovery efficiency} = \text{Hydrochar yield} \times \text{Energy densification} \tag{2.10}
\]

\[
\text{Energy densification} = \frac{\text{HHV of the hydrochar}}{\text{HHV of the feedstock}} \tag{2.11}
\]

2.3.4. Applications

**Power generation**

HTC can remove a portion of the incombustible alkali materials which participate in ash formation during combustion [3]. Co-combustion has been reported with different weight ratios of the biomass to coal [98]. Parshetti and Balasubramanian [99] used a ratio of 50% and defined a combustion characteristic factor (CCF) parameter to address the ease of ignition, firing velocity, and burnout temperature by Equation (2.12):

\[
\text{CCF} = \frac{\left(\frac{dw}{dt}\right)_{\text{max}}}{\left(\frac{dw}{dt}\right)_{\text{mean}}} \frac{\left(\frac{dT}{dt}\right)_{\text{mean}}}{\left(\frac{dT}{dt}\right)_{\text{Th}}} \tag{2.12}
\]
Where \( \frac{dw}{dt}_{\text{max}} \) is the rate of weight loss (% min\(^{-1}\)), \( \frac{dw}{dt}_{\text{mean}} \) is the average burning velocity (% min\(^{-1}\)), \( T_i \) is the ignition temperature (K), and \( T_h \) is the burnout temperature (K).

They indicated that in comparison to raw biomass, the addition of hydrochar improves combustion characteristics due to the removal of a considerable amount of volatile matter and increasing carbon content. Furthermore, their results indicated that combining the hydrochar and coal will result in the decrease of gaseous emission pollutants namely \( \text{CO}_2 \), \( \text{CH}_4 \), \( \text{SO}_2 \), \( \text{NO} \) and \( \text{CO} \). Lin et al. [100] tried to determine how the temperature of the process can affect combustion characteristics of hydrochar fuel from paper sludge. They performed HTC at 180, 210, 240, 270 and 300 °C and found out that performing HTC at 210 °C will result in the highest energetic recovery efficiency.

In addition, their thermogravimetric analysis showed that by increasing the temperature of the process, the ignition combustion of the hydrochar would increase due to a larger reduction in the volatile matter. A similar trend was observed for burnout temperature due to an increase in fixed carbon. Similar research and more detailed results on combustion kinetics of hydrochars are performed by Yang et al. [101], Islam et al. [102] and Gao et al. [103].

The key characteristics that should be targeted to use hydrochar for power generation are not only higher fixed carbon and energy content but also lower ash. The lower the inorganic materials such as Si, K, Na, S, Cl, P, Ca, Mg, and Fe, the cleaner and more efficient combustion. This will result in less fouling, slagging and corrosion in the boilers and less release of toxic emissions to the air [104]. All these characteristics are highly related to the type of feedstock and the process conditions. In terms of the energy content of the hydrochars, it was stated that the higher reaction severity will result in higher energy content, however, the costs of increasing the severity should be considered. Moreover, finer particle size and PW recycling would have positive effects on energy content. Regarding the ash content, it has been shown that increasing the temperature of the HTC process reduces the ash content of the obtained hydrochar. Smith et al. [105] compared the hydrochars obtained from HTC at two different temperatures based on alkali content. It was shown that alkali content almost halved while the temperature was increased from 200 °C to 250 °C.

Soil amendment
Generally, the main expected advantages of using hydrochar for soil amending are nutrient release, mineralization, carbon sequestration, and germination and growth of different crops. Hydrochar can improve soil fertility by absorbing nutrients on its surface and preventing them from being lost by leaching [106]. Also, a higher fertilization efficiency, water holding capacity, and lower N\textsubscript{2}O volatilization emissions caused by animal manure usage are other positive effects of mixing hydrochar with soil [107]. Nitrogen is absorbed as ammonia by plants and used in their growth mechanism. However, they release N\textsubscript{2}O to the atmosphere which is considered as a GHG. Higher amounts of nitrogen also can pollute underground waters by nitrate contamination. Hence, nitrogen levels should be below a certain threshold. Bargmann et al. [108] studied the effect of several hydrochars on soil’s nitrogen dynamics and plant growth. One of their interesting results was that hydrochars with high C: N ratio decreased plant's N content. Hence, one of the key characteristics of a suitable hydrochar is low N content.

Regarding the carbon sequestration, desirable O/C and H/C ratios of the hydrochar have been reported as less than 0.4 and less than 0.6 respectively [109]. Considering the nutrient release, the presence of C, Ca, and other micronutrients, such as Mg, Zn, Cu, Na, and Cl can help the growth of the crops. However, the suitable ranges of these substances should be considered. For example, a high concentration of Na and Cl will increase the electrical conductivity of the soil that can be harmful to the growth of sensitive crops [110]. Another important characteristic of the hydrochar for soil amendment is the porosity. The features like nutrients and water retention capacity are highly dependent on porosity. Nutrients like phosphorus are slowly absorbed by the soil but it can be removed easily by water due to raining or irrigation. The porous structure of hydrochar can hold these nutrients in the soil. Also, the retention of the water by the porous structure can decrease the water demand. The higher the porosity the better water storage [111].

Hence, the hydrochars should be engineered to obtain the characteristics required. In general, it could be said that higher severities of the HTC process or any other method of increasing the carbon content such as finer biomass particle size or PW recycling, would satisfy the carbon sequestration better. Also, using catalysts to activate the hydrochars and increase their porosity can improve water retention.

**Separation**
Hydrochar can be used for separating gases such as carbon dioxide, hydrogen sulfide and nitrogen from flue gas streams [112] or to remove heavy metals and contaminants from water especially if it is activated physically or through acidic/alkaline activation [113]. The HTC process can be modified to produce hydrochar with specific properties depending on the type of contaminants targeted for adsorption. Demir-Cakan et al. [114] determined that HTC of glucose in the presence of acrylic acid will result in hydrochars suitable for removing heavy metals such as Cd$^{2+}$ and Pb$^{2+}$ from the water. Semerciöz et al. [115] activated hydrochar from grapefruit peels with potassium hydroxide and increased their adsorption capacity by 52% to separate Cu$^{2+}$ from water streams. Increasing temperature, pH and the initial Cu$^{2+}$ concentration of the solution had a positive effect on the adsorption capacity. The porosity of the hydrochars is categorized as microporous, mesoporous and macroporous with pore diameters of less than 2 nm, 2-50 nm, and more than 50 nm respectively [116]. The average surface area is reported to be a maximum of 10 m$^2$/g and 150 m$^2$/g for mesoporous and microporous respectively [117]. After breakage of lignocellulosic bonds, the presence of oxygenated functional groups, phenolic, aromatic, and aliphatic compounds, contributes to high porosity (less than 1 nm) in the hydrochar [118] [68]. This can help in absorbance of CO$_2$ as its molecular size is 0.23 nm [119]. Also, the presence of nitrogen compounds increases CO$_2$ capture [120]. Using metal oxide based catalysts has shown to increase the nitrogen-containing compounds [121].

The main considerations for the hydrochar to be used as an adsorbent are surface area, pore-volume, surface charge, and surface functionality [104]. The methods to achieve these characteristics rely on the activation of the hydrochar. The functionality of the hydrochars can be improved by chemicals during or after the process. The increase in the severity of the reaction can increase the surface area and pore volume by removing more volatile matter of the hydrochar. Moreover, as the temperature of the HTC process increases, the pH of the hydrochar decreases. The decreased pH may be suitable for removal of some contamination in water [122].

2.3.5. Types of biomass for HTC

One of the major benefits of using HTC is its high flexibility on the choice of the feedstock. Lignocellulosic biomass is just one broad type of potential feedstocks for HTC. Although the general structure of lignocellulosic biomass can be given by Figure 2.2, the differences of the leaves, softwood, and hardwood should not be disregarded. Their structural difference will result
in different behavior during the HTC process resulting in different yields, energetic and porous properties.

The trees of which the hardwoods can be obtained are deciduous. This means that they lose their leaves which are usually broad and flat in the fall. The trees of softwoods are conifers which means they have needles rather than traditional leaves that can be retained during the winter. It is worthy to note that, although the average hardwood is harder and more durable than the average softwood, there exist hardwoods that are softer than some softwoods. The main differences between hardwood and softwood rely on their structure. Hardwoods have vascular tubes that transfer water throughout. Cross-sectionally, these tubes look like pores that create a wood grain pattern which increases the density and workability of the wood. Instead of pores, softwood has linear tubes for transferring water and nutrients [56]. Regarding the cell substances, while both have a similar percentage of cellulose (around 50%), hardwoods have 20-25% of lignin, but softwoods have 25-35%. Hence, the percentage of hemicellulose in hardwood is higher [10]. Other differences that can be mentioned are hardwood being heavier and denser and softwoods being more fast-growing.

The leaves structure is adopted for efficient photosynthesis and hence they are usually broad to have more surface area for absorbing the light. In a leaf, there are networks of veins to support the structure and transport substances. The outcomes of HTC depend strongly on the type of leaves. Some of them like oak leaves can be categorized as hard biomass due to having hard tissues made of crystalline cellulose scaffolds. By contrast, soft ones such as pine needles do not consist the crystalline cellulose scaffolds. In addition to the hemicellulose, cellulose, and lignin, each of these types has additional components that will interfere in the HTC process. For example, oak leaves have terpenes, tannins and polyphenols and pine needles contain terpenes, oils, and waxes. It has been shown that the hydrochars obtained from soft structures contain hydrophilic and water-dispersible carbonaceous nanoparticles in the size range of 20-200 nm, coexisting with some larger structures. Regarding the HTC process, they first get liquefied and then carbonized. The obtained carbon nanoparticles can find many applications. The hydrochars obtained from hard leaves and tissues have a more continuous phase, that is perforated by a sponge-like, continuous system of nanopores [11].
In addition to the variety of different lignocellulosic biomass, HTC can also be used for wastes such as sewage sludge, animal manure, and municipal solid wastes which have significantly different structures. However, the focus of this research was on lignocellulosic biomass as they are the most abundant biomass source and their structure follows a general pattern.

2.4. Main challenges of HTC

2.4.1. Kinetic model

Kinetic modeling refers to the mathematical description of changes in properties of the system of interest, as a result of changes in operating parameters such as time and temperature [123]. The order, interactions, and severities of the reactions in HTC are complex and different from one feed to another which makes modeling the degradation kinetics of HTC difficult.

The first step in modeling the kinetics is collecting data (hydrochar yields regarding the temperature and time) by performing HTC experiments. Afterward, unknown data which are kinetic parameters (order of reaction, activation energy, and frequency factor) are found by considering the Arrhenius equation through multilinear regression as a fitting data method or other mathematical and statistical approaches using Matlab or other programming software [124]–[126].

By collecting experimental data of the reaction time versus the hydrochar yield, it has been seen that the reaction rates can be split into two stages (Figure 2.3). The rate of the first stage is significantly faster than the second one. It can be said that activation energy for the first stage is smaller than the second one and the process can be modeled with better accuracy if two stages are considered. Hence, for the kinetics of HTC, a modified model which was first proposed by Prins et al. [127] for torrefaction can be used (Figure 2.3). The feed (compound A) will be converted to an intermediate solid (compound B) after separation of the first volatile stream (V1), and then another volatile stream (V2) will be released to give the final product (compound C).
Figure 2.3: Schematic of kinetic modeling of HTC based on research on torrefaction

All the four processes shown by Figure 2.3 can be explained by a simple first-order Arrhenius Equation (2.13):

\[ k_i = A_i \times \exp \left( \frac{-E_{a_i}}{R \times T(t)} \right) \]

Due to the complexity of the differential Equation (2.13), it is usually assumed that the reaction temperature remains constant with respect to time. In other words, the heating up period of the HTC experiment is not usually considered. Alvarez-Murillo et al. [128] for the first time, considered both the heating up process and reaction temperature for the kinetic modeling. Afterward, the overall process can be described by the differential equations (2.14-2.18):

\[
\begin{align*}
\frac{\partial M_A}{\partial t} &= -k_1 \times M_A \\
\frac{\partial M_B}{\partial t} &= (k_1 \times M_A) - (k_2 \times M_B) \\
\frac{\partial M_C}{\partial t} &= -k_2 \times M_B \\
\frac{\partial M_{v1}}{\partial t} &= k_{v1} \times M_A \\
\frac{\partial M_{v2}}{\partial t} &= k_{v2} \times M_B
\end{align*}
\]

\[ K_1, \text{ and } K_2 \text{ can be defined by equations (2.19) and (2.20):} \]

\[ K_1 = k_1 + k_{v1} \]

\[ K_2 = k_2 \]
\[ K_2 = k_2 + k_{v2} \]  

(2.20)

Activation energy and the pre-exponential factor of the equations above can be found from literature as initial guesses. Then by solving the equations simultaneously, the mass yield for each phase can be found. If the values are in accordance with the experiments, the initial guesses are correct, but if not, they should be altered. As there are eight guesses, specific algorithms such as a trust-region-reflective algorithm or genetic algorithm can be used [129].

The other method to predict the reactions is using DOE techniques to find an interrelationship among the process factors (e.g. temperature, time, water: biomass ratio) and the desired response value (e.g. hydrochar yield, HHV, energetic recovery efficiency). For this purpose, based on the experimental conditions a DOE method should be chosen (e.g. factorial design, split-plot design, Latin square design). The ANOVA table of all the independent parameters that may have an effect versus the responses of the parameter of interest will show which parameters and interactions have significant effects and will lead to finding a statistical linear or non-linear equation. For instance, Kambo [10] found the following relationships for mass yield and HHV of the hydrochars with respect to time, temperature and water to biomass ratio (R).

\[
\text{Mass yield} = 170.5 - (0.44 \times T) - (0.3 \times t) - (0.51 \times R) \tag{2.21}
\]

\[
\text{HHV} = 5.79 - (0.07 \times T) + (0.41 \times t) - (0.12 \times R) + (2.12 \times 10^{-3} \times T \times t) - (7.8 \times 10^{-6} \times T \times R) + (7.2 \times 10^{-3} \times t \times R) \tag{2.22}
\]

It is worthy to note that the empirical equations in the literature are mainly used for the same feedstocks. For instance, applying the Equation (2.21) for the corn husk studied in reference [4] results in 49.9% of hydrochar yield which is 16% lower than what has been reported by the study. For loblolly pine and Miscanthus of references [50] and [47], the difference of the predicted mass yields and the experimental results are 0.5% and 5% respectively. The values obtained from Equation (2.22) for the HHV of these references are also not reliable due to the large difference with the experimentally measured data.

There are other empirical models in the literature (e.g. [130], [131]) where second-order models are presented to express the changes in mass yield with respect to the same process factors.
Although this method of prediction can provide useful information, their application is restricted to similar feedstock and experimental conditions.

The main problems with the available kinetic models are as follows:

- The kinetic models found are specific to the type of feedstock. In other words, there is no generic model by which kinetic behavior of any feedstock under HTC conditions can be studied. This is because each lignocellulosic biomass has a different percentage of hemicellulose, cellulose, and lignin.
- The temperature of the process is assumed to be constant and the models do not consider the changes with time and space.

Figure 2.4 shows the suggested steps for finding a more accurate and generic kinetic model. As it is shown, firstly pure hemicellulose (xylan), cellulose and lignin (kraft) should be provided. HTC on each of these feedstocks at different temperatures and times will result in the initial required information for kinetic modeling (temperature, time, and mass yields) (step 1). To have a more accurate model, a reliable heat transfer model should be incorporated (step 2). This step will be discussed in further detail in section 2.5.2. Next, the kinetic model for each of these fundamental feedstocks will be developed (step 3). Afterward, a similar kinetic model for some ordinary feedstock (e.g., sawdust, Miscanthus, sugarcane Bagasse) with known percentages of hemicellulose, cellulose and lignin will be performed (step 4). Then by using statistical methods a correlation between the amount of feedstock and the kinetics of a general feedstock will be found (step 5). The aim is predicting the kinetics of any kind of lignocellulosic biomass by entering its composition to the model.

It should be noted that the use of this method to define a generic model for biomass is quite difficult. The behavior of the biomass constituents alone is different from their behavior in the wood structure. One reason can be due to the longer times required for the water to reach the reactive compounds. Hence, the interactions of the constituents should be taken into account and will probably add to the complexity of the model. These interactions can be found when the mathematical model is compared with the results of real biomass. Déniel et al. [132] considered the HTL on the model compounds of food processing residues to understand the fundamentals of the process. They also mentioned that due to the complex composition of each feedstock, a global reaction scheme, including kinetic aspects, would be very difficult to achieve. Hence, they focused on some of the pure compounds including fiber (mainly cellulose, hemicellulose, and lignin),
proteins, lipids and some mixtures such as protein and sugars to find the interactions. They concluded that the interaction reactions between molecules of different natures impact the yield and quality of the products.

**Figure 2.4. The suggested steps for finding a generic kinetic model**

**2.4.2. Heat transfer model**

The economic feasibility of HTC is highly dependent on its energy consumption. Idris O’Sule [133] studied heat transfer mechanisms of torrefaction and developed a mathematical solution for the process by assuming the samples as a cylinder with known dimensions and properties. He used COMSOL Multiphysics to obtain heat generation profiles. A similar investigation was performed by Babu and Chaurasia [134] for the pyrolysis of solid particles. However, regarding heat transfer of HTC, there is no comprehensive study in the literature. Although the thermal conductivities of different biomass samples were determined by Ogedengbe [135], the main difficulty with modeling heat transfer in HTC is determining the mechanisms inside the reactor during the process. The properties of biomass such as density, porosity, and permeability change due to unexplored chemical reactions [75]. Álvarez-Murillo et al. [128] modeled HTC heat transfer for cellulose by assuming the reaction to involve just water. They considered an HTC batch reactor receiving heat from an enclosed oven and modeled radiation and convection using COMSOL Multiphysics. Baratieri et al. [136] developed a lumped capacitance method for heat transfer of HTC, but they also considered that the
reactor had only water in it. Also, the aim of these investigations was to find the temperature profile inside the reactor for use in kinetic modeling and not to calculate the energy requirement for biomass treatment.

The unique and complex properties of the water-biomass mixture which change with time, temperature, and unknown reactions during the process make modeling heat and mass transfer difficult. Having information about the reactions is important because if a reaction is exothermic, the heating source can be partially or completely turned off in some stages, and a great amount of energy can be saved. HTC is known as an overall exothermic process. However, the initial reaction of HTC (hydrolysis) is endothermic [137]. Hence the activation energy for hydrolysis should be provided by external heating. At higher temperatures and longer times, the reactions of sugars like monosaccharides (which is an exothermic reaction) dominate the process gradually [138], hence there is a chance to compensate for the heat loss during the process by promoting exothermic reactions. However, to date, no HTC process has been maintained without external energy supply [139], [140].

Yan et al. [30] tried to find the heat of reaction for HTC of loblolly pine. Firstly, to find the heat of formation for the feed, they considered Equation (2.23) for the combustion where x and y can be determined from the ultimate analysis.

\[
CH_xO_y(s) + \left(1 + \frac{x}{4} - \frac{y}{2}\right)O_2(g) \xrightarrow{\text{yields}} CO_2(g) + \left(\frac{x}{2}\right)H_2O(l)
\]  

(2.23)

The heat of combustion (ΔHc) of biomass solids was found with a bomb calorimeter, then by knowing the heat of formation of the products in Equation (2.23), the heat of formation of biomass was determined. Then, the heat of reaction was calculated from the difference between the heats of formation of the products and reactants. For simplification, it was assumed that the gas product is all CO₂ and the PW is all acetic acid. Finally, by having enthalpies of the input and output streams, the heat of reaction was obtained.

Their results also indicated that by increasing the temperature of the process, the reaction becomes less endothermic. Cuvilas et al. [141] performed HTC with long residence times and found the overall process to be exothermic. Table 2.5 indicates the energy balance of their work. The heat of reactions has also been reported as 500-800 kJ/kg [141]–[143].
### Table 2.5. Energy balance data of HTC

<table>
<thead>
<tr>
<th>Treatment conditions</th>
<th>Wood</th>
<th>Water</th>
<th>Acid</th>
<th>Pretreated wood</th>
<th>Acetic acid</th>
<th>Precipitates</th>
<th>Water</th>
<th>Acid</th>
<th>Gas</th>
<th>Heat of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 °C, 150 min</td>
<td>-0.183</td>
<td>-256.14</td>
<td>-</td>
<td>-1.79</td>
<td>0.0</td>
<td>-0.11</td>
<td>-256.14</td>
<td>-</td>
<td>-0.81</td>
<td>-2.53</td>
</tr>
<tr>
<td>180 °C, 350 min</td>
<td>-0.183</td>
<td>-256.14</td>
<td>-</td>
<td>-2.29</td>
<td>0.0</td>
<td>-0.17</td>
<td>-256.30</td>
<td>-</td>
<td>-1.03</td>
<td>-3.47</td>
</tr>
</tbody>
</table>

The main aim of the energy modeling of HTC is to make the process less energy-intensive. Hence, the time and amount of energy released during the exothermic reactions should be found. The process should then be tailored in a way that increases and facilitates the exothermic reactions. Unfortunately, none of these aims have been achieved to date. The main problems with the available energy models are as follows:

- The analytical models in the literature do not consider the medium of HTC properly. The porous nature of the biomass and the changes in the characteristics of biomass and water mixture with time and increasing temperature have not been considered.
- The enthalpy of the reaction found by the enthalpy of the formation only provides a general overview of the whole energy balance of the process. Again, the time and amount of energy released by exothermic reactions cannot be found by this method.

The following experimental, analytical and simulation procedure can help to address the above gaps:

a) Finding the enthalpy of the whole process:

The procedure to achieve this goal is depicted in Figure 2.5. As can be seen, the empirical formula of the feed and the hydrochar can be obtained by determining the values of C, H, N, S, and O through ultimate analysis. Moreover, the composition of gas and liquid by-products can be distinguished after characterization by GC and HPLC respectively. The general equation shown in the last step of Figure 2.5 can be used to find the enthalpy of the whole process based on Equation 2.24.

\[
\Delta H_{\text{reaction}} = \sum \Delta H_f^{\text{products}} - \sum \Delta H_f^{\text{reactants}}
\]  

(2.24)

The unknown parameters in this equation are enthalpies of formation of the hydrochar and the feed. To find these unknown parameters, the combustion equation can be written and by performing bomb calorimetry experiments for both the feed and hydrochar and finding the
enthalpy of the combustion from them (HHV), enthalpy of formation of the feed and hydrochar can be found.

It should be mentioned that the ash content is not considered due to the fact that it is incombustible. Moreover, the amount of ash is usually small, and the composition of ash varies depending on the feedstock. Hence, in the equations given in Figure 2.5, the biomass and the hydrochar are considered as ash-free.

![Diagram of HTC process]

**Figure 2.5. The procedure to find the enthalpy of the HTC process**

b) Finding the heat loss during the process by using the governing equations:

The general heat loss equation from the reactor can be written based on the conditions of the experiment and geometry of the reactor. Assuming a cylindrical shape for the reactor and using an electrical circuit model and a lumped system as shown by Figure 2.6, the heat loss can be obtained from Equation (2.25) and (26). Another assumption is that the reactor is equipped with a stirrer. The stirrer ensures maintenance of the same temperature throughout the whole reactor. These equations can provide reasonable information regarding the heat loss during the operation of the reactor in the set temperature of the process. This is especially true in the case of developing the equations for a continuous reactor (where the temperature of the reactor remains constant instead of raising from the environment
temperature), the heat loss shows the amount of energy required by exothermic reactions of HTC to sustain the process without external energy requirement.

\[ Q = \frac{T_{\infty 1} - T_{\infty 2}}{R_{\text{tot}}} \]  

(2.25)

\[ R_{\text{tot}} = R_{\text{conv1}} + R_{\text{cyl}} + R_{\text{conv2}} = \frac{1}{(2 \pi r_1 L)h_1} + \frac{\ln(r_2/r_1)}{2 n L K} + \frac{1}{(2 \pi r_2 L)h_2} \]  

(2.26)

Figure 2.6. Modeling the heat loss during hydrothermal carbonization

c) Experimental and computational method to find energy consumption during HTC:

During the HTC experiment, a temperature controller is usually incorporated to maintain the temperature of the reactor at the desired setpoint. An energy analyzer can be also incorporated into the setup in which by measuring the current and the voltage, the energy provided by the external heater during the heating up and constant temperature stage can be monitored (Figure 2.7, part A).

In addition to this experimental approach, COMSOL Multiphysics software provides appropriate tools for modeling the HTC process (Figure 2.7, part B). The simulation can be performed by combining heat transfer in porous media and chemical reactions module. The required information for the chemical reaction module can be obtained from the kinetic modeling explained previously. Moreover, the required data for heat transfer in porous media, such as permeability and porosity, can be obtained experimentally or from the literature [144].

The model developed by COMSOL software can be verified by the experimental approach to finding energy consumption, once it is verified the simulation can be used to assess the effects of varying different parameters to find out the best operational conditions for performing HTC in terms of energy consumption (Figure 2.7, part C). Moreover, after verification of the model,
the energy released by the exothermic reaction may be found by taking the difference between the model with and without chemical reactions module activated.

![Figure 2.7. Energy modeling of HTC experiment: A) schematic of the experimental setup to find energy consumption, B) Schematic of modeling in COMSOL Multiphysics, C) Schematic of Comparison of the experiment and model’s energy consumption](image)

The experimental, simulation and modeling parts can ensure accurate information about energy consumption. The next step would be to manipulating the reactions and tracking their effect on energy consumption. For example, the reactions of glucose after the initial hydrolysis of the biomass is the main exothermic reaction in the process [138]. It is known that the hydrolysis of glucose takes place quickly during HTC and can produce a wide range of products such as acetic acid and HMF [145]. Considering HMF production, glucose goes under an isomerization and produces fructose. It has been reported that this reaction in the presence of extra water becomes -3.87 kcal/mol exothermic [146]. After this, the obtained fructose will proceed through dehydration to produce HMF which is also reported to be 33.1 kcal/mol exothermic [147]. When the amount of glucose is increased in the process, the released energy can be absorbed and can reduce the overall energy requirement of the process.
Also adding a portion of hydrogen peroxide may help the process to be more energy sustained as it will decompose to oxygen and water in an exothermic reaction [148].

2.4.3. Continuous reactor

A continuous reactor will clearly reduce the required energy and water consumption rate for hydrochar production significantly. One of the main challenges is to design a pump that can introduce the feed (or the feed and water mixture) against the high pressure of the reactor. Although few corporations in Europe, namely INGELIA [149], BIOKOL [150], ANTACO [151], AVALON Industries [152], and SUNCOAL [153] have claimed to perform HTC at an industrial scale, there is no detail of their pumping system and process.

Hoekman et al. [70] used a modified twin-screw extruder (TSE) as a reactor to perform fully continuous and fast (with a reaction time of 20-30 sec) HTC process. The raw biomass was rapidly taken from one side and the hydrochar was delivered on the other side. The TSE reactor was equipped with hot water injection and band heaters between the inlet and outlet. As the reaction time was too low, the concept of severity factor was used to compare the obtained hydrochars with those produced in batch reactors. Although the physical characteristics of the obtained hydrochars from the TSE reactor were different from the hydrochars from the batch reactor, they had similar energy densification and palettization behavior. It is also worthy to note that the hydrochars obtained from this TSE system were then used by Liu et al. [154] in a life cycle study. They mixed these hydrochars with coal fines and determined that electricity generated from the co-formed products has significantly lower GHG intensity and slightly higher life cycle energy use than coal-generated electricity. In another work, Hoekman et al. [155] designed a large scale semi-continuous reactor using an auger-equipped tubular reactor system that conveys raw biomass trough a zone of hot pressurized water and deposits the solid hydrochar product in an accumulator maintained at a lower temperature and showed that the hydrochars obtained by this method are similar to the ones obtained by small-batch reactors.

Stemann and Ziegler [142] proposed a simulation of a continuous HTC system. They used EES software to calculate energy consumption and determined that energy consumption decreases considerably due to recycling. According to their model, biomass consisting of 60% moisture is preheated to 100 °C. Next, in a lock hopper, it is mixed with steam coming from a flash tank downstream of the process. Afterward, hot water and an external steam generator will help it reach
the HTC required temperature (210 °C) and biomass to water ratio (1:7). The heat of reaction was found by differential scanning calorimetry as 500 kJ/kg (exothermic). However, due to utilizing the PW in the reactor, it can be as high as 800 kJ/kg. Their study showed that energy demand is related to both heat of reaction and water content. To perform the HTC without major energy demand, the heat of reaction should meet the sensible energy needed to heat up the biomass with certain water content. Another industrial-scale simulation was proposed by Ching [143]. They assumed heat of reaction as 500 kJ/kg from Stemann and Ziegler [142] and other design assumptions such as water to biomass ratio 1:1 from Erlach and Tsatsaronis [156]. Then they calculated the plant's total energy consumption including steam for heating the reactor and electricity for pelletizing and chipping the biomass feed. By performing sensitivity analysis for the heat of reaction, they found out if the heat of reaction varies between 600 kJ/kg and 400 kJ/kg, the amount of required steam for heating and keeping the reactor at the desired temperature would be 0.7 ton/h and 1.6 ton/h respectively.

Continuous reactors need a more elaborated system to convey the feedstock as a stream while maintaining high pressure in the reactor. This can be performed with a hydraulic or screw pump or a system of locks where the biomass is brought step by step to a higher pressure [76]. Also, mixing the biomass with higher amounts of water and chopping the biomass to finer particles can help the pumping. An alternative is to use several reactors in parallel (semi-continuous) such that the feedstock can always be fed in one of the reactors without waiting for the previous process to cool down and the pressurized warm PW of the previous reactor can enter the next reactor.

2.4.4. Large-scale studies

The integration of HTC with other renewable/conventional processes cannot only make the whole process more energy-efficient, but it can also present more desired products. Reza et al. [157] combined AD with HTC. They used wet digestate from an AD in the thermophilic situation (50-60 °C) as feed for an HTC process and showed that this results in a greater amount of energy per 1 kg of raw biomass (20% and 60% more than HTC alone and AD alone respectively). A reverse process may be a good idea for future studies. The alkali content of the hydrochar reduces considerably compared to raw biomass. This alkali content is dissolved in the PW. The pH of the PW is between 2.7 and 3.5 and has a high load dissolved TOC content (50 to 100 mg/L). By applying this PW into an AD system, hydrolysis, which is the limiting factor for AD system, can take place faster. Alkali metal in the PW is also expected to contribute to more biogas yield.
In another research study, Reza et al. [38] indicated that a mixture of 10% hydrochar from HTC and 90% char from torrefaction would result in a durable pellet with higher energy density. This is because the hydrochar fills the void spaces and makes solid bridges between torrefied biochar particles. HTC can also be combined with pyrolysis and gasification [158], [159]. Liu et al. [160] showed its combination with pyrolysis improves the adsorption capacity for contaminants like Cr$^{6+}$, Cd$^{2+}$, and atrazine. They pyrolyzed hydrochars at 350, 500 and 650 °C for 2 hours and named it pyro-hydrochar. They indicated that while the surface area of the hydrochar was slightly higher than that of biochar (obtained from pyrolysis solely), the surface area and the durability of pyro-hydrochar was significantly higher than both.

As no real industrial scale HTC system is in operation, there exists a considerable gap in the economic evaluation of HTC systems. Results in literature are based on many simplifications and scale-up of experimental results. By increasing the amount of products, the production costs can be reduced. This is because the cost of the reactors, pumps and other equipment does not increase with the same factor of the size of the equipment [161]. According to Vogel [162], the relationship between capacity increase, and a change in investment cost can be given by Equation (2.28):

$$I_2 = I_1 \left( \frac{\text{C}_{\text{ap}2}}{\text{C}_{\text{ap}1}} \right)^{0.67}$$

(2.28)

However, finding accurate factors like the exponential constant here (0.67) and other operational changes requires more research.

To consider environmental and economic evaluations, LCA can be applied to compare HTC systems with other alternative treatments. Benavente et al. [163] used LCA to compare environmental impacts associated with treating olive mill waste by HTC with aerobic composting, AD, and incineration. Their research considered the consumption and production of materials and energy, together with the pollutant emissions generated over the entire life cycle of each treatment approach. They also discussed the avoided emissions due to not burning conventional fuel for energy production. Upstream processes, such as waste collection and transport, were not investigated as they were assumed to be the same for all scenarios. The functional unit of their study was considered as one kg of fresh feedstock (olive mill waste). However, to have a more accurate model regarding the HTC-based scenario they should have considered a de-ashing system and the impacts of burying ash are the landfills. Nine of the impact categories assessed in their
work were climate change, human toxicity (cancer and non-cancer effect), photochemical ozone formation, terrestrial acidification and eutrophication, freshwater eutrophication and ecotoxicity, and marine eutrophication. Their results indicated that if HTC is accompanied by subsequent hydrochar combustion for energy recovery, it can be more environmentally advantageous than composting and AD. The HTC scenario of their study was composed of the main HTC reactor, rotary dryer for drying the obtained hydrochars and a combustor combusting a combination of hydrochars and auxiliary materials. The emission to the air occurs in all steps, and the emission to water occurs by the disposal of the PW in the HTC and combustion of hydrochars due to their alkali contents. The main reason for the environmental superiority of incineration with energy recovery to HTC was the toxic materials released to the environment by the PW of HTC which indicates the significance of the PW management in the HTC process and its recovery.

Reißmann et al. [164] reviewed the technological, economic and environmental aspects of hydrothermal processes with pyrolysis and torrefaction for dealing with biogenic residues with high moisture content in Germany and concluded that the hydrothermal process has better technical performance and lower climate footprints. The main reason for having less environmental impacts is that hydrochar contains less alkali content than biochar (solid product of other thermochemical processes) and is rich in nutrients [165]. They considered energy efficiencies and global warming as their comparison criteria. Depending on the feedstock, the boundary of the LCA studies may change but generally, it starts with collecting the waste from the farms, supplying to the plant, performing the HTC process on it, pelletizing the hydrochar, transportation and incineration in a plant and then utilizing the heat. A similar LCA was performed by Ahamed et al. [166] comparing a combined HTC system and oil refinery system (for the transesterification of PW with acid treatment which produces glycerol and bio-diesel) with an incineration system and an AD one. One tonne of food waste, system boundary including collection, processing, waste conversion and disposal of food waste and three outputs namely electrical energy (using biodiesel with 35% efficiency), hydrochar and glycerol were considered in their study. Their LCA results showed the proposed HTC and refinery combination is more favorable when the oil content of the feedstock is more than 5%. In general, it could be concluded that the main issues to be considered in a comprehensive LCA work regarding hydrochar utilization, is defining the perimeter of the scenarios which does not neglect the challenges. Such a perimeter not only includes the preparation
and transformation steps but also the post-treatment issues caused by HTC such as PW management, slagging and fouling due to the ash content, and high costs of the required energy.

The combination of the biomass recovery processes based on a circular economy concept (where there is no waste) needs more investigation. As there is presently no industrial-scale HTC process, finding real data for the HTC seems difficult. Using the modeling and experimental investigation proposed in the previous sections can provide more realistic data outputs. Then, different process integrations can be proposed based on the feedstock and desired products and they can be compared using LCA studies. Figure 2.8 proposes a combination of HTC, AD, and gasification. The PW from HTC can be harmful to the environment if it is disposed, on the other hand, due to its acidic nature, it can facilitate hydrolysis which is the limiting reaction in the AD. On the other hand, the gas released during the HTC is mostly CO₂ which can go to gasification to produce syngas.

![Figure 2.8. Schematic of a combination of HTC, AD, and gasification](image)

In order to perform an LCA study, all of the influential process units should be considered separately. Figure 2.9 proposes the combination of HTC with transesterification and Rankine and Brayton power cycles. This proposed system is mainly useful when the PW contains more oil so that transesterification can provide biodiesel to be used in a gas turbine [166]. As shown in Figure 2.9, the wet hydrochar is utilized in a Rankine cycle after it is dried in the drier. The boiler combusts the dry hydrochar and provides superheated steam for the steam turbine. The steam
expands in the blades of the turbine, generating power and delivering low-pressure steam to the condenser. The condenser converts the steam to water which is pumped to the boiler again. Before reaching the boiler, the water passes from heat exchanger 2 to reduce the boiler’s duty. On the other hand, the liquid by-product of the HT goes to a transesterification system and by using methanol and NaOH, glycerin and biodiesel are produced [167]. The biodiesel then enters the combustion chamber of a Brayton cycle and its combustion reaction with the compressed air rotates the gas turbine blades and provides more electricity. The gas turbine’s exhaust is at 560 °C, hence, before releasing this hot stream to the atmosphere, its energy is transferred to the HTC process water by the heat exchanger 1 and to the Rankine cycle process water by the heat exchanger 2. Wherever electricity was required, the power generated by the steam turbine is used. However, it should be mentioned that this is an example of how systems can be integrated and reduce energy costs and environmental impacts. In commercial scales, the whole system proposed by Figure 2.9 could be complex and some of the components may not be there.

![Diagram](image)

**Figure 2.9. Proposed system by integrating HTC, transesterification, and Rankine and Bryton cycles**

### 2.5. Conclusion

Converting high moisture content biomass to valuable products is more justified with HTC than any other thermochemical process. This study aimed to provide a review of the current knowledge and challenges for finding the barriers and suggest how to tackle them. It was found that the
barriers are mainly due to the lack of knowledge about the chemistry and heat and mass transfer mechanisms during the process and lack of reliable data from continuous HTC reactors. Experimental setups together with numerical approaches were clearly explained to model heat and mass transfer mechanisms in the porous structure of the biomass inside the reactor and find the chemical reactions and kinetics of the process. Once reliable knowledge is obtained, the models should be developed for new continuous reactors and industrial designs. By finding data from these modelings and designs, HTC’s potentials for combination with other processes (e.g., torrefaction, AD, gasification) can be assessed. Then the best operational conditions and optimizations regarding energy and exergy efficiencies and economic and environmental aspects can be found. Finally, LCA can help to evaluate and compare several scenarios of renewable process integrations and answer the concerns of decision-makers and society for finding the best options for energy supply in the future.
Chapter 3. Effects of process water recycling and particle size on HTC

This chapter discusses the effects of recyclability of process water and particle size on the hydrochar. To investigate the water recycling effect, HTC experiments were performed on sawdust using recycled water in a batch reactor. Moreover, to study the particle size effect, 3 small reactors containing specific particle sizes of biomass were placed in a larger reactor simultaneously to ensure consistency in the process condition. The results showed that the process water recycling increases the mass yield (MY) and higher heating value (HHV) of the solid product by 12% and 2% respectively after the first recycle. Physicochemical properties of hydrochar were studied by carrying out the ultimate and proximate, HHV, thermogravimetric (TGA) coupled with Fourier transform infrared spectroscopy (FTIR), and Brunauer–Emmett–Teller (BET) analysis and results are discussed. Regarding the particle size study, higher mass yield, a decrease in heating value and an increase in total organic carbon in the process water were observed by increasing the particle size.


3.1. Introduction

Although HTC’s ability to convert biomass to fuel has been proven by several in-lab experiments, there are other important factors that should be considered for an industrial process including the effect of water recycling and particle size. Regarding the effects of water recycling, there are few studies in the literature that deal with only the mass yield and HHV of the process. None of the mentioned studies have investigated the effects of recycling water in different HTC temperatures and residence times. Moreover, this study characterizes the products with TGA, FTIR, and BET to find the reasons for the changes in the quantity and quality of the hydrochar. The experiments were performed in three different set temperatures and three different residence times. The ultimate and proximate analyses, HHV test, pH test, TOC test, TGA, FTIR, and BET analysis were performed to have a comprehensive comparison of the products.
The second part of this chapter deals with the effects of the biomass particle size in HTC. Three smaller reactors containing feeds with different particle sizes were placed in a larger reactor to ensure that the process conditions for all particles remained the same. The differences in the mass yield and HHV were then discussed. Moreover, TOC testing of the process waters was performed.

3.2. Material and methods

3.2.1. Feed
Sawdust produced from hardwood and green bean were used to run all HTC experiments for the water recycling and particle size experiments.

3.2.2. HTC tests
Regarding the study on recycling effects on the product, the HTC experiments were conducted using the Parr 600 mL series 4560 mini reactor equipped with magnetic stirrer. Approximately 20 g of sawdust was used for each experiment. The HTC setup is shown in Figure 3.1.

![Figure 3.1. Hydrothermal carbonization setup](image)

A dry biomass to water mass ratio of 1:10 was used for the water recycling study. The mixture of sawdust and water was stirred until the sawdust was completely submerged in the water. For the first run, 200 ml of water was used and for each recycle, the process water obtained from the previous experiment (around 150 ml) was mixed with enough water to make the ratio 1:10 again. As some portion of the process water was in the wet hydrochar and another portion was separated
for characterization tests, 150 ml was selected for the next cycles to ensure consistency. After holding the reactor at the process’ set temperatures (180, 220 and 260 °C) for the determined residence time (40, 80 and 120 min), the reactor was immediately submerged into iced water until the temperature decreased to below 30 °C. The liquid–hydrochar mixture was removed from the reactor and separated using filter paper. The solid sample was placed inside a tin crucible and left open to room conditions to dry for approximately 48 h. Hydrochar yield was calculated as the ratio of the weight of obtained hydrochar to the initial biomass weight. Similarly, the gas yield can be found as the mass of the gas produced per unit mass of dry raw biomass sample, and the liquid yield can be calculated by the difference. Figure 3.2. shows the method for recycling the process water used in this experiment.

![Schematic of experimental design for studying the recycling effect on HTC](image_url)

Figure 3.2. Schematic of experimental design for studying the recycling effect on HTC

For investigating the effects of particle size on the product, the feeds used were green bean and hardwood. The raw feeds with three different mean particle size ranges were placed in the three small reactors. The size of the vessels was considered based on the size of the main reactor, so the three vessels would fit in the main reactor. The sizes of the particles were selected such that the particles could easily be submerged in the water and fit in the vessels. The vessels were 1.27 cm × 7.62 cm stainless steel pipe nipples each with two 1.27 cm stainless steel end caps. The vessels were then placed in a 600 ml Parr reactor which contained water and was stirred. The Parr reactor acted as an enclosure to ensure the process conditions were consistent for each small reactor. Figure 3.3. depicts the designed experimental setup for studying the effect of particle size. After a residence time of 40 min in the pre-set temperature of 200 °C, the 3 reactors were cooled down, the hydrochar was separated using filter paper and the mass yield was measured.
3.2.3. Product characterization

The proximate analysis for determining ash, volatile matter (VM), and fixed carbon (FC) content was performed as per ASTM standards [33] on the obtained hydrochar. The ultimate analysis was conducted using a Flash 2000 Elemental Analyzer (Thermo Fisher Scientific, Waltham, MA, USA). The HHV and thermal decomposition of the raw and hydrothermally carbonized samples were analyzed via IKA-C200 bomb calorimeter (IKA Works, Wilmington, NC, USA) and TGA coupled with FTIR spectrometer (TGA: SDT-Q600, FTIR: Thermo Scientific Nicolet 6700, TA instruments-Waters LLC, New Castle, USA). For the TGA and FTIR test, approximately 12 mg of a sample was used in each test and each test was repeated 4 times. The analysis done was with a heating rate of 10 °C /min and the temperature was increased from room temperature to approximately 750 °C. The selected temperature and heating rate are similar to the ones used in a previous hydrochar TGA experiment [168] [63]. Since the TGA was used to simulate combustion, the air was used as the oxidizer at a flow rate of 50 mL/min. The TGA experiments were also repeated with nitrogen to investigate the presence of volatile matter in the porous structure of the hydrochar.

Regarding the BET analysis, the samples were placed in the degassing module of a Quantachrome 4200e Surface Area and Pore Analyzer. Afterwards, the hydrochar was prepared for the analysis by vacuum degassing at room temperature for about 3 hours. All the samples were reweighed to account for the mass loss (if any) and then placed in the analyzer for multipoint BET analysis. The
tubes were calibrated before each run using helium gas. The adsorption isotherm was recorded for relative pressures ranging from $0.05 < P/P_0 < 0.97$ using nitrogen as an adsorbate gas at $-196 \, ^\circ\text{C}$. The surface area was then calculated using the BET region of the adsorption isotherm where the cross-sectional area of the condensed N2 gas was assumed to be 16.2Å. The specific area was estimated for relative pressure values between 0.05 and 0.35. The average pore size and total pore volume were also analyzed, they were estimated from the adsorption branch of the isotherm and at the closest relative pressure to unity ($> 0.96$). In addition, the pH values of the liquid samples were measured using a digital probe meter (Thermo Orion pH meter, model 210 A). A Shimadzu TOC-ASI analyzer was used to measure the TOC of the process water.

TOC was determined by a TOC meter (Model: TOC-VCPN, Shimadzu Corporation, Kyoto, Japan). In the TOC analyzer, the organic carbon is converted to carbon dioxide by an oxidizing gas (oxygen) and is measured by an infrared detector. The inorganic forms of carbon (IC: usually carbonate and bicarbonate) are separated from the total organic value by subtraction.

### 3.3. Results and discussion

#### 3.3.1. Process water recycling effect

The results on the variation in mass yield, pH of the process water, HHV, densification factor (ED), and energy recovery factor (ERF) with recycling for different temperatures and residence times are presented in Table 3.1. The experimental runs were replicated three times to ensure reproducibility. Equations 3.1 and 3.2 are used to find the energy densification factor and energy recovery efficiency.

\[
\text{Energy densification} = \frac{\text{HHV of hydrochar}}{\text{HHV of feedstock}} \quad (3.1)
\]

\[
\text{Energetic recovery efficiency} = \text{Hydrochar yield} \times \text{Energy densification} \quad (3.2)
\]

It should be noted that, in addition to the hydrochar yield, the gas yield was found as approximately 5-10% and hence the liquid yield can be found from the difference of 100% and the summation of solid and gas yields. Recycling was found to have a positive effect on the mass yield of the hydrochar. However, this positive increment is more significant after the first recycle. The average of the increment of the hydrochar mass yield after the first recycle for all cases is 10.26 % while the second recycle increases the mass yield of the first recycle by an average of only 1.65%. Weiner et al. [87] found a similar trend for the mass yield increase of paper feedstock. Their first and second recycles resulted in 14% and 2% increase in the initial and first mass yields respectively.
Table 3.1. Variation of hydrochar mass yield, pH, HHV, densification factor (ED), and energy recovery factor (ERF) with recycling for different temperatures and residence times

<table>
<thead>
<tr>
<th></th>
<th>pH of PW</th>
<th>MY (%)</th>
<th>HHV (MJ/kg)</th>
<th>ED (%)</th>
<th>MY (%)</th>
<th>HHV (MJ/kg)</th>
<th>ED (%)</th>
<th>MY (%)</th>
<th>HHV (MJ/kg)</th>
<th>ED (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No recycle</td>
<td>3.55</td>
<td>64.65</td>
<td>19.51</td>
<td>1.07</td>
<td>69.19</td>
<td>63.20</td>
<td>21.03</td>
<td>1.15</td>
<td>72.91</td>
<td>1.25</td>
</tr>
<tr>
<td>One recycle</td>
<td>3.54</td>
<td>71.18</td>
<td>19.86</td>
<td>1.09</td>
<td>77.54</td>
<td>68.02</td>
<td>21.40</td>
<td>1.17</td>
<td>79.85</td>
<td>1.27</td>
</tr>
<tr>
<td>Two recycle</td>
<td>3.53</td>
<td>71.91</td>
<td>20.25</td>
<td>1.11</td>
<td>79.88</td>
<td>71.34</td>
<td>21.81</td>
<td>1.20</td>
<td>85.35</td>
<td>1.30</td>
</tr>
<tr>
<td>220 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No recycle</td>
<td>2.81</td>
<td>50</td>
<td>24.12</td>
<td>1.32</td>
<td>66.15</td>
<td>49.08</td>
<td>24.69</td>
<td>1.35</td>
<td>66.47</td>
<td>47.14</td>
</tr>
<tr>
<td>One recycle</td>
<td>2.79</td>
<td>62</td>
<td>24.56</td>
<td>1.35</td>
<td>83.53</td>
<td>61.95</td>
<td>25.08</td>
<td>1.38</td>
<td>85.23</td>
<td>59.14</td>
</tr>
<tr>
<td>Two recycle</td>
<td>2.78</td>
<td>63.41</td>
<td>24.6</td>
<td>1.35</td>
<td>85.57</td>
<td>63.37</td>
<td>25.47</td>
<td>1.40</td>
<td>88.54</td>
<td>60.53</td>
</tr>
<tr>
<td>260 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No recycle</td>
<td>2.65</td>
<td>44.85</td>
<td>25.38</td>
<td>1.39</td>
<td>62.44</td>
<td>43.79</td>
<td>25.71</td>
<td>1.41</td>
<td>61.76</td>
<td>42.90</td>
</tr>
<tr>
<td>One recycle</td>
<td>2.63</td>
<td>56.65</td>
<td>25.78</td>
<td>1.41</td>
<td>80.11</td>
<td>56.69</td>
<td>26.17</td>
<td>1.44</td>
<td>81.38</td>
<td>55.40</td>
</tr>
<tr>
<td>Two recycle</td>
<td>2.62</td>
<td>59.54</td>
<td>26.29</td>
<td>1.44</td>
<td>85.86</td>
<td>57.57</td>
<td>26.50</td>
<td>1.45</td>
<td>83.69</td>
<td>55.94</td>
</tr>
</tbody>
</table>

It can be observed that recycling at 180 °C resulted in the lowest mass yield increase. When the HTC process temperature was changed from 180 to 220 °C, a significant increase in percentage mass yield change was observed. However, when the temperature was increased from 220 to 260 °C, the percentage of mass yield change was smaller.

Regarding the HHV, a slight increase was observed after each recycle. For instance, while the HHV of the raw sawdust was measured as 18.23 MJ/kg, the HHV of the hydrochars from HTC-220 °C-40 min without recycle, with one recycle and with two recycles were 24.12 MJ/kg, 24.56 MJ/kg and 24.6 MJ/kg respectively. This represents a 1.82% increase after one recycle and a 2% increase after two recycles in comparison to no recycle. The difference between the mass yield increase and HHV increase may be attributed to the carbon content of the added material by recycling to the initial hydrochar not being significantly higher.

The simultaneous increase in mass yield and HHV of the hydrochars by recycling leads to a more significant enhancement of the energy recovery efficiency defined by Eq. 2. While the energy recovery efficiency without recycling was 66.17%, it was increased by around 9.33% and 10.53% after the first and the second recycles for hydrochars obtained from HTC-220 °C-40 min. Hence, increasing the number of recycling cycles appears to result in higher energy recovery efficiency.

To discuss the reasons for observing these changes, the changes in process water should be considered. It has been shown that acidity can have a positive effect on the mass yield in
hydrothermal reactions [10]. Hence, the acidity of the process water obtained from HTC experiments performed at different temperatures and recycle numbers for 40 min of residence time was measured and reported in Table 3.2. The pH of the process water was decreased when the process temperature was increased. HTC-180 °C dropped the pH of the deionized water to around 3.5 while the value for HTC at 220 and 260 °C are around 2.8 and 2.6 respectively. With the same temperature rise of 40 °C, the reduction in the pH value was more significant when the temperature was increased from 180 °C to 220 °C (21%) than from 220 °C to 240 °C (5%). By increasing the temperature, more acidic components will be formed in the process water due to the decomposition and depolymerization reactions of biomass, hence the pH decreases with the temperature [88]. The process water obtained at 260 °C had the highest acidity and hence it increased the mass yield by recycling more than the process water obtained from HTC at lower temperatures could. As Reza et al. [45] showed, with an increase of the feedwater pH, there is an increase in the sugar that remains in the liquid product. When this liquid is used in the next cycle as the process water, it leads to an increase in mass yield. This is likely due to the fact that during HTC, glucose starts reacting at 160 °C through intermolecular condensation and consequently aromatization (carbonization) occurs, and thus the mass yield of glucose increases with increasing temperature up to 260 °C [41]. Another explanation may be the precipitation of lignin by acidic solution [169]. When the pH is lower, the lignin precipitates, resulting in an increase in mass yield. Moreover, as shown in Table 3.2, the pH slightly decreases by recycling.

The acidity of the process water of HTC-220 °C is only slightly lower than that of HTC-260 °C. As a result, the mass yield enhancement due to the acidity of the process water at 220 °C is also very close to that of 260 °C. Moreover, the residence time does not influence the mass yield increment remarkably and as it has been shown in other works, process temperature plays a more important role in characteristics and the mass yield of the hydrochar than the residence time [170][40].

To have a better sense of how the temperature and the residence time can affect the process, severity factor (SF) was calculated. SF is defined based on Arrhenius equation [70], [137] as shown in Equations 3.3 and 3.4:

\[
R_0 = t_0 \cdot e^{\left(T-100\right)/14.75}
\]

\[
SF = \log R_0
\]
where $R_0$ is the reaction ordinate (min), $t$ is reaction time (min) and $T$ is the reaction temperature (°C). The severity factor then can be found as the logarithm of the reaction ordinate ($\log R_0$).

Figure 3.4. shows the relationship between SF for a different time and temperature conditions with the higher heating value of obtained hydrochars. It is clear from the graph that increasing temperature and time will increase the severity factor resulting in higher HHV. The highest slope in increasing the energy content can be assigned to severity factors between 4.3 to 5.3. Severity factor beyond 5.8 does not show significant increase in the heating value of the hydrochar. However, in some applications the little improvement in the HHV may be important and it may be optimal to increase the severity to values around 7. Hence, considering the increase in mass yield as shown in Table 3.1. after recycling and severity factor, HTC-220 °C-40 min has been chosen as optimum and has been used for further analysis.

![Figure 3.4. Energy content as a function of severity factor](image)

Table 3.2 shows the TOC analysis of the process water and the proximate and ultimate analysis of hydrochar.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>TOC of process water (g/L)</th>
<th>Ultimate analysis (wt%)</th>
<th>Proximate analysis (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Raw</td>
<td>-</td>
<td>49.22</td>
<td>6.10</td>
</tr>
<tr>
<td>No recycle</td>
<td>23.61</td>
<td>62.78</td>
<td>5.49</td>
</tr>
<tr>
<td>1 recycle</td>
<td>30.73</td>
<td>64.13</td>
<td>5.24</td>
</tr>
<tr>
<td>2 recycles</td>
<td>34.13</td>
<td>65.23</td>
<td>5.14</td>
</tr>
</tbody>
</table>
The TOC analysis shows the total carbon in the process water from all organics and carbon-containing compounds. From Table 3.2, it can be seen that the TOC increases with increase in recycle, however the increase is more significant for first recycle as compared to second recycle. The first recycle increases the TOC of the process water from 23.61 g/L to 30.73 g/L, while the subsequent recycle increases the TOC by only 3.40 g/L. The increase in TOC of the process water can be attributed to the release of acidic and suspended compounds in the process water, which would be added in each recycle. However, the increase of TOC is less by the second recycle in comparison to the first one. As proposed by Uddin et al. [86], in each recycle, the organic soluble is produced which results in higher TOC, but at the same time, they can be deposited on the porous structure of the hydrochar which can result on smaller increase in TOC. If these rates become equal, there will be an equilibrium concentration and hence, the TOC will remain constant with more recycles. Kambo et al. [88] conducted the HPLC analysis of the process water with five recycles. They reported the major component in the process water to be acetic acid, levulinic acid, glycolic acid, formic acid, and HMF. They found difference between the calculated organic carbon and the measured organic carbon, which indicated the presence of other organic carbon not detected by HPLC. Furthermore, they also found insignificant changes in TOC of process water after third recycle.

Table 3.3 also shows the ultimate and proximate analysis of the raw sample and obtained hydrochars. As expected, the carbon content in hydrochar increases from 49.22% to 65.23 with second recycle. Similarly, the oxygen concentration reduces from 44.57% to 29.44%. Subsequently, fixed carbon increased from 17.80% To 38.68%. It has been shown that the acidity of HTC process water facilitates decarboxylation and dehydration reactions, which increases the carbon content of the hydrochar [26].

About 2 mg of dried and ground sample was needed for each test. The analyzer gave the result for carbon (C), hydrogen (H), nitrogen (N) and sulfur(S) content, and the oxygen content must be calculated using Equation 3.5 below.

$$O\% = 100\% - C\% - H\% - N\% - S\% - ASH\%$$ \hspace{1cm} (3.5)

Like the HHV test, the ultimate and proximate tests were performed 3 times on each hydrochar and the average values were considered.
Table 3.3 compares the results of other HTC studies with the result from the current work. Given the variability in the type of biomass and the operating condition, the results could not be exactly compared, however, the results from the present study are in the range of values obtained from other works.

Table 3.3. Results of HTC on sawdust in literature

<table>
<thead>
<tr>
<th>Ref</th>
<th>Feed</th>
<th>Temp. (°C)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>HHV (MJ/kg)</th>
<th>Carbon content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>Hardwood Sawdust</td>
<td>220</td>
<td>40</td>
<td>50.01</td>
<td>24.12</td>
<td>62.78</td>
</tr>
<tr>
<td>[171]</td>
<td>Sawdust</td>
<td>200</td>
<td>30</td>
<td>54.44</td>
<td>22.91</td>
<td>-</td>
</tr>
<tr>
<td>[172]</td>
<td>Eucalyptus Sawdust</td>
<td>250</td>
<td>120</td>
<td>40</td>
<td>-</td>
<td>69.70</td>
</tr>
<tr>
<td>[173]</td>
<td>Bamboo sawdust</td>
<td>210</td>
<td>60</td>
<td>68.50</td>
<td>22.40</td>
<td>52</td>
</tr>
<tr>
<td>[174]</td>
<td>Eucalyptus sawdust</td>
<td>220</td>
<td>60</td>
<td>48.50</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

To have a better understanding of the effects of recycling on the obtained hydrochars, TGA and BET analyses were performed. The air TGA and DTG graphs of the raw sample and the hydrochars prepared by HTC-220 °C-40 min, with and without recycle are presented in Figure 3.5a and 3.5b respectively. The heating rate and the airflow rate are 10 °C/min and 50 ml/min respectively. It is shown that the samples obtained from HTC with recycled process water are different in terms of combustion characteristics after around 330 °C and they need slightly lower temperatures to undergo complete thermal decomposition. Compared to the raw biomass, the hydrochars are more stable and until around 330 °C. The weight loss of the hydrochars can be categorized into three zones. The first zone occurs from 30 °C to 290 °C for all of the hydrochars. This zone is attributed to the dehydration and release of volatile compounds during the devolatilization process. The dehydration zone is similar for all the hydrochars irrespective of the recycle number. The second zone starts from 290 °C for all hydrochars. The temperature intervals are 290-455 °C, 290-440 °C for one recycle and 290-420 °C for two recycles. The weight losses are very close for all hydrochars but the ones with recycle need a lower temperature to finish this stage. This zone is related to the initial combustion of hydrochar where the whole hemicellulose part is degraded and leads to the rapid decline in weight loss. In addition, the cellulose and lignin are slightly degraded in this zone. Finally, in the third zone, the char undergoes combustion until the final yield is reached at the burnout temperature. In this zone, the remaining hydrochar from zone 2, which is mostly cellulose and lignin, is further oxidized. The weight loss in zone 3 depends on the reactivity of the substrate.
components. By looking at zone 3, one can see that the hydrochar with no recycle has a slightly sharper slope than the chars with recycle. This means that the additional mass yield of the chars with recycle is not as reactive as the initial substrate. Future studies can focus on the type of material which is added to the hydrochars by recycling and investigate their degradation behavior solely.

Another TGA experiment was performed by using nitrogen instead of air but at the same test condition (heating rate and nitrogen flow rate were 10 C/min and 50 ml/min respectively). The nitrogen TGA for all the hydrochars was very similar to each other as illustrated in Figure 3.6. Considering the raw biomass, the figure shows that weight loss occurs in three stages. The first and the third stage are minor, while the second stage shows the major weight loss. The initial weight loss can be due to the moisture content at around 100 °C, as well as the release of organic matters, which occurs at 270 °C for the raw sample and 330 °C for the hydrochars. After this minor stage, a major decomposition starts in all the samples. For the raw sample, from 270 to 370 °C, the weight dropped by 62% (to 24% of the initial weight). For the hydrochars, the major weight loss stage started at 330 °C and ended around 690 °C, which decreased the weight from 92 to 54% of the original sample’s weight. The third stage occurs after this where the slope of the weight loss decreased significantly for both raw sample and hydrochars. From Figure 3.6 it can be established that the nitrogen TGA cannot reveal the effect of recycling on the weight loss. This may be mainly because most of the weight obtained by recycling is lost during the TGA with nitrogen.

Figure 3.5. a. Air TGA, b. Weight percentage graphs obtained by Air TGA of hydrochars prepared by HTC-220 °C-40 min
Figure 3.6. Nitrogen TGA results of hydrochar prepared by HTC-220 °C-40 min

Figure 3.7. FTIR Plots of a) raw sample and hydrochars prepared by HTC-220 °C-40 min: b) without recycle, c) with one recycle and d) with two recycles
The main peaks shown in the figures are in the region between 2400-2240 cm\(^{-1}\) and 736-605 cm\(^{-1}\), both showing the evolution of CO\(_2\). Other than this gas, small peaks can be seen at times less than 20 min and bands 3750-3350 cm\(^{-1}\), showing the release of moisture. The main reason for having small absorbance (around 0.2) in this region might be due to drying of the samples before the FTIR analysis. Moreover, small bands could be seen in the region between 2240-2060 cm\(^{-1}\) corresponding to evolution of CO which can be mainly due to incomplete combustion.

To further study the porous structure of the obtained hydrochars, the BET analysis was conducted for the three samples. An isotherm analysis with nitrogen adsorption-desorption at -196 °C has been performed. The isotherms of the samples are depicted in Figure 3.8.

![Figure 3.8. Nitrogen adsorption-desorption isotherms for different hydrochars obtained by HTC-220 °C-40 min](image_url)

The pore structures of all samples appear to be of Type III isotherm. It can be seen from the graph that recycling does not have a significant effect on adsorption and the obtained hydrochars do not have considerable porosity.

3.3.2. Particle size effect

In this section, the temperature of the HTC process was set as 200 °C and the water to biomass ratio was 1:12. Furthermore, not only woody biomass was studied but also bean was used as the feedstock. The reason for selecting a lower temperature in comparison to the previous experiments was to ensure that the temperature is not too high to degrade the biomass thoroughly regardless of its type and size. Also, the advantage of choosing bean was the ease of chopping and providing
the required sizes. However, as bean can easily be dissolved at higher temperatures and pressures, the particle size effect was also studied by choosing hardwood.

The obtained mass yields, HHV and energy recovery efficiency of the HTC for the beans and the hardwood are reported in Table 3.4 with respect to the sizes of the particles. It is worthwhile to note that the HTC and the characterization tests have been repeated three times and the average values have been reported. The HHV of the raw samples was measured as 18.23 and 19.6 MJ/kg for the hardwood and bean respectively.

Table 3.4. Hydrochar mass yield, HHV and energy recovery efficiency of different sizes of green bean and hardwood by HTC at 200 °C and 40 min

<table>
<thead>
<tr>
<th>Raw biomass particle size</th>
<th>Green bean</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>Hardwood</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass yield (%)</td>
<td>HHV (MJ/kg)</td>
<td>Energy recovery efficiency (%)</td>
<td>Mass yield (%)</td>
<td>HHV (MJ/kg)</td>
<td>Energy recovery efficiency (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.25-3 cm</td>
<td>61.7</td>
<td>22.21</td>
<td>75.17</td>
<td>60</td>
<td>23.57</td>
<td>72.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.75-1.25 cm</td>
<td>60.9</td>
<td>22.42</td>
<td>74.89</td>
<td>58.9</td>
<td>23.73</td>
<td>71.31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Less than 0.25 cm</td>
<td>60.2</td>
<td>22.65</td>
<td>74.8</td>
<td>57.3</td>
<td>24.13</td>
<td>70.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As it is presented in Table 3.4, HTC of smaller particle sizes resulted in a lower mass yield and higher HHV. Generally, by reducing the sizes of the biomass, water can penetrate in the pores of the biomass easier and a greater surface area would be available to enhance the rate of heat and mass transfer and consequently, the reaction kinetics resulting in disintegration and separation of the lignocellulosic matrix. A greater proportion of the biomass is converted, thus resulting in lower mass yields. However, due to an increase in decarboxylation and dehydration reactions, the carbon content of the hydrochars obtained from lower particle sizes would increase resulting in a higher HHV. The lignin part of the biomass combines with and reinforces cellulose fibers via physical and chemical bonds in the cell wall as a filling and binding agent. Between hemicellulose, cellulose, and lignin, hemicellulose is the easiest to degrade and lignin is the most difficult one. It has been shown that the lignin portion of the biomass would experience an increase in degradation when the particle sizes decrease [96]. Size reduction can also have the potential for reducing the crystalline characteristic of cellulose [97]. Reduction in crystallinity improves the mass transfer characteristics and facilitates the hydrolysis as the first hydrothermal reaction. Knowing that lignocellulosic biomass like sawdust can have about 50% cellulose and 30% lignin [49], the lignin
and cellulose would experience a more effective conversion when the particle size is smaller. The purpose of particle size reduction is to increase the particle’s accessibility for achieving higher degrees of hydrothermal reactions. However, the size reduction can increase energy costs. To have better judgment for selecting the particle size for an HTC system, it is useful to also consider the energy recovery efficiency rather than HHV or mass yield alone. Larger biomass particles may have slightly higher energy recovery factor values than smaller particles. For example, although the HHV of the hydrochar obtained from HTC of hardwood of particle sizes 1.25-3 cm is 2.37% lower than that obtained from hardwood with less than 0.25 cm particle sizes, its energy recovery efficiency is 2.28% higher. These results can suggest performing a study prior to hydrothermally carbonizing of any kind of biomass to find what size can be more efficient and economically justified.

Comparing the bean and hardwood hydrochars in Table 3.4, it can be observed that changes in the particle size affect the mass yield and HHV more in HTC of hardwood than HTC of the bean. For example, the difference in the mass yields of samples obtained from HTC of the largest and smallest particles is 2.49% and 4.71% for the bean and hardwood respectively. Similarly, the percentage difference in the HHV of the hydrochar obtained from the feed with smallest and largest sizes is 1.98% and 2.37% for bean and the hardwood respectively. This can be explained by the fact that the bean has a softer texture, dissolves more easily in water and undergoes more severe reactions than hardwood. These differences show the importance of conducting research for finding the optimum size of different kinds of biomass prior to performing the HTC process.

The TOC test for the process water of the hardwood samples was conducted. The results indicate that for the large (1.25-3 cm), medium (0.75-1.25 cm), and small samples (less than 0.25 cm), the total organic carbons are 25.75 g/L, 23.8 g/L and 20.44 g/L respectively as demonstrated in Figure 3.9. The values obtained here are in the range of the ones observed by Kambo [10]. By having finer raw biomass, a higher proportion of carbon would be retained in the hydrochar than in the liquid. In other words, the results of this TOC test are in accordance with the results reported in Table 3.4. Higher HHV of the hydrochars was obtained from HTC of smaller particle sizes, indicating higher carbon contents in the hydrochar. At the same time, the process water obtained from HTC of smaller particle sizes has less carbon content.
Figure 3.9. TOC results of the obtained process water from HTC of different particle sizes of hardwood at 200 °C and 40 min

3.4. Conclusion

The effects of recycling the process water and particle sizes of the feed on the hydrothermal carbonization of biomass were investigated in this research. Both issues can greatly affect the technical and economic feasibility of industrial HTC systems. To achieve the goals of this study, several tests, designs, and feedstocks were used. Regarding the process water recycling effect, it is obvious that the demand for freshwater and energy for heating up the water can be significantly reduced by recycling. This investigation compared the hydrochar obtained from sawdust with no recycling, one recycle and two recycles of the process water. The mass yields obtained from HTC tests in three different residence times (40 min, 80 min, and 120 min) and three different temperatures (180 °C, 220 °C, and 260 °C) showed that the process temperature has a more significant effect on the mass yield than the residence time. The mass yield change was attributed to the changes in the reaction condition due to recycling the process water with a lower pH compared to the initial water. It was also observed that acidity increases due to an increase in the temperature of the process. However, the difference in acidity of the process water at 220 °C and 260 °C was not significant. Hence, the HTC process at 220 °C and 40 mins was selected for investigating the effects of recycling water. It was shown that recycling not only increases the mass yield but also increases the HHV and consequently enhances the energy recovery efficiency. While the energy recovery efficiency without any recycling was 66.17%, it increased to 80.17% and 82% after the first and the second recycles respectively. These changes were attributed to the increase in the acidity of the process water from recycling, which facilitates the decarboxylation and dehydration reactions. However, after two cycles the reactions reached equilibrium. In addition, TGA, FTIR, and BET analysis were performed on the selected samples.
The TGA indicated that the combustion behavior of the hydrochars obtained with recycled water is different which is due to the addition of materials with less reactivity than the usual hydrochar. This may be a result of the presence of tiny solid particles in the process water obtained from the previous HTC cycle, which accumulates in the pores of the hydrochar. Moreover, BET analysis showed that recycling does not have a significant effect on adsorption and the obtained hydrochars do not have considerable porosity.

Considering the effect of particle size in HTC, it was shown that although the energy content of the hydrochars from large biomass (1.25-3 cm) was 2.37% less than that of small biomass (less than 0.25 cm), the energy recovery efficiency of the larger particle was 2.28% more. This is due to the higher mass yield experienced in large particles (4.71% higher than small particles). In addition, the TOC test of the process waters indicated that the liquid products obtained from HTC of larger biomass are more enriched in carbon. Smaller particle sizes undergo higher conversion due to an increase in the surface area for heat and mass transfer resulting in hydrochars with higher amounts of carbon. However, it may not necessarily mean energy recovery efficiency can be enhanced, and research should be done on material by material basis before performing HTC on a large scale, to find the optimum particle sizes.

In conclusion, the results of this research emphasize the importance of process water recovery during HTC and the necessity of understanding the particle size effect on the products and performance of HTC systems, especially when it comes to industrial scales. The impacts of these issues were shown by different tests and experimental designs. However, depending on the purpose of the HTC process, more research on these factors can be conducted before designing the process.
Chapter 4. Prediction of hydrothermal carbonization with respect to the biomass components and severity factor

The goal of this chapter is to establish a link between the composition of biomass and the expected hydrochar from HTC. Based on the experimental design found from response surface methodology, the biomass components, namely pure cellulose, hemicellulose, and lignin, were submitted in different combinations into 39 HTC experiments with severity factors (SF) of 3.83, 5.01, and 6.19. Using the experimental data, an attempt was then made to predict the mass yield (MY), higher heating value (HHV), carbon content (C%), and energy recovery factor (ERF) of the hydrochars according to the biomass composition and the process severity. The results revealed that the interactions between the biomass components do not have a major effect on the hydrochar characteristics whereas the interaction between cellulose and SF is the most significant. Moreover, it was shown that after the lignin content, the hemicellulose content has the highest positive impact on HHV and C% of the hydrochar. An optimization study showed that with a focus on minimizing the SF, while the HHV is maximized, biomass with a cellulose content of 40%, hemicellulose of 35%, and lignin of 25%, under the severity of 4.41 will be the most suitable case for HTC treatment. Finally, a comparison between the predictions and the experimental data in the literature suggests that the proposed equations can provide a good evaluation of the HTC of several biomass feedstocks especially when the amount of ash and extractives are low.


4.1. Introduction

The delay in the commercialization of HTC is mainly due to unknown reaction orders, interactions, and intensities. In addition, the kinetics of the reactions are feed dependent and this hinders the development of a reliable model that can predict the amount and quality of the hydrochar after performing HTC at given conditions. In other words, the results found in each study are specific to the type of feedstock used in the study. Hence, there is no generic model to predict the behavior of different feedstock under HTC conditions.
Studying the HTC of the main biomass components (cellulose, hemicellulose, and lignin) can help to find generic equations and rules for the prediction of the products based on their fiber composition and the severity of the process. Hence, finding acceptable predictions of the MY, HHV and C% with respect to the biomass composition and the SF of the HTC are the main goals of the current chapter. The approach to achieve the goal of this research consists of first performing HTC on the synthesized biomass samples consisting of one, two, and three biomass components at different severities and then finding the MY, HHV and C% of the obtained hydrochars. The next step is finding a correlation based on the obtained information using response surface methodology in Design Expert Version 11. The possible interactions by mixing the biomass components are also considered. Finally, the results are compared with hydrochars of real biomass and the possible errors are explained.

It should be noted that the model proposed in this chapter, can be considered only for the second generation of biomass because instead of cellulose, hemicellulose, and lignin, the third generation of biomass consists of lipid, protein, and carbohydrates [63], [175]. In addition to this, the presence of ash and water extractives are not considered in this model. This is mainly due to their low content in most of the lignocellulosic biomass, their variable composition and to prevent the complexity of the model.

4.2. Material and methods

4.2.1. Feed

Pure hemicellulose (H2125), cellulose (435236), and alkali lignin (370959) were purchased from Sigma-Aldrich Canada Co. as the model components of the biomass. These materials were then mixed or used solely in several HTC experiments (Figure 4.1-a). The characteristics of the purchased materials are given in Table 4.1. The ultimate, proximate, and HHV analyses that are explained in the coming sections were utilized to find the data in Table 4.1.

Table 4.1. Ultimate, proximate, and HHV analysis of the biomass main components

<table>
<thead>
<tr>
<th>Component</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>Ash</th>
<th>Volatile matter</th>
<th>Fixed carbon</th>
<th>HHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>42.1</td>
<td>5.8</td>
<td>0.3</td>
<td>0.1</td>
<td>51.7</td>
<td>0</td>
<td>93.6</td>
<td>6.4</td>
<td>15.80</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>41.9</td>
<td>5.2</td>
<td>0.3</td>
<td>0</td>
<td>51.1</td>
<td>1.5</td>
<td>76.7</td>
<td>21.8</td>
<td>15.02</td>
</tr>
<tr>
<td>Lignin</td>
<td>62.3</td>
<td>4.7</td>
<td>0.5</td>
<td>2</td>
<td>28.1</td>
<td>2.4</td>
<td>47.2</td>
<td>50.4</td>
<td>25.60</td>
</tr>
</tbody>
</table>
4.2.2. HTC experiments

The HTC experiments were conducted using a Parr one-liter series 4571 high-pressure reactor equipped with a precise temperature controller and a cooling loop (Figure 4.1-c).

![Figure 4.1. Experimental setup: a) the pure and synthesized feedstock, b) The three small reactors placed in the main reactor, c) The main reactor equipped with temperature controller and cooling loop](image)

Considering the high number of the required experiments, and to save time without jeopardizing the consistency and accuracy of the results, three small vessels were built (Figure 4.1-b). The size of the vessels was considered based on the size of the main reactor, such that the three vessels would fit in the main reactor. The information about the development and the size of these vessels can be found in another paper [95]. Each of the vessels in each run contains 2 g of pure or mixed sample. Hence, the weight of each component can vary in a range of 0-2 g in the vessels. 10 ml of water was added and stirred in each vessel (1:5 biomass to water ratio). The temperatures of the HTC experiments were set as 180, 220 and 250 °C and the residence time was 30 min for all experiments. Three replicates were performed for each experimental data point. The number of experiments and the percentage of each component is explained in Section 4.2.5. As the real biomass starts degradation from around 180 °C, and this research tries to model the HTC of real biomass by mixing the biomass components, this temperature was selected as the minimum temperature of the experiments. Moreover, 250 °C was selected as the maximum temperature due to the reactor limitations. In addition, as residence time has a considerably lower impact than temperature, and its effects can be addressed by the severity factor, a relatively low time was considered (30 min).

Based on the selected time and temperature of each experiment, severity factor (SF) is defined by Equations (4.1) and (4.2) [70], [137]:

$$R_0 = t \cdot e^{(T-100)/14.75}$$

(4.1)
\[
\text{SF} = \log R_0 \tag{4.2}
\]

where \( R_0 \) is the reaction ordinate (min), \( t \) is reaction time (min) and \( T \) is the reaction temperature (°C).

To indicate the impacts of reaction time and temperature together, reaction severity (SF) given by Equations (4.3) and (4.4) is defined based on Arrhenius equation [70]:

\[
R_0 = t \cdot e^{(T-100)/14.75} \tag{4.3}
\]

\[
\text{SF} = \log R_0 \tag{4.4}
\]

where \( R_0 \) is the reaction ordinate (min), \( t \) is reaction time (min) and \( T \) is the reaction temperature (°C). The severity factor then can be found as the logarithm of the reaction ordinate (\( \log R_0 \)).

The severity factor is widely used by the researchers for describing the hydrothermal processes. This equation assumes a first-order reaction with an Arrhenius temperature dependence. Abatzoglou et al. [71] proposed this equation using a reference temperature of 100 °C, however, the concept of severity was originally introduced by Genlesse and Reuter [72] to address the effects of time and temperature for cracking of the oils. They indicated that a temperature rise of 17 °C halves the required time for getting the same results.

\[
\text{SI} = 2^{t\cdot[(T-480)/17]} \tag{4.5}
\]

Where SI is the time-temperature index, \( T \) is the temperature and \( t \) is the time.

Similarly, in hydrothermal carbonization, as shown in Equation (4.3), 14.75 °C is the temperature increase which has an exponential relation with reaction order to produce the same changes in the hydrochar [70].

### 4.2.3. Characterizations of the hydrochars

MY was calculated as the ratio of the weight of obtained hydrochar to the initial biomass weight. The proximate analysis for determining ash, volatile matter (VM), and fixed carbon (FC) content was performed on the raw material as per ASTM standards [33]. The ultimate analysis was conducted using a Flash 2000 Elemental Analyzer (Thermo Fisher Scientific, Waltham, MA, USA) on the hydrochar and raw material. HHV was measured via IKA-C200 bomb calorimeter (IKA Works, Wilmington, NC, USA). The energy recovery factor (ERF) was then calculated from Equation (4.6):

\[
\text{ERF} = \text{MY} \times \frac{\text{HHV}_{\text{hydrochar}}}{\text{HHV}_{\text{feedstock}}} \tag{4.6}
\]
Where $HHV_{\text{hydrochar}}$ and $HHV_{\text{feedstock}}$ are the HHV of the hydrochar and feedstock respectively in MJ/kg and are obtained from bomb calorimetry experiment. Although ERF is defined by an equation from the mass yield and HHVs of the biomass and hydrochar, it is often used as an important measure to assess the feasibility of HTC processes. Usually, with an increase in SF, MY and ERF decrease, but HHV increases. However, some papers have reported that due to the type of the feedstock, or the process condition, by increasing SF of HTC, MY, and HHV have increased and resulted in an increase in ERF [176].

4.2.4. Response surface methodology

Response surface methodology (RSM) explores the relationships between several explanatory variables and one or more response variables. The main idea of RSM is to use a set of designed experiments to obtain an optimal response [177]. In the current study, RSM was used to find the relations between the variables reported in Table 4.2, with the responses including MY, HHV, C%, and ERF (Table 4.3).

4.2.5. Build information

In this study, a flexible design structure (combined, and user-defined) was performed to accommodate a custom model for the HTC process. Cellulose, hemicellulose, lignin, temperature and time have been considered as variable factors. These factors are representative of lignocellulosic biomass and process condition. For simplicity, SF was replaced by both temperature and time. Table 4.2 presents the design factors and their defined ranges.

<table>
<thead>
<tr>
<th>Component/Factor</th>
<th>Name</th>
<th>Units</th>
<th>Type</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cellulose</td>
<td>%</td>
<td>Mixture</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>Hemicellulose</td>
<td>%</td>
<td>Mixture</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>C</td>
<td>Lignin</td>
<td>%</td>
<td>Mixture</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>D</td>
<td>Severity Factor</td>
<td>-</td>
<td>Numeric</td>
<td>3.83</td>
<td>6.19</td>
</tr>
</tbody>
</table>

HHV, MY, C%, and ERF were used as response factors and are given in Table 4.3.

<table>
<thead>
<tr>
<th>Response</th>
<th>Name</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>HHV</td>
<td>MJ/kg</td>
</tr>
<tr>
<td>R2</td>
<td>MY</td>
<td>%</td>
</tr>
<tr>
<td>R3</td>
<td>C%</td>
<td>%</td>
</tr>
<tr>
<td>R4</td>
<td>ERF</td>
<td>%</td>
</tr>
</tbody>
</table>
According to the variables of the study, a total of 39 runs were suggested by Design-expert 11 (Stat-Ease, Inc., Minneapolis, USA) in randomized order and the output responses were obtained via HTC experiments. Table 4.4 shows the I-optimal design matrix with 39 experimental runs. The standard deviation for HHV, MY, C%, and ERF were 0.48, 1.40, 2.34, and 1.18, respectively.

<table>
<thead>
<tr>
<th>Component 1</th>
<th>Component 2</th>
<th>Component 3</th>
<th>Factor 4</th>
<th>Response 1</th>
<th>Response 2</th>
<th>Response 3</th>
<th>Response 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
<td>A: Cellulose</td>
<td>B: Hemicellulose</td>
<td>C: Lignin</td>
<td>D: SF</td>
<td>HHV</td>
<td>MY</td>
<td>C%</td>
</tr>
<tr>
<td>1</td>
<td>16.67</td>
<td>16.67</td>
<td>66.67</td>
<td>6.19</td>
<td>28.90</td>
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<td>27.71</td>
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<td>0.00</td>
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<td>20.47</td>
<td>71.41</td>
<td>50.90</td>
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<td>0.00</td>
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<td>73.50</td>
<td>71.31</td>
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<td>41.67</td>
<td>41.67</td>
<td>6.19</td>
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<td>28.30</td>
<td>54.72</td>
<td>68.11</td>
</tr>
<tr>
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standard deviation

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<th>HHV</th>
<th>MY</th>
<th>C%</th>
<th>ERF</th>
</tr>
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<tr>
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<td>1.40</td>
<td>2.34</td>
<td>1.18</td>
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4.3. Results and discussion

4.3.1. Experimental results

The results of the 39 HTC experiments and characterization of the obtained hydrochars are given in Table 4.4. These results were then entered into the Design Expert software as inputs. As expected, the highest HHV (30.41 MJ/kg) and C% (71.31%) occurs when the sample is solely made of lignin and the severity factor is at its highest (6.19). Whereas, the lowest HHV (18.26 MJ/kg) occurs at the lowest SF and when the sample is only made of cellulose. This is mainly due to the fact that at low SFs, the hemicellulose undergoes significant carbonization and increases the HHV, but cellulose starts the main carbonization at medium SFs. Other than these easily observable results from Table 4.4, the relations and interactions of the parameters can be of interest which is described in the following sections.

4.3.2. Data Analysis and statistical significance of each model

An adequate functional relationship between the four output responses of the HTC and input variables is developed using response surface study. This relationship between the design factors and output responses can be modeled using a quadratic polynomial equation due to its higher accordance with the experimental results of the current study in comparison to other equations. Analysis of variance (ANOVA) was used to determine the statistical significance of each model and is given in the supporting information. Considering the level of significance as 5%, The Model F-value implies that all models are significant. The predicted $R^2$ in the models is in reasonable agreement with the Adjusted $R^2$ of 0.99 (i.e. the difference is less than 0.2). In the below sections, the effects and the interactions of the design parameters on HHV, C%, ERF, and MY are investigated.

4.3.3. Higher Heating Value (HHV)

Response surface methodology was employed to analyze the effects of each parameter on HHV. According to the methodology described in Section 4.3.1, the mathematical relationship between the dependent and independent variables, and the value of the regression coefficient of the respective equation were calculated. The final equation in terms of actual factors is as follows:
This equation demonstrates the variation of HHV by changing the design factors. The equation for HHV in terms of the design factors and Figure 4.2-a illustrates that cellulose exhibits the highest negative effect on HHV with a coefficient of -54.74 while lignin has a linear positive effect with a coefficient of 26.64. This is due to the fact that the C% and HHV of lignin are already high without carbonization. Moreover, the results reveal that the effect of hemicellulose on HHV is negligible. Considering hemicellulose and cellulose, HHV and C% of hemicellulose is slightly lower than that of the cellulose, however, hemicellulose starts to carbonize from lower severity factors which finally will have a better contribution in increasing the HHV and C% of the final hydrochar. The proposed equation shows that the interaction between cellulose and severity factor is the most significant interaction whereas it does not detect considerable interactions among components. Among the biomass components, only interaction of lignin and hemicellulose increases the HHV.

As shown in Figure 4.2-b, the effect of a change in cellulose, hemicellulose and lignin values on HHV are noticeable when the severity factor is more than 5.4. This is in accordance with the findings in other experimental studies [95]. Another interesting observation from Figure 4.2-b is that the effect of the biomass components' percentage on HHV is more significant in lower SFs than the higher ones.
Figure 4.2. 3D response surface plot of HHV considering the interactions of the biomass components and severity factor

4.3.4. Mass yield (MY)

Equation (4.8) for the MY in terms of design factors indicates that cellulose and hemicellulose with a coefficient of 243.4 and 132.85 respectively have the highest positive effects, whereas the interaction between cellulose and severity with a coefficient of -61 was the highest negative linear effect on MY. The interaction plot (Figure 4.3) shows that when the severity factor is less than 4.42, the effect of biomass components changes on MY is more dominant as compared to when the severity factor is more than 4.42.
Figure 4.3. Contour plot of MY considering the interactions of biomass components and severity factor

4.3.5. Carbon content (C%)

C% is the main indicator of carbonization level, thus its value directly relates to the hydrochar or solid fuel quality. The final equations for C% in terms of design factors and mixture components indicate that cellulose has the highest negative effect on the carbonization with a coefficient of -91.42 while the most effective factors on the carbonization of biomass were related to the lignin and hemicellulose (with a coefficient of 84.86 and 70.18 respectively). On the other hand, the most significant interaction between the parameters was observed between cellulose and severity.
factor with a coefficient of +50.33. Both 3D surface and counterplot (Figure 4.4) depicts that when the severity factor is more than 5.01, the effect of changes in mixture components on C% is less obvious as compared to when the severity factor is less than 5.01.

<table>
<thead>
<tr>
<th>C% =</th>
<th>Impact</th>
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<tr>
<td>-91.42253</td>
<td>C</td>
</tr>
<tr>
<td>+70.17892</td>
<td>H</td>
</tr>
<tr>
<td>+84.85954</td>
<td>L</td>
</tr>
<tr>
<td>-0.309030</td>
<td>C × H</td>
</tr>
<tr>
<td>-1.90956</td>
<td>C × L</td>
</tr>
<tr>
<td>+50.33209</td>
<td>C × SF</td>
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<tr>
<td>+0.429702</td>
<td>H × L</td>
</tr>
<tr>
<td>-3.38168</td>
<td>H × SF</td>
</tr>
<tr>
<td>-10.47161</td>
<td>L × SF</td>
</tr>
<tr>
<td>-3.95784</td>
<td>C × SF²</td>
</tr>
<tr>
<td>+0.417360</td>
<td>H × SF²</td>
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<tr>
<td>+1.23801</td>
<td>L × SF²</td>
</tr>
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</table>

Figure 4.4. 3D response surface and contour plot of the C% considering the interactions of biomass components and severity factor

### 4.3.6. Energy recovery factor (ERF)

ERF is usually an indicator of the feasibility of the proposed system. The final equation for ERF in terms of SF and mixture components is given as Equation 4.10. In this case, cellulose, hemicellulose, lignin and their first order interaction with severity factor have been considered as significant model terms. According to the coefficient values, hemicellulose has a significant positive impact on ERF with a coefficient of 105.99. On the other hand, the only noticeable
interaction between the parameters was observed between cellulose and severity factor with a coefficient of 50.07. As seen in Figure 4.5 in a lower amount of cellulose (<45 wt%), ERF decreases linearly with increasing severity factor. However, in a higher amount of cellulose, ERF reaches its maximum of 92.42 and then starts decreasing. In general, the results show that the role of hemicellulose and interaction between cellulose and severity factor in selecting biomass and adjusting HTC operational factors are very important to reach a high ERF.

\[
\text{ERF} = -19.81985 \ C + 105.98844 \ H + 89.01126 \ L + 50.06871 \ C \times SF + 0.684217 \ H \times SF + 2.73377 \ L \times SF - 5.36956 \ C \times SF^2 - 0.713270 \ H \times SF^2 - 0.500776 \ L \times SF^2
\]  

(4.10)

![Design-Expert® Software](image)

Component Coding: Actual
Factor Coding: Actual

Energy recovery (%)

- Design points above predicted value
- 73.9534
- 96.4208

X1 = A: Cellulose
X2 = B: Hemicellulose
X3 = D: SF

Actual Component
C: Lignin = 33.3333

Figure 4.5. 3D surface of the ERF for the interaction of biomass components and severity factor
4.3.7. HTC optimization

According to the obtained results, biomass components, similar to the severity factor, could play a significant role to produce a high-quality solid biofuel. It is clear that the higher the severity factor of the process, the higher the degree of the carbonization and as a result, the HHV of the hydrochar. However, one of the arguments against HTC is the high energy intensity of the process. Hence an optimization goal can be defined as minimizing the SF but maximizing the HHV. Design-expert software was used to perform this optimization. Considering real biomass feedstocks, the allowable ranges for changes in the content of cellulose, hemicellulose, and lignin were taken from Ref. [9]. The constraints imposed to reach the maximum HHV are given in Table 4.5. As stated earlier, the goal of this optimization is to reach a high-quality hydrochar from biomass with an optimum content of cellulose, hemicellulose, and lignin and with the lowest possible energy-intensive condition.

Table 4.5. Constraints imposed to reach the optimal condition

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<th>Lower Limit</th>
<th>Upper Limit</th>
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<td>is in range</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>B: Hemicellulose</td>
<td>is in range</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>C: Lignin</td>
<td>is in range</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>D: SF</td>
<td>minimize</td>
<td>3.832</td>
<td>6.188</td>
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<tr>
<td>HHV</td>
<td>maximize</td>
<td>18.26</td>
<td>30.41</td>
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</table>

Table 4.6 presents the predicted values of design mixture components (hemicellulose, cellulose, and lignin contents) and severity factor together with the prediction of the responses according to the defined constraints. As it is reported, biomass with a cellulose content of 40%, hemicellulose of 35%, and lignin of 25%, under the severity of 4.41 can be the most desirable case for HTC treatment. However, there are other close enough solutions with slightly lower desirability that can be considered as good options too. These findings can be a great guide for the selection of the feedstock and conditions that are more suitable for HTC.

Table 4.6. Response surface results based according to the imposed constraints

<table>
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<th>Lignin</th>
<th>SF</th>
<th>HHV</th>
<th>MY</th>
<th>C%</th>
<th>ERF</th>
<th>Desirability</th>
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<td>59.301</td>
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4.3.8. Validation of the solutions

The obtained process parameters in Table 4.6 were tested experimentally. Similar to what was explained in the experimental section, 2 g of the mixture was synthesized using 0.8 g (40%) cellulose, 0.7 g (35%) hemicellulose, and 0.5 g (25%) lignin. The prepared sample was mixed with 10 g water and undergone a severity factor of 4.41 (T= 200 °C, t=30 min) and then the obtained hydrochar was characterized. The comparison of the results with the values indicated in Table 4.6 shows that the percentage error is never higher than 1%. Therefore, the accuracy of the optimum model is validated.

4.3.9. Comparison of the results with real biomass

Table 4.7 is presented to compare the values found by the model developed in this work with the experimental results of different woody biomass reported in the literature.

It should be noted that the equations proposed in this study cannot be used or will show considerable errors for HTC of algal biomass (third generation), the second generation of biomass with a significant amount of ash or extractives, and catalytic hydrothermal reactions. In addition, the differences in the predictions with the experimental results can be due to one of the followings:

- The presence of the water extractives and ash content in the real biomass
- Physical bonds and higher interactions between the components in the real biomass
- Errors of measuring the accurate contents of the components
- Other experimental errors
- Regarding the MY, the highest differences can be seen where the percentages of ash and extractives are high. The MY predictions for corn stover and rice hulls with about 34% ash and extractive content and wheat straw with about 13.5% have a relatively high error. For other biomass types, however, the MY prediction is in good agreement with the experimental results. The HHV predictions show a good agreement with the experiments with the highest error of -2.47 MJ/kg for corn stover. The C% is also mostly in good agreement with the results found in the experiments except for the corn stover where there is a 10.35% difference.
Table 4.7. Comparison of the predicted parameters by the obtained equations with the data reported in the literature

<table>
<thead>
<tr>
<th>Sample name And ref.</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
<th>Ash + Extractive (%)</th>
<th>Severity factor</th>
<th>MY (%)</th>
<th>MY pred. (%)</th>
<th>HHV (MJ/kg)</th>
<th>HHV Pred. (MJ/kg)</th>
<th>C %</th>
<th>C% Pred.</th>
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<td>24.12</td>
<td>26.47</td>
<td>62.78</td>
<td>60.7</td>
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<td>38.8</td>
<td>36.3</td>
<td>11.5</td>
<td>13.4</td>
<td>5.41 (260 °C, 5 min)</td>
<td>47</td>
<td>45.77</td>
<td>25.7</td>
<td>24.24</td>
<td>61.2</td>
<td>56.23</td>
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<td>10.66</td>
<td>13.43</td>
<td>5.41 (260 °C, 5 min)</td>
<td>58</td>
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<td>24.22</td>
<td>61.73</td>
<td>56.5</td>
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<td>14.73</td>
<td>4.72</td>
<td>6.19 (260 °C, 5 min)</td>
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<td>26.89</td>
<td>67.43</td>
<td>64.74</td>
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<td>48.45</td>
<td>29.92</td>
<td>17.12</td>
<td>4.51</td>
<td>3.53 (180 °C, 15 min)</td>
<td>66.1</td>
<td>75.62</td>
<td>18.45</td>
<td>19.03</td>
<td>45.52</td>
<td>47.80</td>
</tr>
<tr>
<td>Tahoe mix [31]</td>
<td>50.7</td>
<td>18.2</td>
<td>23.8</td>
<td>7.3</td>
<td>6.04 (255 °C, 30 min)</td>
<td>48.53</td>
<td>50.28</td>
<td>28.03</td>
<td>26.54</td>
<td>70.06</td>
<td>63.01</td>
</tr>
<tr>
<td>Loblolly pine [31]</td>
<td>55.4</td>
<td>11.5</td>
<td>30</td>
<td>3.1</td>
<td>6.04 (255 °C, 30 min)</td>
<td>50.13</td>
<td>54.60</td>
<td>28.39</td>
<td>27.88</td>
<td>71.27</td>
<td>66.09</td>
</tr>
<tr>
<td>Corn stover [31]</td>
<td>29.7</td>
<td>26.3</td>
<td>9.5</td>
<td>34.5</td>
<td>4.86 (215 °C, 30 min)</td>
<td>56.62</td>
<td>38.28</td>
<td>20.04</td>
<td>17.57</td>
<td>51.03</td>
<td>40.68</td>
</tr>
<tr>
<td>Rice hulls [31]</td>
<td>39.8</td>
<td>14.9</td>
<td>11.3</td>
<td>34</td>
<td>6.04 (255 °C, 30 min)</td>
<td>55.44</td>
<td>34.22</td>
<td>17.89</td>
<td>18.76</td>
<td>47.35</td>
<td>44.99</td>
</tr>
</tbody>
</table>

4.4. Conclusion

The results of HTC of different feedstocks vary considerably due to the changes of composition from one feed to another. Hence, developing equations to predict the hydrochar’s characteristics with respect to the biomass composition and process condition is beneficial. Hydrochars produced by HTC with different severity factors on the mixtures of the main components of lignocellulosic biomass (cellulose, hemicellulose, and lignin) were characterized in terms of their MY, HHV, C%, and ERF. The number and conditions of the experiments were suggested by Design Expert software such that it can then establish the relations and equations of the feedstock and process parameters with the hydrochar characteristics. The final equations were validated with secondary experiments on the optimized mixture (40% cellulose, 35% hemicellulose, and 25% lignin, selected based on the minimum SF but maximum HHV) to ensure the accuracy of the fitted models. Errors of less than 1% for all of the responses showed that the models fit
perfectly with the experimental data. Then the model was tested with experimental data of HTC on 10 different real biomass and it was shown that the model is reliable especially at low ash and water extractives contents. The equations can reveal important information for the design and feedstock selection of an HTC plant. For instance, it was found that the higher the lignin and the lower the cellulose contents in the raw biomass, the higher the energy content of the hydrochar. Moreover, it was observed that by selecting the suitable biomass feedstock (with compositions shown in Table 4.5) with as low SF as 4.5, MY of around 67%, and HHV of around 25 MJ/kg can be obtained.
Chapter 5. Development of a mathematical model for hydrothermal carbonization of biomass: Comparison of experimental measurements with model predictions

The present chapter aims to develop a mathematical model for hydrothermal carbonization (HTC) by incorporating heat transfer rate, reaction kinetics, and the porous structure of the biomass for the first time using various modules of COMSOL Multiphysics software. HTC experiments on pine wood particles using a batch reactor were performed to calibrate the model. Operating parameters such as temperature, residence time, biomass to water ratio, and power consumption were recorded, and the obtained products were characterized via ultimate analysis, and bomb calorimetry experiments. Experimental results validate the predictions of the developed model. It is observed that the predicted energy consumption was considerably deflected from the experimental value when the reactions during the processing and porosity of biomass were not considered. The model predicted that a well-insulated, sealed, and continuous reactor can decrease the power consumption significantly when aqueous phase is recycled for heat integration and recovery. Hence, the developed model can potentially be used as a first step in designing an industrial reactor for hydrothermal conversion of biomass, which may attract investors and policy makers for commercialization of this technology.

A version of this chapter entitled “Development of a mathematical model for hydrothermal carbonization of biomass: Comparison of experimental measurements with model predictions” is under review for publication in “Energy”, Elsevier.

5.1. Introduction

The objective of this paper is to step forward in modeling the HTC process by addressing the gaps mentioned above. Pinewood particles were prepared and introduced to the HTC reactor to undergo treatment at 220 oC for one hour. The reason for selecting this feedstock was that the lignocellulosic biomass is increasingly regarded as a potential renewable source for bioenergy and chemical production due to its abundance [29]. Another advantage of using lignocellulosic biomass is that they all have a similar fibrous structure and the obtained results from one research can be used in other works for comparisons and verifications. Although the selection of the biomass should comprise many different factors such as availability, geographical condition, and energy content, perhaps the most important factor could be the cost of the feedstock which
significantly affects the economic feasibility of the process [32]. The focus on low cost biomass such as wood residues could lower the operating cost. In addition, for developing mathematical model that fits different kinds of lignocellulosic biomass, the focus on the reference materials such as hemicellulose, cellulose, and lignin is of great importance. Before moving towards the modeling, some of the required data were obtained experimentally. An energy meter and temperature logger were connected to the heat supplier and the reactor’s outer surface respectively to monitor the changes and the feedstock and the obtained hydrochar were characterized. Regarding the modeling part, COMSOL Multiphysics was used which is a well-known finite element software and is capable to address the interactions of different physics with acceptable solution accuracy and consistency (Figure 5.2). First, the 3-D geometries of the reactor and the biomass were created. Then heat transfer in solids, heat transfer in liquids, and heat transfer in porous media modules were selected for the body of the reactor, the water, and the biomass respectively. Moreover, chemistry and mass transfer in diluted species modules were selected to account for the chemical reactions and mass transfer during the process. To find the kinetic parameters of the reactions, HTC experiments were performed at 3 different temperatures (180 °C, 220 °C, and 250 °C) and 4 different times (30 min, 60 min, 120 min, and 180 min) and the solid mass yields after each experiment were recorded. Afterward, the Levenberg–Marquardt algorithm was used to fit a kinetic model with the experimental data. Finally, the kinetic parameters including the pre-exponential factor and the activation energy were found. COMSOL provides the means of coupling the modules to each other by supplying specific dependent parameter(s) of one module from another module and so on. The required data of the simulation were found by performing experiments, from the literature, and from the software’s data bank. The approach and the work explained in this research are important steps towards commercializing HTC. Despite the need for this kind of research, no similar study has been reported. This study investigates the heat transfer of HTC with consideration of the reactions and porosity of the biomass for the first time. The methods explained here use process knowledge from experiments and develop a reliable heat and mass transfer model that can be used for proper investigations of HTC. Knowing that the expenses and the time required to find experimental data from HTC experiments are high, this research can help the researchers and consequently the decision-makers and investors to a great extent.
5.2. Material and methods

5.2.1. Feed

A good representative of lignocellulosic biomass is pine wood which is abundant in North America. Pinewood was provided from a tree farm in Ontario, Canada, chopped and stored in sealed plastic bags until undergoing the HTC process.

5.2.1. HTC experiments

HTC of the pinewood particles was performed in a batch reactor, Series 4560 (Parr Instrument Company, Moline, IL, USA). Prior to the process, 100 g dry weight of the biomass was mixed with around 500 g of distilled water (1:5 biomass to water ratio) and stirred to ensure that the biomass is fully submerged and soaked. Then the reactor lid was placed and sealed. Afterward, nitrogen gas was injected into the reactor, increasing the pressure to around 2 MPa to ensure that the pressure of the water is always above the saturation pressure. Then, the reactor was heated up from room temperature to 220 ± 5 °C and kept at this temperature for one hour.

The temperature of the reactor was controlled via a temperature controller, model CNI-CB120SB (Omega, Stamford, CT, USA) by reading the temperature inside the reactor from a K-type thermocouple. The temperature controller was connected to a heater around the reactor. The temperature was monitored every 20 seconds by connecting two thermocouples to the temperature logger. Meanwhile, an energy analyzer, model Fluke 435-II (Fluke Corporation, Everett, Washington, USA) was connected to the cables connecting the power supply, temperature controller, and the heater to measure the power consumption of the system continuously. The schematic of this setup is shown in Figure 5.1.

Figure 5.1. Experimental setup schematic
After the process, the reactor was detached from the set-up and immediately quenched with cold tap water. When the inside temperature dropped to below 30 °C, the heater was removed from the reactor and the solid part was separated using 20 μm filter papers. The separated solid part (hydrochar) was then dried in a muffle oven at 105 °C for 24 h for further analysis. Knowing the masses of the initial raw biomass and obtained hydrochar, the mass yield of the hydrochar can be found using the following equation:

\[
\text{Mass yield} = \frac{\text{mass of dried hydrochar}}{\text{mass of initial biomass}} \times 100
\]  

(5.1)

In order to collect the required experimental points for modeling the reaction kinetics, the same HTC procedure was repeated at three different temperatures (180 °C, 220 °C, and 250 °C) and at four different times (30 min, 60 min, 120 min, 180 min).

5.2.2. Proximate, ultimate, and bomb calorimetry analysis

After producing hydrochars via HTC, the samples undergo characterization experiments. The main purpose of performing these experiments for this study is for finding the empirical formula of the hydrochar and raw biomass and deriving the representative chemical reaction during the process. The proximate analysis was carried out in a Model Thermolyne F48055-60 bench-top muffle furnace (Thermo Fisher Scientific, Waltham, MA, USA) per ASTM standard [179], the main purpose of which was to find the ash content of the samples.

The ultimate analysis (CHNSO) test was conducted using a Flash 2000 Elemental Analyzer (Thermo Fisher Scientific, Waltham, MA, USA). About 2 mg of dried and the ground sample was needed for each test. The analyzer found the content of carbon (C), hydrogen (H), nitrogen (N) and sulfur(S) for each sample. Then the oxygen content was calculated using Equation (5.2)[34].

\[
O\% = 100\% - C\% - H\% - N\% - S\% - \text{ASH}\%
\]  

(5.2)

The higher heating value (HHV) tests were performed via IKA-C200 bomb calorimeter (IKA Works, Wilmington, NC, USA). About 0.5 g of each sample was placed in a crucible, and then the crucible was placed in the vessel. After, pressurizing the vessel with oxygen and placing it in a water bath, the sample was ignited. The machine recorded the temperature of the water before and after the ignition, and the HHV was then calculated accordingly.
5.2.3. Schematic of the model, geometry, and materials

Figure 5.2 is a schematic of the modeling section and the connection of different modules in COMSOL.

The size and the shape of the reactor have significant effects on the operation of an HTC process and its final products. Generally, the strongest structure to hold the high pressure of the reactor content is spherical. However, due to requirements of large volumes, cylindrical structure is the best alternative. In a cylindrical reactor, the pressure is evenly distributed and there is no concentration of force in any specific area. This is mainly because a cylindrical shape has a lower surface area in comparison to rectangular and other shapes of the same volume, and as a result lower amount of stress is exposed to the walls of the reactor and there is no break down point in the structure.

The geometry of the problem represents the reactor’s body and accessories, and the biomass particles. All dimensions of the reactor and accessories were measured precisely using a caliper. Figure 5.3 shows the geometry created in COMSOL. The reactor is made of stainless steel with an inner diameter of 6 cm and a height of 19.6 cm. Knowing that the density of the pine particles is
0.6 \text{ g cm}^{-3}$, in order to make 100 g of the biomass and 1:5 biomass to water ratio, a number of 400, 7.5 mm cube particles were developed to represent the biomass and were distributed evenly in the reactor.

**Figure 5.3. The geometry of the studied HTC system simulated in COMSOL**

The mesh that was utilized for the geometry shown in Figure 3 was constructed as a physics controlled mesh. Physics controlled mesh in COMSOL conducts the meshing of the domain automatically and adapts it based on the equations to be solved. The mesh was manually refined inside the reactor to achieve higher accuracy. Different types of the mesh, i.e., coarse, medium, and fine were used and the problem was converged in all cases with negligible improvements. Therefore, fine type of the mesh was used.

The boundary condition of the heat transfer for the bottom, and surrounding of the reactor is the uniform heat supplied by the heater, whereas for the top of is the convective heat transfer with the room temperature.

**5.2.4. Heat transfer model**

After defining the geometry, the heat transfer models were developed. By selecting the materials for each domain in COMSOL, the properties of that material such as specific heat, thermal conductivity, and density were considered from the software’s data bank.
As shown in Figure 5.3, the bottom and sides of the reactor are in contact with the heater, while the top is in touch with the room atmosphere, wasting some energy by convection. The heat penetrates from the sides and bottom of the reactor by conduction to the mixture of the water and biomass. Heat transfer in solids module is used for the conduction of the heat from the heater and the convection from the top parts of the reactor. Heat transfer in liquids module is used for the water inside the reactor and heat transfer in porous media module is used for the biomass.

The temperature increase by the heater was from room temperature (22 °C) to the setpoint (220 °C). The heat is initially provided by the heater with a capacity of 640 W. If the temperature goes beyond the setpoint, the controller turns the heater off. This was entered in COMSOL with a conditional statement presented by Equation (5.3):

\[ P_{\text{Heater}} = \text{If} \ (T_{\text{ave}} < 220 \, ^\circ\text{C}, 640 \, \text{W}, \text{else} \ 0 \, \text{W}) \]  

Where \( T_{\text{ave}} \) is the average temperature of the reactor content and \( P_{\text{Heater}} \) defines the power of the heater. In addition to the heat provided by the heater, the heat of reactions plays a role in varying the temperature of the reactor content from the set point. The tolerance considered for the temperature control was ± 5 °C for both experiment and the model.

As it was stated, prior to performing the HTC experiment, the pressure was increased to around 2 MPa. Shortly, after the heating process starts, the pressure inside the reactor increases. The pressure changes with respect to the temperature were monitored via a pressure gauge during the experiment and were given to the model. The maximum pressure was seen at 220 °C as 5.25 MPa.

The heat flux, \( \dot{q}_{\text{conv}} \), in \( \frac{\text{W}}{\text{m}^2} \) from the parts of the reactor that are exposed to the room temperature due to convection was modeled by the following equation:

\[ \dot{q}_{\text{conv}} = h \cdot (T - T_{\text{atm}}) \]  

In Equation (5.4), \( h \) is the convective heat transfer coefficient \( \left( \frac{\text{W}}{\text{m}^2 \cdot \text{K}} \right) \), \( T \) is the temperature of the surface which changes with time, and \( T_{\text{atm}} \), is the room temperature (22 °C). The convective heat transfer coefficient were estimated in COMSOL by considering the Nusselt number, thermal conductivity of the material and the characteristic length [128], [180].
The general heat transfer equation for solid and liquid parts of the model which can account for conduction, convection and heat source from the chemical reactions is given by Equation (5.5).

\[ \rho \cdot c_p \frac{\partial T}{\partial t} + \rho \cdot c_p \cdot u \nabla T = \nabla \cdot (k \nabla T) + \dot{Q} \]  

(5.5)

Where \( k \) (W m⁻¹ K⁻¹), \( \rho \) (kg m⁻³), and \( c_p \) (kJ kg⁻¹ K⁻¹), are the thermal conductivity, density, and heat capacity of each material, \( u \) is the velocity vector (m s⁻¹), \( t \) is the time (s), \( T \) is the temperature (°C), and \( \dot{Q} \) (W m⁻³) is the heat flow released from the reactions which is one of the inputs from the chemical reactions section to the heat transfer section [181].

Finally, as biomass is a porous medium, the heat transfer is a combination of conduction in the solid volume, and convection in the pores. The porosity of the biomass was measured by submerging the biomass with known volume in the water, finding the volume of the displaced water (which shows the volume of the solid part) and using Equation (5.6):

\[ \theta_s = \frac{V_t - V_d}{V_t} \]  

(5.6)

Where \( \theta_s \) represents the porosity, \( V_t \) stands for the total volume of the biomass sample (cm³), and \( V_d \) indicates the volume of the displaced water (cm³). A porosity of 0.54 was found for the pine particles used in this study which is in line with the literature [182]. It should be noted that the water displacement method mentioned for measuring the porosity is the most simple and inexpensive method. For higher reliability, other methods such as mercury porosimetry, helium pycnometry, and image analysis could be performed [183]–[185]. This porosity is assumed to be constant during the process. The governing equations for this section, are as follows:

\[ (\rho \cdot c_p)_{eff} \frac{dT}{dt} + (\rho \cdot c_p)_f \cdot u \cdot \nabla T + \nabla \cdot \dot{q} = \dot{Q} \]  

(5.7)

\[ \dot{q} = -k_{eff} \nabla T \]  

(5.8)

In these equations, \( \dot{q} \) denotes the net rate of heat conduction into the unit volume (W m⁻³). The second expression in Equation (5.7) i.e. \((\rho \cdot c_p)_{f} \cdot u \cdot \nabla T\), involves the multiplication of the fluid’s (water) density and heat capacity and the rate of temperature change in a volume element due to convection (u.\( \nabla T \)). Overall the second expression accounts for the rate of heat transfer due to convection per unit volume of the pores (W m⁻³) [186]. Moreover, \((\rho \cdot c_p)_{eff} \) which stands for the effective volumetric...
heat capacity \((\frac{J}{m^3 K})\), and \(k_{\text{eff}}\), effective thermal conductivity \((\frac{W}{m K})\), can be found by Equations (5.9), and (5.10):

\[
(\rho \cdot c_p)_{\text{eff}} = \theta_s \rho_s c_{p,s} + (1 - \theta_s) \rho_f c_{p,f}
\]

\[(5.9)\]

\[
k_{\text{eff}} = \theta_s k_s + (1 - \theta_s) k_f
\]

\[(5.10)\]

Where \(\theta_s\) represents the porosity, \(\rho_s\), \(c_{p,s}\), and \(k_s\) are the density, heat capacity and thermal conductivity of the solid part of the biomass, and \(\rho_f\), \(c_{p,f}\), and \(k_f\) are those of the void part of the biomass.

It is also worth mentioning that the BET analysis on the same sample shows that the pore structures of the samples appear to be of Type III isotherm. [95]. The surface area of the samples increased from around 4 m\(^2\)/g to 8.24 m\(^2\)/g after HTC at 220 °C. Meanwhile, the average pore sizes were around 6-7 nm. The pore sizes of the samples did not experience a significant change. Regarding their pore diameter, they were categorized in the mesoporous range.

**5.2.5. Chemistry model**

The chemistry and transport of diluted species in porous media modules in COMSOL were used to simulate the reactions. As it was stated in the introduction, during HTC, several reactions with unknown intensities and orders occur which makes addressing all reactions in this extremely complicated. However, by characterizing the products and the feed, the overall reaction can be defined [187].

To achieve this aim, empirical formulas of the raw biomass and the obtained hydrochar after experimentally carbonizing the biomass at 220 °C for an hour, were found from the ultimate analysis. Regarding the liquid by-products, as around 90% of the liquid is acetic acid [88], the whole liquid by-product in the reaction is considered to be acetic acid. As for the gas by-product, \(CO_2\) has been considered for the same reason [5]. As investigating the detailed reactions occurring during HTC is beyond the scope of this study, a first-order reaction rate and Arrhenius equations were used to represent the overall chemical reactions [128].

\[
C_{1.47}H_{2.23}O + H_2O \rightarrow C_{2.72}H_{7.4}O + CO_2 + CH_3COOH
\]

\[(5.11)\]

It is worth mentioning that, by increasing the initial pressure of water prior the start of the process, it is ensured that water remains in the subcritical region. The increase in the pressure increases the
density of the water and results in higher solvent power compared to water vapor. Moreover, in the subcritical region, due to high availability of ions in the water environment, ionic reactions take place [188]. Hence, due to the decrease in the polarity of water and increase in its ionic products, better solubility of organic compounds and increased catalytic activities for acid-base reactions such as hydrolysis of the bio-polymers of the biomass are expected [132]. It should be noted that the impact of water formation was neglected. Although this is the common approach in the literature, a recent study by Pecchi et al. [189] indicates that the calculation of the enthalpy change of the HTC process is more accurate and the process appears as more exothermic as the temperature increases when the water formation is accounted for. To find the overall heat of reaction of Equation (5.11), the enthalpy of formation of the reactants and the products are found and applied in Equation (12):

\[ \Delta H_{\text{reaction}} = \sum \Delta H_f^{\text{products}} - \sum \Delta H_f^{\text{reactants}} \] (5.12)

The enthalpy of formation for the known substances like CO$_2$, and CH$_3$COOH, can be found from the literature. However, due to the unique chemical formulas of the biomass and hydrochar, their heats of formation are gotten from bomb calorimetry experiments. The combustion reactions of the biomass and the hydrochar that take place in the bomb are given by Equations (5.13), and (5.14).

\[
\begin{align*}
\text{C}_{1.47}\text{H}_{2.23}\text{O} + 1.52 \text{O}_2 & \rightarrow 1.11 \text{H}_2\text{O} + 1.47 \text{CO}_2 \quad \text{H}=-18.23 \text{ MJ/kg} \\
\text{C}_{2.72}\text{H}_{2.74}\text{O} + 2.9 \text{O}_2 & \rightarrow 1.37 \text{H}_2\text{O} + 2.72 \text{CO}_2 \quad \text{H}=-24.12 \text{ MJ/kg}
\end{align*}
\] (5.13) (5.14)

The experiments will provide the heat of reaction value, and as the heat of formation for other participants in reactions (5.13) and (5.14) can be found from thermodynamic tables, the heat of formation of the biomass and hydrochar can be calculated using Equation (5.12). The thermodynamic properties of the compounds like heat capacity, enthalpy, and entropy were entered by CHEMKIN files [190], and other sources [191] to consider the changes in the properties with temperature.

The reaction rate, \( K \) \( \left( \frac{1}{s} \right) \) was found based on the Arrhenius equation:

\[
K = A T^n \cdot \exp \left( - \frac{E_a}{RT} \right)
\] (5.15)
Where \( A \) is the frequency factor \((\text{s}^{-1})\), \( E_a \) is the activation energy \((\text{J mol}^{-1})\), \( T \) is the temperature (K), and \( R \) is the universal gas constant \((8.31 \text{ J mol}^{-1} \text{K}^{-1})\). Finding the values for the kinetic parameters, \( A \), and \( E_a \), requires extensive experimental data.

Most of the kinetic parameters reported in the literature are related to pure substance. However, lignocellulosic biomass like pine, contains hemicellulose, cellulose, and lignin together, and this can deflect the value of kinetic parameters. In this study, the kinetic parameters were found by developing a model based on the Arrhenius equation and fitting that with the solid mass yield obtained from HTC experiments at different temperatures and times.

Transport of Diluted Species in Porous Media module is used to simulate the mass transfer of the species of Equation (5.16). The mass balance due to the reaction and species transport is modeled by the time-dependent diffusion-convection equation.

\[
\frac{\partial c_i}{\partial t} = \nabla \cdot (-D_i \nabla c_i) + u \cdot \nabla c_i = R_i \tag{5.16}
\]

Equation (5.16), shows the changes in the concentration of species \( i \) with time, \( R_i \) refers to the rate term for each species which could be found by multiplying the reaction rate (from Equation 5.15) by the corresponding stoichiometric coefficient. \( u \cdot \nabla c_i \) indicates the rate of the concentration change in a volume element due to convection, \( D_i \) is the diffusion coefficient for each of the species \((\text{m}^2 \text{s}^{-1})\) and \( \nabla \cdot (-D_i \nabla c_i) \) indicates the rate of concentration change due to diffusion [192]. The diffusion coefficient of carbon dioxide, acetic acid and hydrochar in the water were considered as \( 2.23 \times 10^{-9} \text{ m}^2 \text{s}^{-1} \) [193], \( 12.1 \times 10^{-10} \text{ m}^2 \text{s}^{-1} \) [194], \( 6.73 \times 10^{-10} \text{ m}^2 \text{s}^{-1} \) [50] at the room temperature respectively. The temperature effect on the diffusivity was taken into account by the software, using Stokes–Einstein equation [50].

### 5.2.6. Kinetic model

To develop the kinetic model, the following reaction was considered:

\[
\text{Biomass} \rightarrow \text{Hydrochar} + \text{Liquid} + \text{Gas} \tag{5.17}
\]

Then a similar procedure to Ref. [128] was considered. At a given time, the solid mass yield can be found by adding the mass of the hydrochar \( (m_{HC}) \) and the mass of the biomass \( (m_B) \):

\[
m_s = m_{HC} + m_B \tag{5.18}
\]
Considering the mass of the biomass at the present time, the reaction rate can be found from Equation (5.19):

\[ r = - \frac{dm_B}{dt} = K \cdot m_B \]  

(5.19)

In this equation, \( K \) is the reaction rate constant which was explained by Equation (5.15).

Considering \( m_B0 \) as the initial mass of the biomass, the solid yield can be calculated by Equation (5.20):

\[ SY = \frac{m_S}{m_B0} \]  

(5.20)

The changes in the masses increase with the increase in the temperature and time of the HTC process. As the temperature is dependent on the time (T(t)), the mass yield cannot be easily calculated by resolving the differential equations. Hence, a series of experimental data were fitted by the kinetic model developed in COMSOL to find the optimum pre-exponential factor and the activation energy that can match the experiments. The adjusting parameters in the COMSOL model (A, and Ea) were determined by fitting the experimental SY data using the Levenberg-Marquardt algorithm [128].

5.3. Results and discussion

5.3.1. Experimental results

Table 5.1 shows the data found by ultimate, proximate, and bomb calorimetry experiments performed on the raw and treated biomass at 220 °C for 60 min. The experimental runs were replicated three times to ensure reproducibility. The reported values are the mean of the three runs. The standard deviations for the mass yields, ultimate and proximate analyses, and HHV values were less than 1%, 0.4%, and 2.1% respectively. This information was then used to find the required data for the reaction engineering section (Equations (5.11) - (5.14)). In addition to this, the temperature and power profiles of the experiment are shown in Figure 5.5.

Table 5.1. The results of the ultimate, proximate, and bomb calorimetry analysis of raw and hydrochar treated by HTC-220 °C-60 min

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mass yield (%)</th>
<th>Ultimate analysis (wt%)</th>
<th>Proximate analysis (wt%)</th>
<th>HHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C H N S O Ash FC VM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>-</td>
<td>49.22 6.10 0.01 0 44.57</td>
<td>0.10 17.80 82.10</td>
<td>18.23</td>
</tr>
<tr>
<td>Hydrochar</td>
<td>57.46</td>
<td>63.51 5.33 0.02 0 31.12</td>
<td>0.02 31.24 68.74</td>
<td>24.12</td>
</tr>
</tbody>
</table>
Table 5.2 shows the obtained solid mass yields from HTC experiments at multiple temperatures and times by which the kinetic parameters were estimated.

**Table 5.2. Solid mass yields from HTC experiments at three different temperatures and four different residence times**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Mass yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>30</td>
<td>79.5</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>69.5</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>67</td>
</tr>
<tr>
<td>220</td>
<td>30</td>
<td>62.5</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>56.55</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>52.9</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>50.75</td>
</tr>
<tr>
<td>250</td>
<td>30</td>
<td>48.81</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>43.84</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>42.13</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>41</td>
</tr>
</tbody>
</table>

### 5.3.2. Modeling results

The kinetic parameters were found by fitting the experimental mass yields (reported in Table 5.2) with the model at different temperatures using COMSOL. Figure 5.4 indicates the predicted mass yields at three different temperatures with the corresponding experimental data.

![Figure 5.4. Comparison between the solid mass yield from the experiments and the kinetic model](image-url)
As shown in Figure 5.4, the model fits with a satisfying agreement to the experiment \((r^2=0.99)\). The values of the model parameters that give the best fit of the experimental data are: \(E_a = 73.2 \text{ (kJ/mol)}\), \(A = 5.81 \frac{1}{s}\), and \(n = 1.4\). These data were then entered the Chemistry module of COMSOL integrated models.

Figure 5.5 shows the temperature and power consumption profiles of the experiment and the model. The data for the temperature and the power were recorded every minute, but an average of every 5 min was considered in Figure 5.5. This was especially helpful to show the trend of power consumption, as the on-off control mechanism was used to keep the temperature at the set point. Not only does the temperature profile of the model match that of the experiment but also the power consumption curves of both cases are in good agreement. The temperature rise starts from the room temperature using the maximum capacity of the heater towards the set point of the reaction. After 35 minutes, the temperature hits 220 °C and then the reactor’s content is kept at around the setpoint ± 5 °C for an hour. Hence, the overall time of the process was 95 minutes. The maximum temperature difference between the model and the experiment was 3.39 °C at the end of the process and the difference of the temperature profiles is negligible with \(r^2 >0.99\).

Regarding power consumption, the maximum capacity of the heater (640 W) was used at the beginning of the process. At around minute 20, where the temperature was around 195 °C, the heating slowed down, and in a short time after that, it stabilized the temperature at around 220 °C. The power supplied from the heater was used to compensate for the losses of the system which is mostly by convection from the reactor’s body to the atmosphere at room temperature. At approximately 60 minutes, the consumed power increased again and decreased after 20 minutes. The primary reason for this sudden change can be due to the on-off mechanism of temperature control.
Validation of the predicted temperature and power profile with the experimental data

The highest difference between the model and the experiment is 21 W which occurred at around 80 minutes. This relatively large difference is probably due to slight differences in the control logic used in the temperature controller and the one used by the model (Eq. 3). However, the trend of the power curves and the average consumed powers are close enough. The average power consumptions by the model and the experiment are 464 W and 468 W respectively, and the $r^2$ value is higher than 98.51% which shows this model is a reliable tool to simulate the trend and amount of required power for HTC.

Figure 5.6 shows the predicted changes of the relative mass yields with time by the model by dividing the mass yield of each component by the dry mass yield of the initial biomass (100 g).
The model predicts a final mass yield of 63.2% after 30 min in 220 °C and 55.2% after 60 min. These values are negligibly different with the ones from the experiment (see Table 5.1). Moreover, the trend of the mass yield evolutions is in agreement with other studies [50], [95], [128], [129] where there is an initial slow change at the beginning of the process, then the rate of the reactions accelerates and slows down again at the end of the reaction.

Figure 5.7 indicates the status of the reactor at 4 different times. At the initial stage of the process (A), the whole reactor is at room temperature. At a short while after, the heat starts to penetrate from the sides of the reactor (B). This continues for 35 min at which the temperature inside the reactor reaches 220 °C. Part (C) of Figure 5.7 shows the temperature distribution at a short time before it reaches 220 °C. After 35 min, the reactor remains at 220 °C for an hour with an off-on control mechanism, hence the temperature distribution throughout the reactor remains the same (D).
Figure 5.7. A view of the reactor’s temperature (in °C) distribution at different times

Figure 5.8 compares the energy requirement found by this model with two other cases. In the first case, the effect of chemical reactions was not considered and in the second case, not only the chemical reactions but also the porosity was neglected.
These defined scenarios by the model show how the power requirements will deflect from reality when the chemical reactions and the heat transfer in porous media are not considered. The average power consumptions are 502 W, and 478 W for the first case, and second case respectively which is 39 W, and 15 W, higher than the average power consumed in a real case. It should be noted that in the second scenario, the temperature hit the setpoint 5 minutes earlier, hence the overall process time was 90 minutes.

One of the factors that cause changes in power consumption is heat absorbed and released by endothermic, and exothermic reactions. It is known that the initial reaction pathways in HTC such as hydrolysis are endothermic, however, at higher temperatures and residence times, the exothermic reactions such as the decomposition of monosaccharides will release some heat to the process medium [176]. Now that the model is developed, the heat absorbed or released from the reactions can easily be found by deducting the energy curve where the reaction has not been considered (the yellow curve of Figure 5.8) from where the reaction has been considered (the red curve of Figure 5.8). As it was stated, the difference of the average power consumption in these two conditions is 39 W. Considering 95 min of the process and knowing that the initial biomass feed was 100 g, it can be concluded that the overall heat of reaction is -2223 kJ/kg. This value is in line with the findings of...
Cuviolas et al. [141] that found the heat of reaction from HTC of wood at 180 °C and 150 min as -2530 kJ/kg.

The energy requirements of the HTC process studied here were relatively high, and this can be a disadvantage of the HTC process for consuming a considerable amount of energy for producing value-added products that decrease the energy return on investment. However, it should be noted that there are a variety of applications for the hydrochar obtained by HTC that may not be necessarily priced by the amount of energy used to produce them. Moreover, it should be noted that, in the present study, the required energy was studied for a lab-scale batch reactor. Scaling up the HTC set-ups will significantly decrease the production costs. For instance, if the plant is scaled up by a factor of 10, the investment costs may increase by a factor of less than 5 [161]. Also, the future of HTC reactors will move on to continuous set-ups and wasting the energy of the water that is heated up in each cycle will be minimized. Fortunately, the model proposed in this study can consider some of these improvements.

A continuous reactor can return the water after each cycle with a high temperature (around 180 °C) using high-pressure hydraulic pumps to the reactor and mix it with the new feedstock which is at the room temperature. Moreover, the reactor’s body could be fully insulated to minimize the convective heat losses to the environment. Figure 5.9 shows the system with the energy input and output, as well as the temperature and power curve. The average power consumption in these conditions is 80.3 W considering the external heating and the power consumed by the pump. It only takes 3 minutes for the system to reach the setpoint temperature after which the energy requirement of the process decreases significantly, and after 30 min, it does not need any energy. This is due to efficient insulation, as well as the heat released by the reaction which is sufficient to sustain the process. The total energy input to the system is 303.53 kJ, and the energy output considering the hydrochar yield and its HHV is 1326.60 MJ.
5.4. Uncertainty analysis of the experiments

In this section, the uncertainty analysis of the experiments is presented to assess the accuracy of the results. The uncertainties are due to the accuracy limitations of different measurement devices. The absolute measurement uncertainties provided by the manufacturer (i.e. accuracy) for the K-type thermocouple, OMEGA data logger, and the weighing scale are ±2.2 °C, ±0.3 °C, and ±0.5 g respectively. Using this information for each device, the relative uncertainties of the measured quantities can be calculated based on the propagation uncertainty [195].

The main measured quantities of the experiment that were used to validate the model were temperature, hydrochar mass yield, and power. The relative uncertainty of the power measurements can be found in the manual of the energy analyzer as ±1%. The relative uncertainty associated with the temperature of the reactor content can be found by Equation (5.21).

\[
\frac{\delta T}{T} = \sqrt{\left(\frac{\delta T_{TC}}{T_{TC}}\right)^2 + \left(\frac{\delta T_{DL}}{T_{DL}}\right)^2} \tag{5.21}
\]

Where \(\delta T\), and \(T\) denote absolute accuracy and temperature (°C) respectively, and the subscripts TC, and DL are used to specify the temperature in the thermocouple, and the data logger respectively.

For the setpoint temperature value (220 °C), the relative uncertainty is ±1%. By a decrease in temperature, the uncertainty increases. For instance, at 120 °C, the relative uncertainty is ±1.85%.
Similarly, regarding the mass yield of the hydrochar, Equation (5.22) can be used. In this equation, the weight of the initial biomass and the final hydrochar are considered together because the mass yield is a function of both (see Equation 5.1).

\[
\frac{\delta m}{m} = \sqrt{\left(\frac{\delta m_{WB}}{m_b}\right)^2 + \left(\frac{\delta m_{WB}}{m_{hc}}\right)^2}
\]  

(5.22)

Where \(\delta m\) shows absolute accuracy of the mass, and \(m\) indicates the mass. Also, the subscripts WB, b, and hc specify the weighing balance, biomass, and hydrochar. Using Equation (5.22), the relative uncertainty associated with the measurement of the hydrochar mass yield is \(\pm 1\%\).

5.5. Conclusion

HTC is an emerging technology for converting biomass to bioenergy and other value-added products. Although the outstanding features of this process have been confirmed, more progress is required to adopt it at industrial scales. A numerical model that can address the real heat transfer and energy consumption is necessary to move on to this scale. The models investigated in the literature lack the consideration of the porous nature of the biomass as well as the heat released by the reactions. This study addressed these issues by modeling and experimentation of HTC for pinewood particles at 220 °C for one hour. On the other hand, the heat and mass transfer were modeled by COMSOL Multiphysics software. The temperature, power, and mass profiles of the model were validated with those of the experiment and showed a good agreement. While the overall process consumed an average of 465 W for 95 min, it was shown that without considering the heat released by the reactions and porosity, the estimated power will be far from reality. Finally, in order to address the concerns of high energy intensity of this process, a well-insulated, sealed, and continuous reactor was considered in the model, and it was shown that for each 100 g of the biomass, a total amount of 303.53 kJ energy can be used to convert it to the 55 g hydrochar with a heating content of 1326.60 kJ. This indicates that if HTC can be performed effectively, it can be highly feasible and promising. Future research should focus on developing such systems as well as investigating the means of further reducing input to output energy ratio.
Chapter 6. Product evaluation of HTC: Continuous vs. batch processing

HTC has been relatively well investigated in lab scale, however, due to the high pressure and temperature of the process; critical problems often arise when considering large continuous operations. These problems have not only hindered the commercialization developments of HTC but also have prevented the study of possible changes in the products because of continuous feeding. This study introduces a novel continuous feeding system to feed the new portions of biomass slurry against the high pressure of the reactor. Hence, the biomass is instantly exposed to the desired pressure and temperature, instead of the slow temperature increase from room temperature to the desired temperature and pressure exhibits in batch systems. The physical and chemical characterization tests on the obtained hydrochars reveal interesting information when compared with the hydrochars from the batch operation, particularly in high temperatures, where continuous operation showed a higher degree of carbonization. Higher content of organic-based intermediates, lower cellulose crystallinity, improved hexagonal graphene sheets, surface hydrophobic characteristics, and higher thermal stability were observed at elevated temperature in continuous HTC by TOC, XRD, FTIR, BET, and TGA. The changes are possibly due to the suppression of the secondary polymerization and instead enhanced primary carbonization. The promising conclusion of these results is that by introducing continuous systems in HTC, not only will the time and energy consumption of the process decrease, but also higher qualities of hydrochar are achievable.

A version of this chapter entitled “Product evaluation of hydrothermal carbonization of biomass: Continuous vs. batch processing” is under review for publication in “Biomass Conversion and Biorefinery”, Springer.

6.1. Introduction
HTC has been evaluated extensively in the literature and its advantages are proven, however, there are a number of challenges that have hindered its commercialization. One of the main challenges towards commercialization of the process is the development of a feeding system that can continuously feed the new biomass/water mixture against the high pressure of the reactor [187]. The continuous reactor will not only increase the speed of hydrochar production but also will
reduce the required energy of the treatment as there is no need to heat up the biomass slurry from
the room temperature.

In the current chapter, a novel continuous HTC system is designed and built. The novelty of this
system is in designing the pumping system where the hydraulic force helps the pressure of the new
feed (upstream of the reactor) overcome the pressure of the feed inside the reactor. Hence, when
the valve at the top of the reactor opens, the new feed can enter the reactor. Therefore, in this
configuration, the developed system can receive the biomass/water slurry at room temperature and
pressure, increase the pressure to a higher pressure than the reactor, directly feed it into the reactor
and let it stay for certain reaction time, and then discharge it from the bottom of the reactor. The
other aim of this work is to compare the hydrochar and process water obtained by this continuous
system with that of a batch operated system. Hence, the obtained hydrochars from both
configurations have been thoroughly investigated by performing proximate and ultimate analysis,
bomb calorimetry, TGA, FTIR, and XRD.

6.2. Material and methods
6.2.1. Design of a continuous system
The first challenge was the design of a hydraulic pump that is able to pressurize the mixture of
biomass and water and feed it into the reactor. This system should be able to generate a pressure
of at least 1000 psi and withstand an internal temperature of 285 °C. Another design constraint
considered in the development of the system was the ability to process a 20% biomass (1:5 biomass
to water ratio) input stream. The lower the biomass to water ratio and the smaller the biomass
particle size is, the easier the operation of the pump and piping would be. The details of the
proposed custom system can be seen in Figure 6.1.

Table 6.1 reports the main components of the feeding system. In order to pressurize and move the
provided biomass slurry, a stacked dual-piston-cylinder with the common shaft was designed. In
this system, two stacked cylinders with different diameters were used. The bottom cylinder (driver,
red in Fig 1 A) has a larger diameter, and this creates a mechanical advantage via a common ram
shared with the top cylinder (driven, black in Fig 6.1A).

According to Equation (6.1), the mechanical advantage of the different diameter bores was utilized
to increase the pressure of the top cylinder.

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In this equation, MA indicates the mechanical advantage ratio. Bore 1 indicates the diameter of the bottom cylinder (0.032 m) and Bore 2 is the bore diameter of the top cylinder (0.019 m). Knowing that the cylinder pushes by the hydraulic system with a force of 13.64 kN, using Equation (6.2), a pressure of 47.88 MPa (around 7000 psi) can be achieved which is more than the required pressures.

\[
P = \frac{F}{\pi \cdot \frac{d^2}{4}}
\]

Where P is the pressure in Pa, F is the push force of the cylinder in N, and d is the cylinder diameter in m. Furthermore, the volumetric flow rate of the pump can be found by knowing the cylinder diameter, and stroke from Equation (6.3).

\[
\dot{V} = \frac{(\pi \cdot \frac{d^2}{4}) \cdot h}{t}
\]

In Equation (6.3), \(\dot{V}\) is the volumetric flow rate \(\left(\frac{m^3}{s}\right)\), h is the cylinder stroke (0.15 m), and t is the stroke time (10 s). Hence, a flow rate of 4.33 \(\frac{ml}{s}\) can be achieved.

**Table 6.1. Description of the components of the feeding system**

<table>
<thead>
<tr>
<th>Component</th>
<th>Task</th>
<th>Main specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic cylinder</td>
<td>Piston actualization</td>
<td>6 in stroke, 1.25 in bore dia., ¾ in rod dia.</td>
</tr>
<tr>
<td>Hydraulic hosing</td>
<td>Connect the motor and hydraulic cylinder with the 4-way lever control valve</td>
<td>¼ in hose int. dia., High tensile steel, and rubber</td>
</tr>
<tr>
<td>Adapter sleeve</td>
<td>Connect the shaft and the piston of the hydraulic cylinder</td>
<td>Machined of a steel tube (schedule 80), uses 6 bolts for connection</td>
</tr>
<tr>
<td>Common shaft</td>
<td>Provide the compression to the feed</td>
<td>Schedule 160 steel</td>
</tr>
<tr>
<td>High-pressure connecting-tee</td>
<td>Connect the pumping, feed tank and reactor sides</td>
<td>1 in, high pressure</td>
</tr>
<tr>
<td>4-way lever control valve</td>
<td>Manually control the motion of the hydraulic cylinder</td>
<td>-</td>
</tr>
<tr>
<td>Multifunction hydraulic power unit</td>
<td>Power the hydraulic cylinder</td>
<td>½ HP, AC unit</td>
</tr>
</tbody>
</table>

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The HTC reactor was designed such that it can connect and utilize the high-pressure feed provided by the hydraulic pump. The requirements for the design included the ability to operate under a temperature of 285°C, withstand a pressure up to 1000 psi, and handle a concentration of up to 20% solids. The ability to safely handle temperatures and pressures while remaining airtight was tested by pressurizing the system to varying degrees of pressure and temperature for varying lengths of time. The main components of the reactor are presented in Table 6.2. In addition to considering the ability to receive, process, and deliver the products, the maintenance, and transportation capabilities of the system were also considered. The flange connection at the top of the reactor allows the ease of opening and cleaning whenever required. Moreover, the whole system was designed in such a way that it can be fit on support with wheels at the bottom. This portable design enables the system to easily move from one place to another.

**Table 6.2. Description of the components of the HTC reactor**

<table>
<thead>
<tr>
<th>Component</th>
<th>Task</th>
<th>Main specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heater control unit</td>
<td>Heat up the reactor and maintain the set temperature by a thermocouple connection of heater and the controller</td>
<td>850 W Omega ceramic pipe heater, Omega temperature controller, K-type thermocouple</td>
</tr>
<tr>
<td>Rotating ball valves</td>
<td>Continuously transfer stream to and from the reactor while maintaining pressure</td>
<td>1200 psi at 280 °C, body and seat made of 316 Stainless Steel</td>
</tr>
<tr>
<td>Pressure relief valve</td>
<td>Opens at a specified pressure and releases fluid from inside a pressure vessel</td>
<td>Set pressure: 700 psi</td>
</tr>
<tr>
<td>Reactor</td>
<td>The main chamber for the HTC process</td>
<td>Built of 2 ½ in pipe, 18 in long</td>
</tr>
<tr>
<td>Flange connection</td>
<td>To connect the reactor inlet valve and fitting to the reactor body</td>
<td>Stainless steel and ¾” diameter, 4 3/4” bolts, heavy-duty nuts and washer at each end, high pressure and temperature gasket in between the flange.</td>
</tr>
<tr>
<td>Hand trolley (Reactor support)</td>
<td>To enable moving the whole set up from one place to another</td>
<td>Hand trolley bolted and welded to the reactor body</td>
</tr>
</tbody>
</table>

This custom system was first designed in Solid Works and then was built in the machine shop at the University of Guelph. The system can be divided into three zones. The volume between
Valves 1 and 2 (Zone 1) is around 0.22 Lit, the volume of the reactor (between Valve 2 and Valve 3) is around 1.5 L (Zone 2), and the volume between Valves 3 and 4 (Zone 3) is around 0.1 Lit.

Figure 6.1. A) Solid Works design of the system, and B) built system

6.2.2. Feed

Sawdust produced from hardwood was used to run all HTC experiments. The size distribution of the feed particles was in a range of 500-1000 µm. A 1:10 biomass to water ratio was considered. The biomass and water were completely stirred and then introduced to the feeding hopper of the system.
6.2.3. HTC experiments and characterization of the products

In order to ensure the consistency of the test conditions and to have a fair comparison, the same system was used in a batch mode for the batch experiments. The HTC temperatures for continuous and batch processes were 180, 210, 240, and 260 °C. The corresponding pressures for these temperatures were 253, 305, 510, and 700 psi respectively. The maximum temperature was selected due to the restrictions of the maximum pressure (1000 psi) and for the safety of the operation. The minimum temperature was selected due to the fact that initial changes during HTC occur from around 180 °C [3]. The reaction time at the set point temperature for all experiments was considered as 60 minutes. All of the HTC experiments were performed two times to ensure reproducibility.

After collecting the products from the bottom of the reactor in a bucket, the hydrochar was separated from the process of water using filter papers. The separated hydrochar was dried in an oven at 105 °C overnight. The solid mass yield (MY) of each process was then calculated by dividing the initial mass of the biomass to the mass of the dried hydrochar. Further characterizations were then performed on the dried hydrochars to investigate the physical and chemical differences.

The proximate analysis was conducted using ASTM standards [33] to determine the content of ash, volatile matter (VM), and fixed carbon (FC). The ultimate analysis was performed using Flash 2000 Elemental Analyzer (Thermo Fisher Scientific, Waltham, MA, USA) to find the percentage of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S). The oxygen content was then found by Equation (6.4):

\[
O\% = 100\% - C\% - H\% - N\% - S\% - \text{Ash}\% \quad (6.4)
\]

The higher heating value (HHV) of the hydrochars was measured via IKA-C200 bomb calorimeter (IKA Works, Wilmington, NC, USA). Moreover, the thermal decompositions of the samples were studied by Thermo-gravimetric analysis (TGA) using a TGA machine (SDT-Q600, TA instruments-Waters LLC, New Castle, USA). Fourier-transform infrared spectroscopy (FTIR) tests were carried out to determine the functional groups on the hydrochar surface using Spotlight 200i FT-IR Microscopy System (PerkinElmer, Massachusetts, USA). A small amount of the dried hydrochars (around 5 mg), was placed on the diamond crystal and then secured tightly with a clamp for IR analysis. A total of 32 images at 4
cm⁻¹ resolution were averaged to give the final spectrogram for each sample. The obtained spectra were then analyzed with OriginPro data analysis and graphing software (Version 9, OriginLab Corporation, Northampton, MA, USA).

X-ray powder diffraction (XRD) measurements were conducted to investigate the structural differences of the obtained hydrochars in batch and continuous modes. The measurements were carried out using Rigaku Automated Powder X-Ray Diffractometer (Rigaku, Tokyo, Japan). The copper X-ray tube (wavelength of 1.54 Å) was operated at 40 kV and 44 mA. The measurement scan was performed at 0.1 scans/min, in the range 2θ = 1–30. The depth of the samples was 0.5 mm and they were uniformly speeded in an aluminum surface. The X-Ray spectra were analyzed using the MDI Jade 9 (MDI, Livermore, CA, USA) software.

BET analysis was performed by placing the samples degassing module of a Quantachrome 4200e Surface Area and Pore Analyzer and recording the volume of the adsorbate gas (nitrogen) at -196 °C, and relative pressures ranging from 0.05 < P/Po < 0.97.

In addition to all characterizations on the hydrochar mentioned above, total organic carbon (TOC) of the process water was measured by a TOC meter (Model: TOC-VCPN, Shimadzu Corporation, Kyoto, Japan). Further information regarding the procedure of ultimate, proximate, bomb calorimetry, TGA, BET, and TOC analysis can be found in ref. [95].

6.3. Results and discussion
6.3.1. Characterization of the products

Batch and continuous HTC experiments were carried out to compare the effects of temperature on product distribution and properties. As shown in Table 6.3, in batch and continuous experiments, the reaction temperature was changed between 180 °C and 260 °C, while the reactor pressure changed from 250 to 700 psi, and the reaction time was 60 min for all cases. For both batch and continuous experiments, by increasing the temperature, the solid mass yield decreased, and the carbon content increased, which is in line with other results in the literature [13], [14]. By increasing the temperature from 180 °C to 260 °C, in the batch mode, the hydrochar yield decreased from 69% to 51.76% and carbon content increased from 53.61% to 61.95%. Meanwhile, the decrease of the mass yield for the continuous experiments was from 74.10% to 48.23%, and the increase in the carbon content was from 52% to 64.91%. An interesting observation is that the batch operation in lower temperatures (less than 240 °C) has resulted in higher degrees of
carbonization, however, above 240 °C, the continuous operation results in hydrochar with higher carbon content and heating value. At 260 °C, the continuous operation resulted in around 3.53% lower mass yield, but 2.96% higher carbon content, and, consequently, 2.15 MJ/kg higher energy content than the batch operation.

Table 6.3. Bio-products distribution and properties of batch and continuous operations

<table>
<thead>
<tr>
<th>Condition</th>
<th>Hydrochar Yield (wt%)±1</th>
<th>Elemental and proximate analysis (wt%)± 0.1</th>
<th>Solid Portion ± 0.1</th>
<th>Liquid Portion ± 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>-</td>
<td>-</td>
<td>44.13</td>
<td>6.15</td>
</tr>
<tr>
<td>B-180</td>
<td>69</td>
<td>22.80</td>
<td>53.61</td>
<td>5.56</td>
</tr>
<tr>
<td>C-180</td>
<td>74.10</td>
<td>20.25</td>
<td>5.65</td>
<td>52</td>
</tr>
<tr>
<td>B-210</td>
<td>59.8</td>
<td>30.3</td>
<td>9.9</td>
<td>55.92</td>
</tr>
<tr>
<td>C-210</td>
<td>60.95</td>
<td>29.59</td>
<td>9.46</td>
<td>54.21</td>
</tr>
<tr>
<td>B-240</td>
<td>56.51</td>
<td>35.92</td>
<td>7.57</td>
<td>56.49</td>
</tr>
<tr>
<td>C-240</td>
<td>55.85</td>
<td>34.75</td>
<td>9.40</td>
<td>57.11</td>
</tr>
<tr>
<td>B-260</td>
<td>51.76</td>
<td>39.11</td>
<td>9.13</td>
<td>61.95</td>
</tr>
<tr>
<td>C-260</td>
<td>48.23</td>
<td>38.44</td>
<td>13.33</td>
<td>64.91</td>
</tr>
</tbody>
</table>

To understand why by increase in the operating temperature of HTC, a continuous carbonization can be as good as batch operation or even better, it is beneficial to have a closer look at the carbonization pathways. The final hydrochar in HTC is produced from two different pathways. The first pathway is called solid-solid conversion which results in primary hydrochar. During this pathway, the hydrochars maintains in the original structure of the biomass and depending to the degree of carbonization loses majorly of hemicellulose, some parts of the cellulose and a small amount of lignin [196]. This primary hydrochar is the ready to allow the deposition of some extra solids (secondary hydrochar) on its pores. The second pathway is due to coupling of the fragments in the aqueous phase followed by polymerization which results in the secondary hydrochar [197]. This part of hydrochar that is a result of production of fulfurals and intermediate organic acids and subsequent polymerization as microspheres deposits on the pores of the primary hydrochar and can be subject to many changes depending on the HTC condition [198].

Hence the comparison of the hydrochars obtained from the batch and continuous operations can be assisted by discussion on the degree of formation and carbonization of primary and secondary hydrochars. On the one hand, it can be hypothesized that due to additional time for the increase of temperature to the set temperature in the batch operation, the secondary hydrochar will be more dominant in comparison to continuous operation. On the other hand, the instant exposure of the
biomass to the high temperature and pressure of the process during the continuous operation, significantly enhances the carbonization of the primary hydrochar.

In order to monitor the concentration of organic-based intermediates derived from hydrochar decomposition, TOC analysis was performed. As seen in Table 6.3, the highest TOC (59.11 mg/l) was obtained at C-260. Generally, with an increase in the temperature, the TOC increases, unless the carbonization of some parts of the derived monomers in the process water via consecutive reactions occurs which will result in the further hydrochar formation [57]. This is more pronounced in the batch experiment at 240 °C and 260 °C, where their TOC contents are smaller than the corresponding continuous experiments. This shows that the primary carbonization has the dominant reactions during continuous HTC and overcomes the secondary hydrochar reactions observed in batch HTC.

It is also observed that C-260 has the greatest HHV as it had the highest carbon (64.91 wt%) and lowest oxygen (28.5 wt%). The HHV of the hydrochar at C-260 was 8% higher than that of B-260. The HHV values in all experiments show a linear relationship with the oxygen content. In fact, the rise of temperature coincides with higher deoxygenation resulting in higher HHV [199]. Total carbon retained in hydrochar derived from continuous experiments decreased with the increase in temperature. The reason might be due to the dissolution of surface nitrogen and oxygen-based salts in the liquid, decarboxylation, denitrogenation, and deoxygenation.

**6.3.2. X-ray diffraction analysis of the hydrochars**

Figure 6.2 shows XRD patterns of raw biomass and hydrochars derived from HTC at the temperature of 260 °C. The intensive peaks at 22.45° and 34.25° in raw biomass show the crystalline regions of cellulose [16].
The XRD pattern of the hydrochars can be affected by the degree of degradation of cellulose [21,22]. As shown in Figure 6.2., when the experiment performed at 260 °C, strong peaks recorded from cellulose lost their intensity and became broader which is in association with the transition of the crystalline structure of cellulose into the amorphous [23]. In the case of C-260, another peak related to the graphene sheets structure was appeared at 2θ position of 45.5° showing the formation of graphene sheets among the turbostratic structure of carbon. This phenomenon could result in the conductivity of the hydrochar and make it a potential material for energy storage systems [24].

6.3.3. Thermal decomposition behavior and volatile matter composition

TGA and DTG analysis were conducted to investigate the thermal decomposition behaviors of the samples. As shown in Figure 6.3, The initial weight loss for all samples starts from around 100 °C by the release of moisture and continues by the release of some of the organic matter [25]. The second stage which is the major weight loss occurred from around 275 °C up to 375 °C for the raw sample (68% weight loss). This stage started and ended at higher temperatures for the hydrochars. In general, the higher is the temperature of HTC temperature, the higher temperature is required to start the major weight loss in the TGA analysis. For instance, for B-180 and C-180, the range of the major weight loss was from 300 °C to 575 °C (around 52% weight loss) and for B-260, and
C-260 was from 375 °C to 725 °C (around 40% weight loss). This is why the thermal stability of C-260 was the highest and the one for C-180 was the lowest among the hydrochars.

Figure 6.3. TGA and DTG curves of the hydrochars obtained by batch and continuous operation

The differences in the TGA curves of the hydrochars obtained from continuous HTC with the ones obtained from the batch HTC, reveals interesting information. While the hydrochars obtained at the low temperature from the batch HTC (B-180) were slightly more stable than the continuous HTC (C-180), the trend was reversed by an increase in the temperature. The TGA curves of B-210 and C-210 were almost the same, but at 240 °C, C-240 was more stable than B-240. The most significant difference was observed between C-260, and B-260, where B-260 lost 4% more weight. This indicates that the C-260 hydrochar experienced the maximum removal of volatile matters and was thermogravimetrically the most stable. This trend is highly correlated to the oxygen content of the hydrochar and confirms the enhanced solid fuel quality of the hydrochar. Interestingly, it was found that the continuous HTC reactor could overcome the technical barriers of batch mode at temperatures above 240 °C. This phenomenon confirms the high thermal stability of C-260 and makes it a possible alternative to coal and other conventional solid fuels. It is known that secondary hydrochar consists of volatile organics condensing into the primary hydrochar pores that can devolatilize from the surface during combustion at relatively lower temperatures and decrease the thermal stability of the hydrochar. This phenomenon can result in the lower temperature ignition and reduced boiler efficiency [197]. As the batch operation results in higher amounts of secondary
hydrochar, it can lead to more operational problems during combustion. Most of the studies that have evaluated the feasibility of a continuous HTC plant [142], [200], [201], rely on the data produced or adopted from lab-scale batch reactors, however, the hydrochars produced from a real continuous reactor can show even better performance than the ones from batch operations.

6.3.4. Determination of functional groups

The FTIR analysis of the hydrochars shown in Figure 6.4 was carried out to investigate the functional groups. The detected peaks are reported in Table 6.4.

![Figure 6.4. FTIR spectra of the hydrochars obtained by batch and continuous operation](image)

**Table 6.4. Detected peaks of FTIR analysis of the hydrochars obtained by batch and continuous operation**

<table>
<thead>
<tr>
<th>Detected peak (cm⁻¹)</th>
<th>Class</th>
<th>Structure</th>
<th>High</th>
<th>Low</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3330</td>
<td>Amides</td>
<td>RCONH₂</td>
<td>3335</td>
<td>3325</td>
<td>NH stretch</td>
</tr>
<tr>
<td>3292</td>
<td>Carboxylic acid</td>
<td>RCO-OH</td>
<td>3400</td>
<td>2800</td>
<td>Dimer OH</td>
</tr>
<tr>
<td>2929</td>
<td>Alkanes</td>
<td>-CH₂</td>
<td>2930</td>
<td>2920</td>
<td>-CH₂</td>
</tr>
<tr>
<td>2850</td>
<td>Alkanes</td>
<td>RCH₂CH₃</td>
<td>2800</td>
<td>3400</td>
<td>CH stretch</td>
</tr>
<tr>
<td>1592</td>
<td>Aromatic</td>
<td>C-C in ring</td>
<td>1600</td>
<td>1585</td>
<td>Ar C-C stretch</td>
</tr>
<tr>
<td>1514</td>
<td>Misc.</td>
<td>N=O niroso</td>
<td>1600</td>
<td>1500</td>
<td>N=O niroso</td>
</tr>
<tr>
<td>1457</td>
<td>Alkanes</td>
<td>RCH₂CH₃</td>
<td>1450</td>
<td>1470</td>
<td>CH₂ and CH₃</td>
</tr>
<tr>
<td>1313</td>
<td>Amines</td>
<td>Ar₂NH</td>
<td>1250</td>
<td>1360</td>
<td>Ar-N stretch</td>
</tr>
<tr>
<td>1161</td>
<td>Amines</td>
<td>RNH₂</td>
<td>1030</td>
<td>1200</td>
<td>C-N stretch</td>
</tr>
<tr>
<td>1112</td>
<td>Ethers</td>
<td>R-O-R</td>
<td>1150</td>
<td>1070</td>
<td>C-O stretch</td>
</tr>
</tbody>
</table>
The peaks shown in the range of (3400–2800 cm$^{-1}$) are mainly due to the aliphatic OH stretching vibration of hydroxyl and carboxyl groups [202]. The peaks in the range of 1150-1070 cm$^{-1}$ represent the stretching vibrations of C – O groups. The weakest peaks at these ranges are related to C-260 and C-240, which indicates they have experienced a high degree of dehydration and decarboxylation. Based on the results, the C-260 hydrochar is the most hydrophobic due to showing the least intensity at 3400–2000 cm$^{-1}$. Overall the observations from this section confirm the stronger carbonizations occurring in the continuous HTC above 240 °C. At lower temperatures of HTC, cellulose and hemicellulose can be hydrolyzed into polysaccharides as macro-intermediates. As the temperature increased, the peaks at around 1457, 1592, 1710 and 3292 cm$^{-1}$, corresponding to the carboxylic acids and ester functional groups in polysaccharides, became more pronounced. This phenomenon is in agreement with the XRD spectra of samples in which the crystalline structure of cellulose is transformed into the amorphous structure. Peaks at 1457 and 1592 cm$^{-1}$ are due to the stretching of aromatic lignin bonds (Ar C–C) which is due to the condensation, dehydration, and decarbonization of intermediates [203].

**6.3.5. The porous structure of hydrochars**

BET analysis on all hydrochars was conducted to investigate the changes of the porous structure with batch or continuous treatments. All samples showed the same kinetics of the reaction toward nitrogen adsorption on the biochar surfaces and the type of the porous structure for all of them is hierarchical. However, the hydrochars obtained from continuous operation at high temperatures (especially 260 °C), show increased surface areas. The surface area of the B-180, and C-180 are around 4.6 m$^2$ g$^{-1}$, they increase to around 7.24 m$^2$ g$^{-1}$ at 210 °C for both batch and continuous operation. At 240 °C, the surface area for B-240 is 10.63 m$^2$ g$^{-1}$, while for C-240, the surface area is slightly higher: 12.80 m$^2$ g$^{-1}$. This difference is even more vivid at 260 °C, where B-260 has a surface area of 13.45 m$^2$ g$^{-1}$, but for C-260 a significant increase is observed: 15.09 m$^2$ g$^{-1}$. The observations from BET analysis confirms the previous results and is another indication of the suppression of the secondary hydrochar production at high-temperature continuous HTC. As the reactions in these situations are
more abrupt rather than equilibrium type, the occurrence of primary carbonization is more significant, lowering the deposition of aqueous matters in the pores of the hydrochar and increasing the surface area.

6.4. Conclusion
The development of a novel portable continuous HTC system and characterization of its products were reported. The results showed that the hydrochars obtained from continuous operation below 240 °C were only slightly less carbonized, but above 240 °C showed higher degrees of carbonization. To conclude, the study confirms the necessity to step towards the development of continuous systems for commercialization of HTC and indicates one of the possible configurations. The authors believe that, the transition of HTC from lab-scale batch reactors to commercial scale continuous reactors along with the water and heat recovery is of high necessity by which not only the operational energy and water consumption would decrease, but also this research showed that higher qualities of the hydrochar can be obtained.
Chapter 7. Numerical comparison of a combined hydrothermal carbonization and anaerobic digestion system with direct combustion of biomass for power production

This chapter is This study is aimed at designing and analyzing two scenarios for bioenergy production from undervalued biomass (sawdust). In one of the scenarios (direct combustion or DC), raw biomass is burned in a combustor to provide the heat that is required by the Rankine cycle to generate electricity. In the other scenario (HTC-AD), the raw biomass first undergoes HTC treatment. While the solid product (hydrochar) is used to produce power by a Rankine cycle, the liquid by-product undergoes an AD process. This results in fuel gas production and it can be used in a Brayton cycle to generate more power. Energy and mass balance analysis of both scenarios were developed for each unit process by using Engineering Equation Solver (EES). The required data were obtained experimentally or from the literature. The performances of the proposed systems were evaluated, and a sensitivity analysis was presented to help in finding the best operational conditions.


7.1. Introduction

Research on biomass conversion has been extensively conducted in the lab scale, however, there is a sensible gap regarding the practical and industrial design and environmental assessments. The integration of the biomass treating processes cannot only make the whole process more energy-efficient, but it can also further reduce the waste considerably based on the circular economy [187]. Reza et al. [157] used the digestate from an AD process operating at thermophilic conditions (50-60 °C) as a feed for HTC. The energy recovery of this combination was 20% higher than energy recovery from HTC and 60% higher than the one for AD. The AD-HTC process proposed by Reza et al. [157] can be reversed to HTC-AD [204] such that the biomass is firstly fed to the HTC process where its alkali content dissolves in the process water (PW) and produces hydrochar with lower ash content that is more suitable for boilers [176]. In addition to the use of hydrochar for power generation, the process water can enter an existing AD system. The pH of the PW is in the
range of 2.7-3.5 [88], [95], and hence, it can accelerate the hydrolysis step in AD. As hydrolysis is considered as the limiting factor of AD systems [205], ease of conversion in the AD system is expected. This study is aimed at introducing two different scenarios for bioenergy production using direct combustion for one scenario and a combination of hydrothermal carbonization and anaerobic digestion for the other one. Both scenarios integrate the power cycles and the biomass conversion processes with heat recovery and internal energy supply. The required data for HTC were obtained from lab-scale experiments. These data include hydrochar’s mass yield, heating value, and elemental composition. The governing thermodynamic equations of the systems were developed by Engineering Equation Solver (EES). The main goals of this study are to develop and perform numerical analysis on an integrated HTC-AD scenario for converting biomass to energy, and to compare the performance of electricity production by the proposed method with direct combustion of the raw biomass.

7.2. Material and methods
7.2.1. Feed
Both systems can work with a variety of biomass. For this study, sawdust has been considered as the feedstock which is tiny pieces of wood that fall as a powder from wood as it is cut by a saw [206]. Sawdust is one of the most abundant biomass and it is interesting to know that more than 5 million tons of sawdust surplus was available in Canada alone in 2004 [207].

7.2.2. HTC and characterization tests
Some of the main primary data were obtained by performing lab-scale experiments. The HTC experiments were conducted using the Parr 600 mL series 4560 mini reactor and approximately 20 g of sawdust was used for each experiment. For HTC, dry biomass to water mass ratio of 1:5 was used. After stirring the sawdust and water mixture in the reactor, it was sealed and pressurized by nitrogen gas to ensure the pressure inside the reactor is always above the saturation pressure of water. The reactor was then heated up to 220 °C and kept at this temperature for 40 min. The reactor was then immediately submerged into iced water until the temperature decreased to below 30 °C. The liquid–hydrochar mixture was removed from the reactor and separated using filter paper. The solid sample was placed inside a tin crucible and left in a furnace overnight at 105 °C to dry.

Higher heating value (HHV) test was then performed on the raw feed and solid products of HTC using the IKA bomb calorimeter. Moreover, the proximate analysis and ultimate analysis were
performed on the obtained hydrochar and the raw sample. More details on the procedure of these characterization tests and the composition of the products can be found in Ref. [95].

7.2.3. Description of the first scenario

In the HTC-AD scenario, HTC was scaled up and combined with Rankine, and Brayton cycles and anaerobic digestion process. Figure 7.1 shows the schematic of scenario 1. Biomass is mixed with the hot pressurized water. It is worth mentioning that unlike the experiment mentioned in the previous section; the HTC reactor is not pressurized with the nitrogen gas but is pressurized with the water that enters the reactor using a high-pressure pump. Moreover, the required heat for HTC is provided by a heat exchanger that recovers the heat from the Rankine and Brayton cycles. The main product of HTC is wet hydrochar which is utilized in a Rankine cycle after getting dried in the drier. Table 7.1 is a stream table to help understand the conditions of each stream in the HTC-AD scenario.

![Figure 7.1. Schematic of the hydrothermal carbonization-anaerobic digestion (HTC-AD) scenario](image-url)
<table>
<thead>
<tr>
<th>State Number</th>
<th>Temperature (°C)</th>
<th>Mass Flow Rate (g/s)</th>
<th>Other Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25</td>
<td>16</td>
<td>10% moisture content</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>75</td>
<td>$p = 101$ kPa</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>75</td>
<td>$p = 1800$ kPa</td>
</tr>
<tr>
<td>3</td>
<td>176.6</td>
<td>75</td>
<td>$p = 1800$ kPa</td>
</tr>
<tr>
<td>4</td>
<td>95</td>
<td>10.06</td>
<td>Contains 0.7 g/s of water</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>0.43</td>
<td>Gaseous mixture (mainly CO$_2$)</td>
</tr>
<tr>
<td>6</td>
<td>180</td>
<td>74.3</td>
<td>Including 4.6 g/s mass yield from biomass flow</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>74.3</td>
<td>Mixture of water and acidic components</td>
</tr>
<tr>
<td>8</td>
<td>60</td>
<td>5.56</td>
<td>Including 1.54 g CH$_4$, and the rest is CO$_2$</td>
</tr>
<tr>
<td>9</td>
<td>25</td>
<td>8.38</td>
<td>$p = 101$ kPa</td>
</tr>
<tr>
<td>10</td>
<td>473</td>
<td>8.38</td>
<td>$p = 1717$ kPa</td>
</tr>
<tr>
<td>11</td>
<td>1200</td>
<td>13.94</td>
<td>$p = 1717$ kPa</td>
</tr>
<tr>
<td>12</td>
<td>350</td>
<td>13.94</td>
<td>Gaseous outlet of GT</td>
</tr>
<tr>
<td>13</td>
<td>230</td>
<td>13.94</td>
<td>Gas</td>
</tr>
<tr>
<td>14</td>
<td>132.8</td>
<td>13.94</td>
<td>Gas</td>
</tr>
<tr>
<td>15</td>
<td>50.53</td>
<td>13.94</td>
<td>Gas emission</td>
</tr>
<tr>
<td>16</td>
<td>120</td>
<td>0.7</td>
<td>Steam</td>
</tr>
<tr>
<td>17</td>
<td>50</td>
<td>9.36</td>
<td>HHV = 24,600 [kJ/kg]</td>
</tr>
<tr>
<td>18</td>
<td>120</td>
<td>86.92</td>
<td>Gaseous mixture (mainly CO$_2$)</td>
</tr>
<tr>
<td>19</td>
<td>120</td>
<td>88.05</td>
<td>Gaseous mixtures to sustain AD process</td>
</tr>
<tr>
<td>20</td>
<td>25</td>
<td>88.05</td>
<td>Gas emission</td>
</tr>
<tr>
<td>21</td>
<td>40.53</td>
<td>72.92</td>
<td>$p = 1800$ kPa</td>
</tr>
<tr>
<td>22</td>
<td>45</td>
<td>72.92</td>
<td>Rankine process water</td>
</tr>
<tr>
<td>23</td>
<td>48</td>
<td>72.92</td>
<td>Rankine process water</td>
</tr>
<tr>
<td>24</td>
<td>540</td>
<td>72.92</td>
<td>Superheat steam</td>
</tr>
<tr>
<td>25</td>
<td>280</td>
<td>70.4</td>
<td>$p = 850$ kPa</td>
</tr>
<tr>
<td>26</td>
<td>280</td>
<td>2.52</td>
<td>$p = 850$ kPa</td>
</tr>
<tr>
<td>27</td>
<td>230</td>
<td>2.52</td>
<td>Steam to heat up HTC</td>
</tr>
<tr>
<td>28</td>
<td>54.97</td>
<td>2.52</td>
<td>Hot water</td>
</tr>
<tr>
<td>29</td>
<td>50.53</td>
<td>2.52</td>
<td>Hot water</td>
</tr>
</tbody>
</table>
The liquid by-product of the HTC exchanges its heat with the water stream entering the HTC reactor and then enters into the AD system. The main output of this AD system is a gas stream enriched in methane and hydrogen. This gas stream then enters the combustion chamber of a Brayton cycle and its combustion reaction with the compressed air rotates the gas turbine blades and provides more electricity. The gas turbine’s exhaust is at high temperature [208], [209], hence, before releasing this hot stream to the atmosphere, its heat is transferred to the HTC reactor. If the gas turbine’s exhaust heat is insufficient for the HTC process, excess heat is supplied from the lower stages of the steam turbine of the Rankine cycle. The power that is generated by the steam turbine is used wherever electricity was required (for the pumps and the compressor).

### 7.2.4. Description of the second scenario

As shown in Figure 7.2, in this scenario, the biomass is introduced to the drier as the first processing step in this scenario (direct combustion (DC)) [210]. Afterward, the dried biomass is utilized in a boiler to convert a water stream to steam, which can then produce the power after expansion in the turbine. Table 7.2 reports the stream table of the DC scenario.

![Figure 7.2. Schematic of the direct combustion (DC) scenario](image)
Table 7.2. Stream table of direct combustion (DC) scenario

<table>
<thead>
<tr>
<th>State Number</th>
<th>Temperature (°C)</th>
<th>Mass Flow Rate (g/s)</th>
<th>Other Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25</td>
<td>16</td>
<td>10% moisture content</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>14.40</td>
<td>HHV = 17,800 [kJ/kg]</td>
</tr>
<tr>
<td>2</td>
<td>110</td>
<td>1.60</td>
<td>Steam</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>4.38</td>
<td>Water back to the cycle</td>
</tr>
<tr>
<td>4</td>
<td>110</td>
<td>141.55</td>
<td>Gaseous mixture (mainly CO₂)</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>141.55</td>
<td>Gas emission</td>
</tr>
<tr>
<td>6</td>
<td>40.53</td>
<td>82.80</td>
<td>$p = 1800$ kPa</td>
</tr>
<tr>
<td>7</td>
<td>66.14</td>
<td>82.80</td>
<td>Rankine process water</td>
</tr>
<tr>
<td>8</td>
<td>540</td>
<td>82.80</td>
<td>Superheat steam</td>
</tr>
<tr>
<td>9</td>
<td>160</td>
<td>80.02</td>
<td>Entering superheat steam to low pressure GT</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>80.02</td>
<td>Saturated steam</td>
</tr>
<tr>
<td>11</td>
<td>40</td>
<td>82.80</td>
<td>Saturated water</td>
</tr>
<tr>
<td>12</td>
<td>110</td>
<td>2.78</td>
<td>Steam to help with drying</td>
</tr>
</tbody>
</table>

7.2.5. Assumptions and other required data from the literature

As the systems explained in sections 7.2.3 and 7.2.4 incorporate several types of equipment, several assumptions such as the operational conditions of each equipment should be considered. Moreover, some of the data are not obtained via experiments. Hence, this section clarifies the assumptions and data obtained from the literature. It was assumed that the HTC is scaled up to a continuous reactor and the flow rate of the biomass to this reactor is 0.016 kg/s. The same flow rate was considered for the second scenario. The initial moisture content of the biomass was 10% and a 1:5 dry biomass to water moisture was considered for HTC.

The process water from HTC is acidic and contains water, acetic acid and a number of other organic acids [95]. According to Kambo et al. [88], these organic acids mainly contain acetic acid, 5-Hydroxyl Methyl Furfural (HMF), and levulinic acid. The composition of the process water that was considered in this study is reported in Table 7.3. It is worthwhile to note that a more accurate and detailed research study on HTC should consider the presence of other organic compounds,
such as glycolic acid or formic acid. In this research due to the high number of equations only three of the components were considered.

Table 7.3. Composition of bio-oil from HTC

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Formula</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>CH₃COOH</td>
<td>40</td>
</tr>
<tr>
<td>HMF</td>
<td>C₅H₈O₃</td>
<td>40</td>
</tr>
<tr>
<td>levulinic acid</td>
<td>C₆H₆O₃</td>
<td>20</td>
</tr>
</tbody>
</table>

The chemical reactions of these acids in AD were considered based on Buswell and Muller [211] and are as follows:

\[
\text{CH}_3\text{COOH} \rightarrow \text{CO}_2 + \text{CH}_4 \quad (7.1)
\]
\[
\text{C}_5\text{H}_8\text{O}_3 + 1.5 \text{H}_2\text{O} \rightarrow 2.25 \text{CO}_2 + 2.75 \text{CH}_4 \quad (7.2)
\]
\[
\text{C}_6\text{H}_6\text{O}_3 + 3 \text{H}_2\text{O} \rightarrow 3 \text{CO}_2 + 3 \text{CH}_4 \quad (7.3)
\]

It should be noted that the presence of other elements, such as nitrogen (in other feedstocks such as algae), would result in nitrogen compounds in the bio-oil and bio-gas. Hence, the Equations (7.1)–(7.3) should be updated for other feedstocks. Moreover, the addition of materials that help to buffer pH changes and regulate the pH might be required, as the pH of the organic materials entering the AD is around 3, and most of the commercial AD systems work in a pH range of 6.7–7.8 [212].

The gas composition exiting the HTC was considered to be all carbon dioxide according to Yan et al. [30], due to its considerably higher abundance than other gases. The combustion of the biomass and hydrochar in the boilers, as well as the combustion of the obtained gases from AD in the combustion chamber, was considered with 150% of excess air.

It was also assumed that the system operates at steady-state and steady flow conditions. Moreover, the HTC temperature is 220 °C, and the AD system operates at 35 °C, the process water leaves the HTC at 180 °C, the air consists of 79% nitrogen, and 21% oxygen and the air, biogas and combustion products are considered as ideal gases. Regarding the temperature of the PW, it should be noted that this temperature is highly dependent on the design of a continuous HTC system that can discharge the process water at that temperature. Given that, to date, there is no clear report
regarding such a reactor, a sensitivity analysis will be performed to investigate the effects of lower temperatures of PW. The efficiencies for all exchangers, turbines, and compressors were considered as 80%, whereas for the pumps the efficiency was assumed as 70% [213]. A temperature approach of 10 °C was considered for all heat exchangers. Moreover, the design is such that the required heats for the drier and the HTC reactor are supplied by the boiler and the gas turbine exhaust respectively. The compressor and pumps use a portion of the produced power. Other assumptions considered in the EES codes of the scenarios are reported in Table 7.4.

### Table 7.4. Other assumptions of the integrated scenarios

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat capacity of the biomass (kJ/kg.K)</td>
<td>1.5</td>
</tr>
<tr>
<td>Heat capacity of water at room temperature</td>
<td>4.18</td>
</tr>
<tr>
<td>(kJ/kg.K)</td>
<td></td>
</tr>
<tr>
<td>The heat of vaporization of water (kJ/kg)</td>
<td>2260</td>
</tr>
<tr>
<td>Compressor exit pressure (kPa)</td>
<td>1717</td>
</tr>
<tr>
<td>Compressor compression ratio [209]</td>
<td>17</td>
</tr>
<tr>
<td>Methane heating value (MJ/kg) [214]</td>
<td>55.51</td>
</tr>
<tr>
<td>Flue gas temperature (°C) [215]</td>
<td>150</td>
</tr>
<tr>
<td>Exothermic heat of reaction in HTC (kJ/kg) [26]</td>
<td>765</td>
</tr>
<tr>
<td>The temperature of PW leaving HTC reactor (°C)</td>
<td></td>
</tr>
<tr>
<td>ST inlet temp. (°C)</td>
<td></td>
</tr>
<tr>
<td>GT exhaust temp. (°C) [216]</td>
<td></td>
</tr>
<tr>
<td>Ambient temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>Ambient pressure (kPa)</td>
<td>101</td>
</tr>
<tr>
<td>Maximum combustor temperature (°C)</td>
<td>900</td>
</tr>
<tr>
<td>The temperature of PW leaving HTC reactor (°C)</td>
<td></td>
</tr>
<tr>
<td>Exothermic heat of reaction in HTC (kJ/kg) [26]</td>
<td></td>
</tr>
</tbody>
</table>

7.3. Results and discussion

#### 7.3.1. Experimental results

The experimental results from characterization tests on the raw biomass and hydrochar obtained from HTC at 220 °C and 40 min are reported in Table 7.5.

### Table 7.5. Experimental results from characterization on the biomass and hydrochar

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Yields (%)</th>
<th>Ultimate Analysis (wt%)</th>
<th>Proximate Analysis (wt%)</th>
<th>Calorimetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solid</td>
<td>Liquid</td>
<td>Gas</td>
<td>C</td>
</tr>
<tr>
<td>Raw</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>49.22</td>
</tr>
<tr>
<td>Hydrochar</td>
<td>65</td>
<td>32</td>
<td>3</td>
<td>63.51</td>
</tr>
</tbody>
</table>
Based on the ultimate analysis, and the molar number of the elements, the empirical formula of the raw biomass and the hydrochar can be obtained as $\text{C}_{1.47}\text{H}_{2.23}\text{O}$ and $\text{C}_{2.72}\text{H}_{2.74}\text{O}$ respectively. These formulas were then used in the combustion equations in the boilers.

$$\text{C}_{2.72}\text{H}_{2.74}\text{O} + 2.9 (\text{O}_2 + 3.76 \text{ N}_2) \rightarrow 2.72 \text{ CO}_2 + 1.37 \text{ H}_2\text{O} + 10.9 \text{ N}_2 \quad (7.4)$$

$$\text{C}_{1.47}\text{H}_{2.23}\text{O} + 1.52 (\text{O}_2 + 3.76 \text{ N}_2) \rightarrow 1.47 \text{ CO}_2 + 1.11 \text{ H}_2\text{O} + 5.7 \text{ N}_2 \quad (7.5)$$

It should be noted that the ash content is an important element to consider when it comes to energy production from biomass. The ash content of the feedstock in this study was negligible (0.1%), but this may not be the case for other feedstocks. For instance, according to Phyllis database [217], the sawdust of different woods may contain up to 2% of ash content. In such situations, more treatments, like de-ashing before the combustion or utilizing specific boilers that can handle the ash content of the feedstock, should be considered.

### 7.3.2. Preliminary results from the first and second scenario

The preliminary results of the scenarios that are given in Table 7.6 are based on the assumptions and the calculations discussed above. As can be seen in Table 7.6, the direct combustion of biomass with 10% moisture content shows a better relative performance. The total power that is produced by the DC scenario is 101 kW, which is 5.21 kW higher than the HTC-AD scenario. In addition, the efficiency of the DC scenario is around 2% higher than that of the HTC-AD scenario.

### Table 7.6. Preliminary results of the HTC-AD and DC scenarios

<table>
<thead>
<tr>
<th>Item</th>
<th>HTC-AD Scenario</th>
<th>DC Scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass flow rate (g/s)</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Total produced power (kW)</td>
<td>95.79</td>
<td>101</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>37.37</td>
<td>39.40</td>
</tr>
<tr>
<td>Power by the steam turbine (kW)</td>
<td>90.03</td>
<td>103.10</td>
</tr>
<tr>
<td>Power by the gas turbine (kW)</td>
<td>11.74</td>
<td>-</td>
</tr>
<tr>
<td>Net power consumed by the HTC reactor (kW) (supplied from the boiler and GT exhaust)</td>
<td>6.90</td>
<td>-</td>
</tr>
<tr>
<td>The power produced by exothermic reactions (kW)</td>
<td>11.02</td>
<td>-</td>
</tr>
<tr>
<td>Net energy consumed by the drier (kW) (supplied from the boiler)</td>
<td>1.59</td>
<td>5.92</td>
</tr>
</tbody>
</table>

It is worth reminding the reader here that these results do not consider the complexities of the integration in the HTC-AD scenario and the possible problems with slagging and fouling in the
DC scenario due to the direct use of biomass without treatments. Moreover, it should be noted that the assumptions considered in obtaining the results had significant effects on the results. Out of the many assumptions listed above, the uncertainty that is associated with some parameters warrants further investigation. Hence, in the following sections, the effects of moisture content, HHV, and water in the HTC process on the total produced powers and efficiencies of both scenarios are investigated.

7.3.3. Sensitivity analysis
Biomass moisture content

The moisture content of the biomass is one of the key parameters for selecting a technology that deals with biomass to bioenergy conversion. Figures 7.3a and 7.3b show the effects of this parameter on both scenarios.

![Graph showing effects of biomass moisture content on net power and efficiency](image)

**Figure 7.3. Effects of biomass moisture content on (a) net power, and (b) efficiency of each scenario**

Increasing the moisture content of the biomass feedstock decreased the total power that was produced by both scenarios. With an increase in the moisture content from 0 to 70%, the power that was produced from the HTC-AD scenario dropped from 106.4 kW to 32.24 kW, while, for the DC scenario, it was from 113.30 kW to 27.08 kW. Regarding efficiency, the DC scenario shows a considerable decrease in the overall efficiency with an increase in the moisture content. However, for the HTC-AD scenario, the efficiency showed a slight increase with an increase in the moisture content. This interesting result shows that the main advantage of processes that use
HTC for treating the biomass is when the moisture content is higher. The processes that involve an initial stage of drying exhibit a reduction in efficiency due to higher amounts of moisture, which is energy intensive to remove. The power consumption of the drier in the DC scenario increases from 5.91 kW to 22.39 kW, when the moisture increases from 10% to 50%. As shown in Figure 3, the HTC-AD scenario shows a better performance than the DC one when the moisture content of the biomass is over 40%.

**HHV of the raw biomass and obtained hydrochar**

Higher heating value (HHV) is one of the critical properties when it comes to the design and calculations of thermal conversion systems for biomass. HHV can be considered as a specific property of each biomass as its value is different in one biomass from another. HHV of the hydrochar not only depends on the severity of the HTC process but is also highly dependent on the fiber structure and chemical composition of the biomass [218]. Figures 7.4a and 7.4b show the effects of changes in the HHV of the raw biomass in the net power and efficiency respectively. It is assumed that the HHV of the hydrochar in the first scenario is 6.8 MJ/kg higher than the corresponding HHV of the biomass-based on the results of the experiments (Table 7.5). It should also be noted that the moisture content is as its initial assumption (i.e. 10%).

![Figure 7.4. Effects of biomass HHV on (a) net power, and (b) efficiency of each scenario](image)

Figure 7.4a illustrates that, with an increase in the HHV of the biomass from 12 to 23 MJ/kg, the net power that was produced by both scenarios increases. With HHVs lower than 15.5 MJ/kg, the
DC scenario produces less power and it has lower efficiency. This can be an indication that direct combustion can be a better option when the heating content of the biomass in its raw form is relatively high. For instance, when the lignin content of the biomass is higher [218].

**Water: biomass ratio and the temperature and composition of process water from HTC**

The main feature of HTC that makes it different from other thermochemical processes is it being performed under a water medium. All of the biomass particles in the HTC should be in contact with water; however, it is clear that the more water is used, the more energy is required for the process. Hence, the water to biomass ratio is one of the key parameters for the design of an HTC reactor. Figure 7.5 indicates the effect of water on biomass ratio on the performance of the HTC-AD scenario. As expected, the net power output and efficiency decrease with an increase in the water to biomass ratio. Therefore, it is suggested that the use of water should be minimized after it is ensured that the biomass is fully submerged in the water.

![Figure 7.5](image)

*Figure 7.5. Effects water to biomass ratio on the performance of the first scenario*

The other issue that can affect the HTC-AD scenario is the composition of the process of water entering the AD process. This is highly dependent on the type of biomass and HTC process condition. Figure 7.6 compares the performance of the HTC-AD scenario while considering that 100% of the obtained organic acids are one of the acetic acid, HMF, or levulinic acid. Figure 7.6 shows that the performance of the bioenergy systems improves if the composition of the PW contains more HMF or levulinic acid. The assumptions of 100% of these components are only
from a statistical point of view to show the effects of each of the components clearly and cannot happen in real situation.

![Figure 7.6. Effect of PW composition on the performance of the first scenario](image)

In addition to the parameters discussed above, the PW temperature of the HTC process can play an important role in the reduction of energy usage by the HTC reactor and consequently the whole process. Figure 7.7 indicates the energy consumed by the HTC reactor, as well as, the output power and efficiency of the first scenario while varying the temperature of the PW.

![Figure 7.7. Effect of temperature of PW on the performance of the HTC reactor and overall scenario](image)
While considering a temperature of 220 °C for the HTC process, the ability of the reactor to discharge the process water to the heat exchanger in as high temperature as possible is crucial. The efficiency of the system can increase by around 5% with an increase in the temperature of the discharged PW from 40 °C–190 °C. This again shows the importance of designing reactors that can recover the heat.

7.4. Conclusion

This research investigated two possible scenarios for producing power from biomass. The HTC-AD scenario integrated HTC and AD with power cycles, whereas the DC scenario only utilizes integrated direct combustion of the biomass with the Rankine cycle. It was shown that a 16 g/s sawdust biomass stream with 10% moisture content can produce 95.79 kW power for the HTC-AD scenario, whereas the DC scenario can produce 101 kW. While considering the complexity and potential capital costs of the HTC-AD scenario, the direct use of the biomass might seem like a better option for sawdust. However, it was shown that an increase in moisture content makes the HTC-AD scenario superior in terms of efficiency and produced power. In an integrated system, several parameters can have significant impact on the objective parameters of the system. For instance, it was shown that the benefits of the HTC-AD scenario are more sensible when the initial HHV of the biomass is lower, water to biomass ratio is lower, the type of the biomass generates acids, like HMF in its liquid yield, and there is heat recovery from the HTC unit. Further environmental and economic investigations are required to complete this study.
Chapter 8. Conclusion and future works

This chapter summarizes the major outcomes of this thesis. In addition, the direction of future studies to complete this work is suggested.

8.1. Overall Conclusion

The objective of this thesis was to find the main barriers to the commercialization of HTC and incorporate the suggested solutions to tackle these barriers. After explaining the need to move on to continuous hydrothermal reactors from batch ones, one of the required research was to understand the effects of parameters such as process water recovery and particle size on the hydrochar. In an industrial scale HTC, the pre-processing (shredding and changing the size) of the biomass should be taken into account. In addition, knowing that the water to biomass ratio in HTC is often around 5:1, it is not logical to use a significant amount of water and energy in each run, hence water recovery is necessary.

It was concluded from chapter 3 that although the smaller particle sizes undergo higher conversion due to an increase in the surface area for heat and mass transfer, it may not be necessary to decrease the size of the biomass more than a certain point as the effects can be minor. In fact, the optimum size of particles depends on the process condition and the heat transfer in the reactor and should be obtained in an industrial HTC. It was also shown that recycling not only increases the mass yield but also increases the HHV and consequently enhances the energy recovery efficiency. After 2 recycles the energy yield of HTC at 220 °C, showed around 10% enhancement. The changes were attributed to the changes in the reaction condition due to recycling the process water with a lower pH compared to the initial water. Although the changes after the second recycle would experience saturation, overall the recovery of the process water in HTC is highly recommended.

The main goal of the next two chapters was to find models that can represent the biomass changes in HTC. In chapter 4, the development of equations to predict the hydrochar’s characteristics with respect to the biomass composition and process condition was targeted. Equations for MY, HHV, C% and ERF were developed based on the interactions between the contents of cellulose,
hemicellulose, and lignin as well as the SF. Comparison of the equations with experimental data of 10 different real biomass showed that the equations are reliable especially at low ash and water extractives contents. In chapter 5, a simulation for representing the heat and mass transfer in HTC was presented. This simulation considered the heat of reaction and porosity of the biomass and showed that the previous models without considering these parameters are unreliable.

Chapter 6 reported the design and development of a novel portable continuous HTC system that uses a stacked dual-piston-cylinder with a common shaft attached to a hydraulic pump to feed the biomass against the high pressure of the reactor. Moreover, it was shown that in a continuous operation, due to the enhancement of primary carbonization and suppression of secondary carbonization, higher qualities of the hydrochar can be obtained.

Finally, chapter 7, used the knowledge of HTC obtained in the other chapters and integrated them with other processes namely AD, Rankine, and Bryton cycles, to develop a numerical comparison study between direct combustion and pre-treatment processes. It was shown that an increase in moisture content makes the pre-treatment superior in terms of efficiency and the produced power. In addition, it was found that when the initial HHV of the biomass is lower, water to biomass ratio is lower, the type of the biomass generates acids like HMF in its liquid yield, and there is heat recovery from the HTC unit, the benefits of the pre-treatment scenarios are more noticeable.

8.2. Recommendations for future work

In addition to the studies presented in this thesis, additional work is required to obtain the best advantages of HTC.

- The main focus in this research was on the HTC process itself and studying different varieties of the biomass was out of the scope of this research. Future research should target finding the best HTC operational points for third and fourth generations of biomass in HTC.
- Improving the compositional model (chapter 4) of lignocellulosic biomass under HTC by adding a representative of ash, and a representative of water extractives.
- Finding another compositional model (chapter 4) for algal biomass using representatives of protein, lipids, and carbohydrates.
- Developing a kinetic model for the main components of any kind of lignocellulosic biomass (cellulose, hemicellulose, and lignin) and then finding a comprehensive model to address different feeds.
• Developing a kinetic rate equation for biomass that directly undergoes the desired HTC processing condition in the continuous operation.
• Assessment of the role of glucose and hydrogen peroxide on the energy profile of the HTC, in order to move towards a self-sustain HTC.
• Design of more continuous HTC systems to adapt the most optimum ones in industries.
• Life cycle analysis of industrial-scale integrated HTC and other processes to assess the pollutions and impacts of different sustainable scenarios.
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