University of Nevada, Reno

Effects of process parameters on hydrothermal carbonization

A thesis submitted in partial fulfillment of the
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Chemical Engineering

By

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Abstract

In recent years there has been increased research activity in renewable energy, especially upgrading widely available lignicellulosic biomass, in a bid to counter the increasing environmental concerns related with the use of fossil fuels. Hydrothermal carbonization (HTC), also known as wet torrefaction or hot water pretreatment, is a process for pretreatment of diverse lignocellulosic biomass feedstocks, where biomass is treated under subcritical water conditions in short contact time to produce high-value products. The products of this process are: a solid mass characterized as biochar/biocoal/biocarbon, which is homogeneous, energy dense, and hydrophobic; a liquid stream composed of five and six carbon sugars, various organic acids, and 5-HMF; and a gaseous stream, mainly CO_2. A number of process parameters are considered important for the extensive application of the HTC process. Primarily, reaction temperature determines the characteristics of the products. In the solid product, the oxygen carbon ratio decreases with increasing reaction temperature and as a result, HTC biochar has the similar characteristics to low rank coal. However, liquid and gaseous stream compositions are largely correlated with the residence time. Biomass particle size can also limit the reaction kinetics due to the mass transfer effect. Recycling of process water can help to minimize the utility consumption and reduce the waste treatment cost as a result of less environmental impact.

Loblolly pine was treated in hot compressed water at 200 °C, 230 °C, and 260 °C with 5:1 water:biomass mass ratio to investigate the effects of process parameters on

HTC. The solid product were characterized by their mass yields, higher heating values (HHV), and equilibrium moisture content (EMC), while the liquid were characterized by their total organic carbon content and pH value.

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Introduction

1.1 Background

The industrial revolution in the eighteenth and nineteenth centuries has brought a serious challenge in balancing between the environment and the ever increasing demand for development of modern societies. After Europe and the USA, a recent surge in manufacturing and production in Asia and expected development in Africa will require about 50% more energy in 2030 than was consumed in 2005 [1]. The conventional fossil fuels (e.g. oil, coal, and natural gas), renewable energy sources (e.g. hydro, wind, solar, biomass, and geothermal), and nuclear energy will be the sources to meet that demand. On the other hand, global warming is posing a potential threat due to burning more fossil fuels that produce anthropogenic gases like CO_2, which is responsible for most of the atmospheric temperature rise on our planet. Nuclear energy has a huge potential to take over the fossil fuels, but the nuclear disaster in Japan has posed a barrier to its further application all over the world. Not only that disaster but also a variety of social and political issues, as well as operational safety and permanent waste disposal concerns, however, could limit nuclear energy's widespread utilization in overall energy production [1, 2]. Renewable sources, especially lignocellulosic biomass, one of the largest compared to coal, oil, and natural gas, abundant in most areas, and biodegradable (hydrophilic), is set to become an important contributor to the world energy need with the growing concerns of greenhouse emissions. Recent studies on world energy show that about 10– 14% of the world's energy supply comes from biomass and biomass derivatives [3].

An extensive application of bioenergy can control the environmental issue like greenhouse gas emissions in a substantial and effective way [4]. Ragauskas et al., suggested that the Kyoto agreement to reduce carbon dioxide emissions could be met by replacing fossil fuels with naturally available bio-resources [5]. The fastest growing economies around the world, especially the under-developed and developing countries, parallel the technological development in the world, and research and development activities are forced to study new and bio-renewable energies.

1.2 Energy strategy

The U.S. *Billion-Ton-Update,* published in August 2011, found that there are potentially sufficient biomass feedstocks to meet EISA and RFS mandates, provided that viable, efficient conversion and transportation systems are available [6]. Figure 1.1 represents the predicted amount of potential feedstocks. However, to achieve this, there is a strong need to develop viable technologies to produce secure and affordable biomass. Although plant biomass is the only current sustainable source of organic carbon, biomass feedstocks are marked by their tremendous diversity, that make them rather difficult to characterize a whole due to their fibrous nature, low density, and low heating value. So, they are not considered as an ideal fuel. It is understandable that the available logistics to handle this diverse bio-resource are not sufficient to attain the billion ton goal. A cost effective, easy to implement, sustainable, and environmentally friendly technology is required to move towards the energy security plan. Thus, commercialization and policy support for current and near-term opportunities is needed to grow the industry from its present base, and also research and development to increase the impact, efficiency, and sustainability of bio-energy facilities [5].

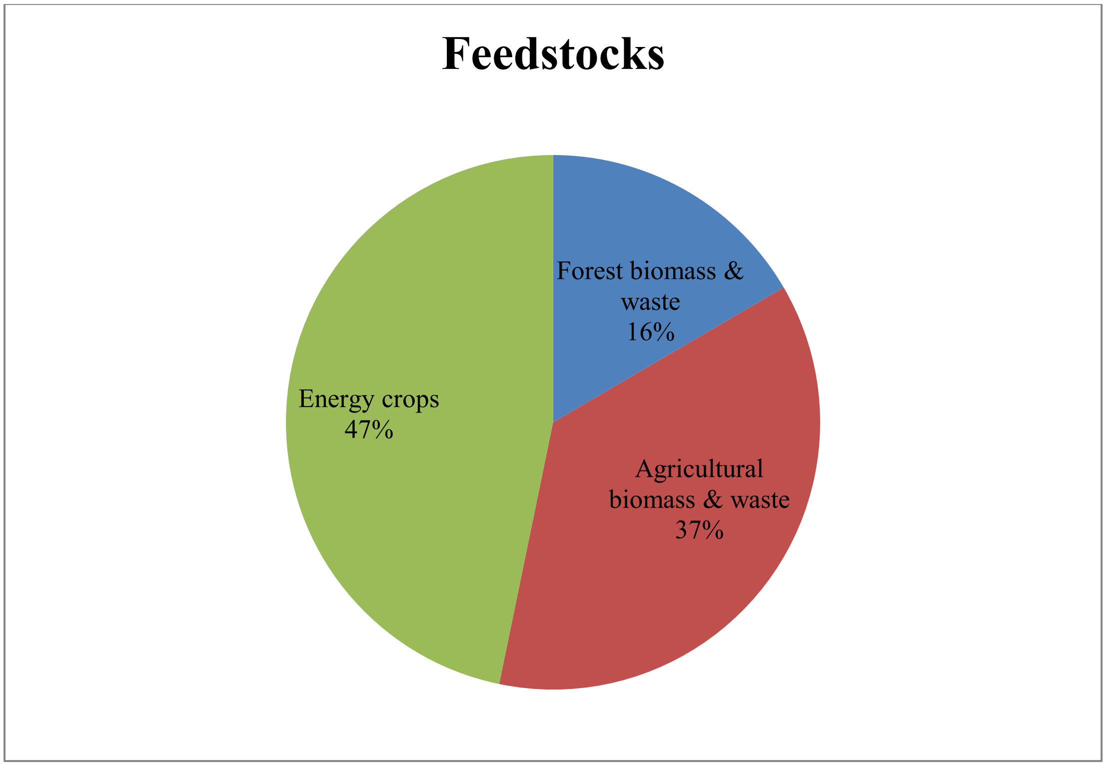

Figure 1.1 Potential forest and agriculture biomass available by 2022 at $60 per dry ton or less, under baseline scenario assumptions [6].

1.3 What is biomass?

Biomass (Greek *bio* meaning *life* + *maza* meaning *mass*), a term for all organic material that stems from plants, includes products, byproducts, residues, and waste from agriculture (straws, hulls, stems, and stalks), forestry and related industries, as well as the non-fossilized and biodegradable organic fractions of industrial and municipal solid wastes. In a broader definition, it also refers to wood, short-rotation woody crops, agricultural wastes, short-rotation herbaceous energy species, wood wastes, bagasse, industrial residues, waste paper, municipal solid waste, sawdust, biosolids, grass, waste from food processing, aquatic plants and algae, animal wastes, and a host of other materials. The major component is cellulose (35–50%), followed by hemicellulose (20–35%), and lignin (10–25%). Proteins, oils, and ash make up the remaining fraction of lignocellulosic biomass [7]. However, the structure of these materials is very complex within the lignocellulosic biomass.

1.4 Why is biomass a source of energy?

Carbon dioxide, produced by combustion of coal or hydrocarbons, fermentation of sugars in beer and winemaking, respiration of all living organisms, dissolution of earth crust, etc., is used by plants through the photosynthesis process to produce carbohydrates that form the building blocks of biomass. The light energy captured from the sun turns into chemical energy that can be used for fuel. Typically, photosynthesis converts less than 1% of the available sunlight to store as chemical energy [8]. If biomass is processed efficiently, either chemically or biologically, extracting the energy stored in the chemical bonds and the subsequent ‘energy’ product combines with oxygen, the carbon is oxidized to produce CO_2 and water. The process is cyclical, as the produced CO_2 is then available to produce new biomass to store further solar energy.

1.5 Structural components of biomass

Biomass is undoubtedly the most versatile raw material available to man. It is burnt as fuel to provide energy, converted into fibers for most paper production, and put to newer uses as a source of industrial chemicals.

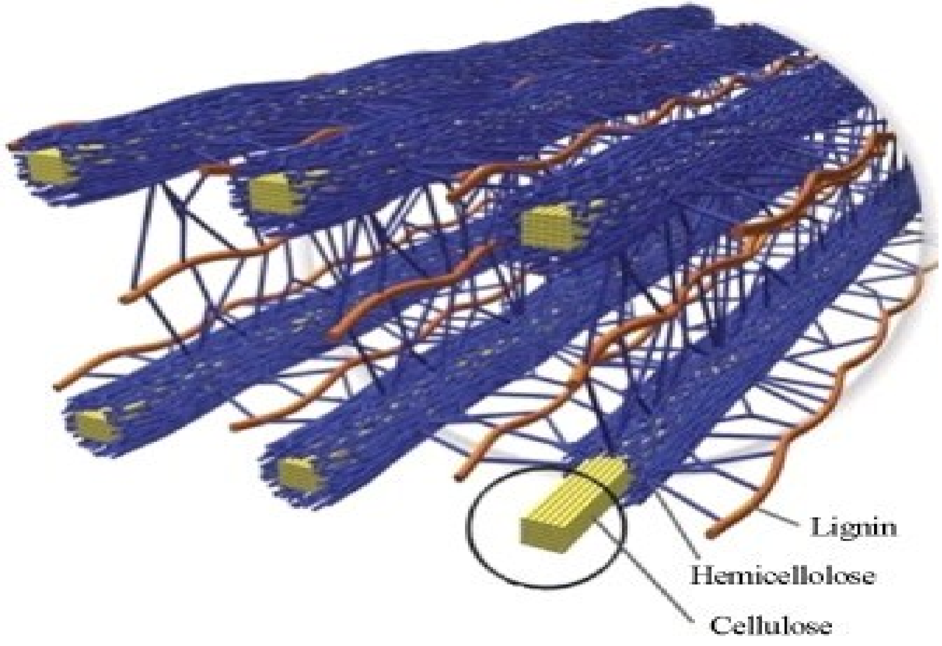

Figure 1.2 Cellulose strands surrounded by hemicellulose and lignin [9].

Typically, lignocellulosic biomass comprises three major fractions – cellulose, hemicellulose, and lignin – plus lesser amounts of minerals (ash) and other compounds often termed *extractives*. Figure 1.2 shows the most expected internal structure of lignocellulosic biomass.

1.5.1Cellulose

Cellulose, about 33~50% of all plant matter, is the most common organic compound on Earth, with an annual production of over 50 billion tons [10]. It is a linear polysaccharide polymer with many glucose monosaccharide units, with an average molecular weight of around 100,000 g. The glucose monomers are connected via β-(1→4)-glycosidic bonds, which facilitate to form hydrogen bonds between and among the sugar molecules. This web of bonding characteristic makes them crystalline, resistant to swelling in water, and resistant to attack by enzymes. Also, the acetal beta linkage

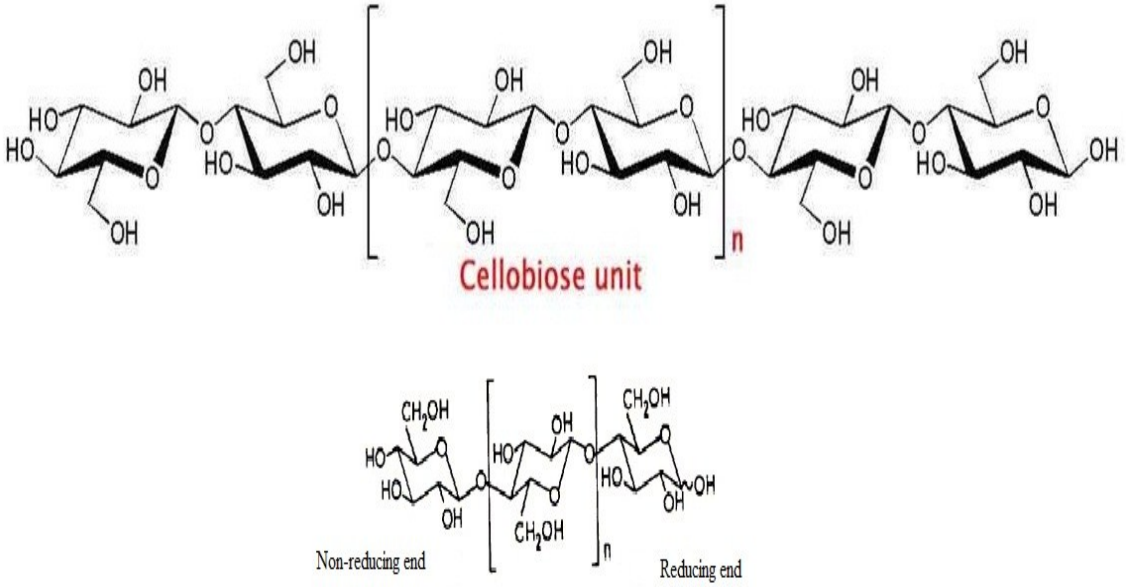

Figure 1.3 Schematic illustration of a cellulose chain [20].

makes it different from starch. Available evidence suggests that cellulose is formed at, or outside, the plasma membrane of a plant cells as it is often found in the protective cell walls of plants, particularly in stalks, stems, trunks, and all woody portions of plant tissues [11-12]. However, cellulose from different biological sources has different properties, and both its physical (crystalline) and chemical structure can affect its behavior. The most accepted hypothesis about cellulose is that fibers are embedded in a lignin-polysaccharide matrix [13-16].

There are six different forms of cellulose crystal structure studied in literature among them cellulose I and cellulose II are the most common [17-19]. Figure 1.3 represents the common structural configuration of a cellulose chain with a reducing and a non-reducing end. In nature, cellulose chains have a degree of polymerization (DP) of approximately 10 000 glucopyranose units in wood cellulose and 15 000 in native cotton cellulose [20].

1.5.2 Hemicelluloses

After cellulose, the second most common polysaccharide in nature, representing about 20–35% of lignocellulosic biomass, is hemicelluloses which are, unlike cellulose, chemically heterogeneous polymers of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and sugar acids, with an average molecular weight of <30,000. Hemicelluloses are embedded in the cell walls of plants, sometimes in chains that form a 'ground' - they bind with pectin to cellulose to form a network of cross-linked fibers [21].

Figure 1.4 shows the typical sugar groups of hemicelluloses. Xylans are the most abundant hemicelluloses. However, this characteristic varies from biomass to biomass, such as hardwood hemicelluloses which contain mostly xylans, whereas softwood hemicelluloses contain mostly glucomannans [23].

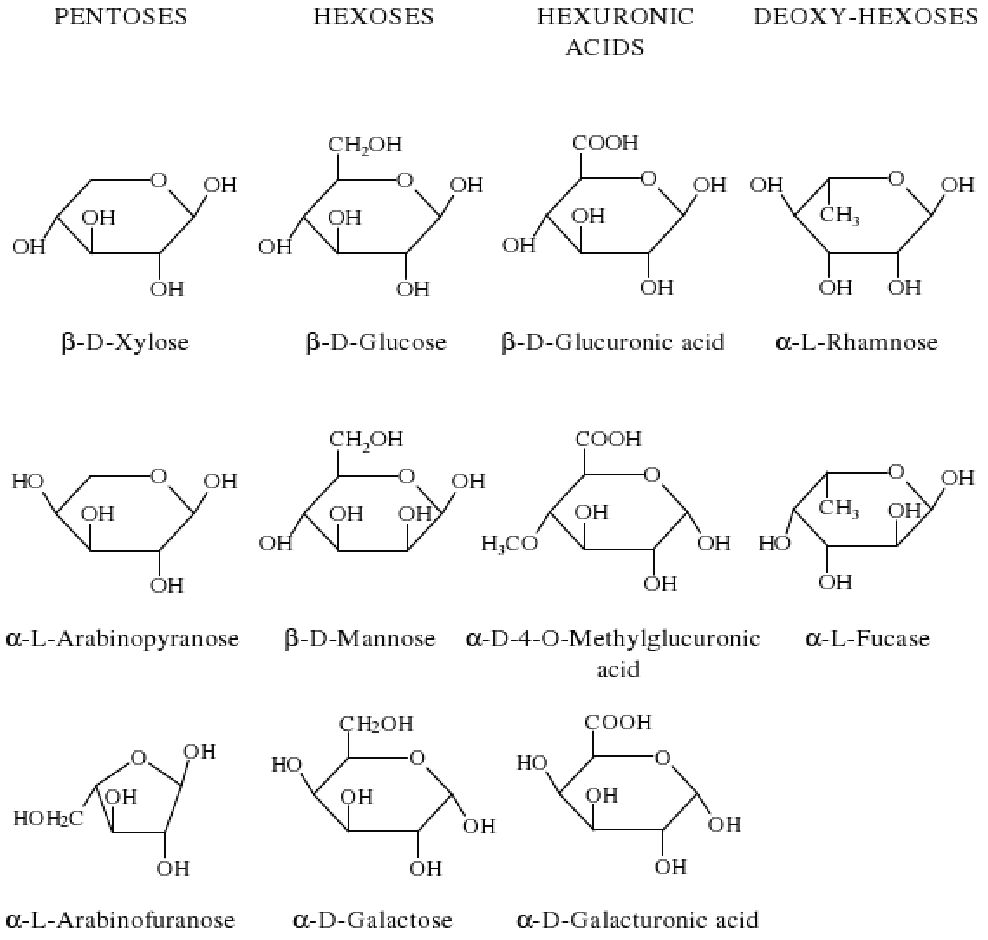

Figure 1.4 (a) Schematic illustration of sugar groups of hemicelluloses [22]

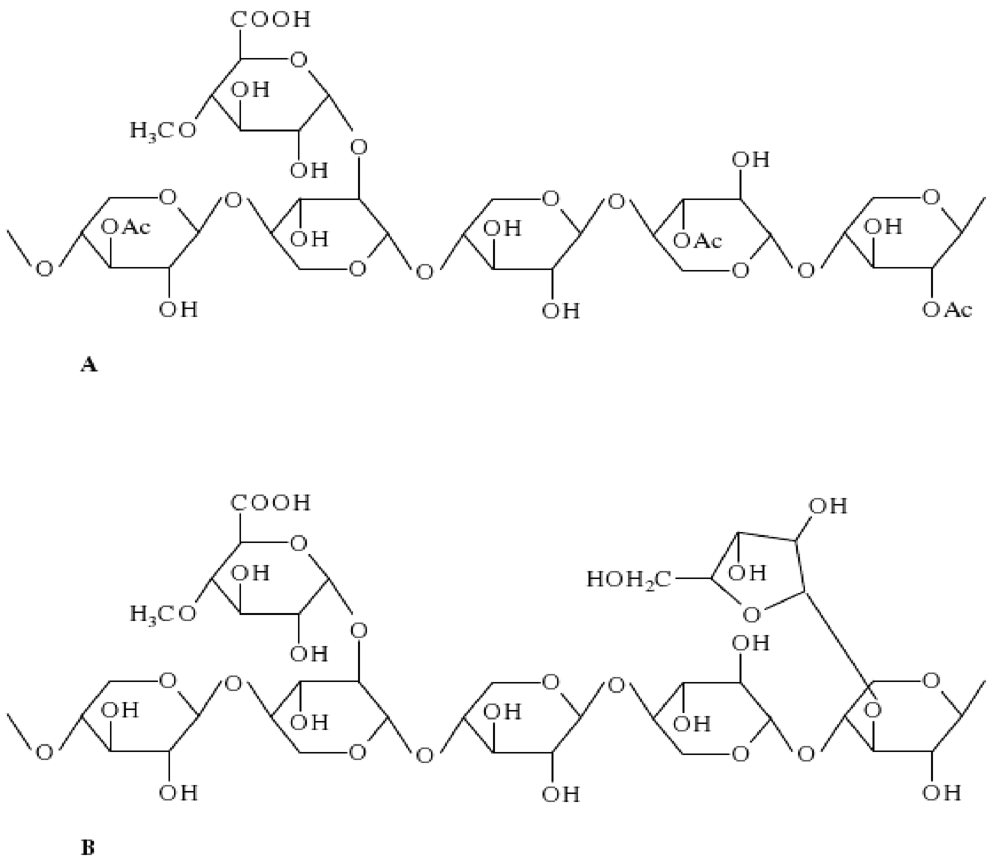

Figure 1.4 (b) Schematic illustration of partial xylan structure for hardwood (A) and softwood (B) [23]

Xylans of many plant materials are heteropolysaccharides with homopolymeric backbone chains of 1, 4-linked β-D-xylopyranose units. Besides xylose, xylans may contain arabinose, glucuronic acid or its 4-O-methyl ether, and acetic, ferulic, and p-coumaric acids. The frequency and composition of branches are dependent on the source of xylan [24]. Xylans from different sources, such as grasses, cereals, softwood, and hardwood, differ in composition [21]. Hemicelluloses consist of shorter chains (500–

3,000 sugar units) as opposed to (7,000–15,000 glucose molecules per polymer) seen in cellulose.

1.5.3 Lignin

The most complex structural component of lignocellulosic biomass, representing about 10–30% of total biomass, is lignin, which is the generic term for a large group of aromatic polymers resulting from the oxidative combinatorial coupling of 4-hydroxyphenylpropanoids [25-26]. It is difficult to define lignin from a common point of view because of its unusual heterogeneity and lack of a predefined primary structure. Lignin monomers deposit in the walls of secondarily thickened cells, making them rigid and impervious. It is widely accepted that hydroxycinnamyl alcohols (or monolignols), coniferyl alcohols and sinapyl alcohols, with typically minor amounts of p- coumaryl alcohols, are the primary building blocks of complex lignin matricies [27]. Figure 1.5 shows a part of the complex building block of woody biomass.

It is believed that lignin provides the structural support through strengthening of biomass and is covalently linked to hemicellulose [28]. It also plays an important role in transporting water in plant stems. The polysaccharide components of plant cell walls are highly hydrophilic and thus permeable to water, whereas lignin is more hydrophobic. The crosslinking of polysaccharides by lignin is an obstacle for water absorption to the cell wall. Thus, lignin makes it possible for the plant's vascular tissue to conduct water efficiently [29].

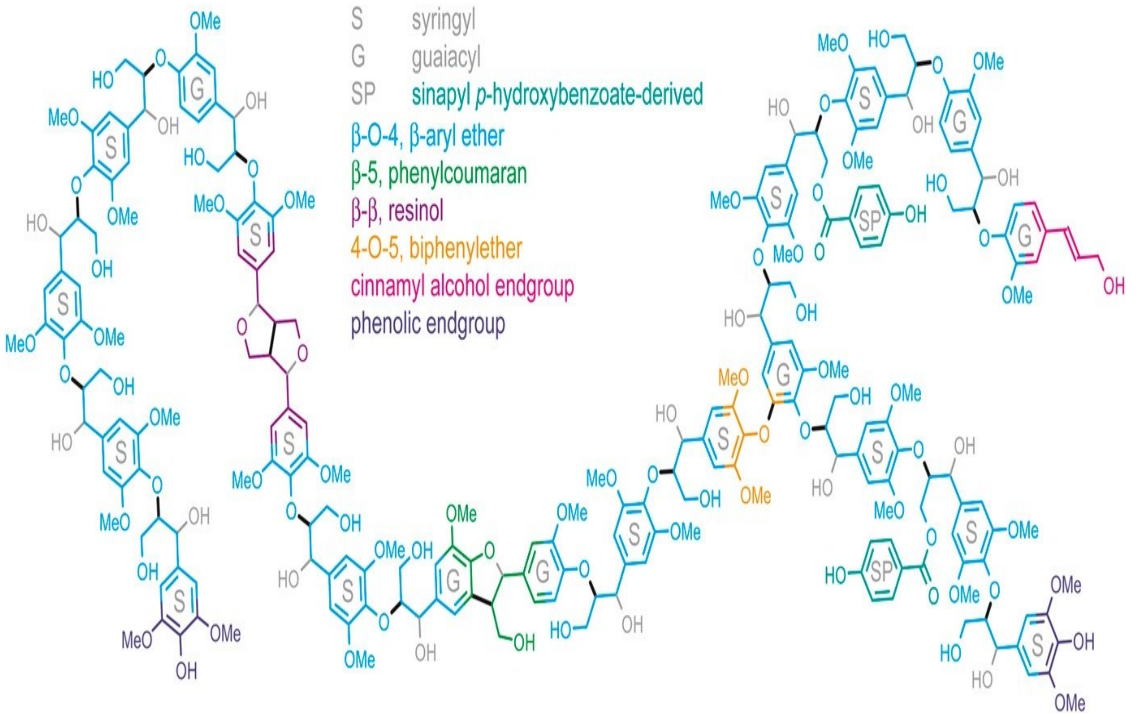

Figure 1.5 Representation of a lignin polymer from poplar, as predicted from NMR-based lignin analysis [30].

1.5.4 Extractives

Extractives are non-structural materials of lignocellulosic biomass, which have low molecular weight and are soluble in neutral solvents. They represent only about 4-10% of the total weight of dry wood, and the contents of extractives vary among wood species, geographical site, and season. These water soluble materials include inorganic material, non-structural sugars, and nitrogenous material, resin, fats, waxes, fatty acids and alcohols, terpentines, tannins and flavonoids, esters, and triglycerides, among others

[31]. Resin canal and ray parenchyma cells contain most of the extractives in biomass, with small amounts in the middle lamella and cell walls of tracheids. Inorganic material in the water soluble material may come from both the biomass and any soluble material that it is associated with the biomass, such as soil or fertilizer. Different plant species have different application of these extractives (e.g. toxic extractives are used as a protective means against fungi and termites) [32].

1.6 Bioenergy conversion routes

Renewable agricultural and forestry resources have been used since ancient times as fuels and raw materials for numerous products. Over the time and also with the development of modern technology, researchers have tried to develop a viable route to convert the diverse sources of lignocellulosic biomass for fuels, heat, power, chemicals, materials, foods and feeds in cost effective and environmentally attractive means. Depending on the nature of biomass, a number of paths have been proposed and developed which include fractionation, densification (briquetting, pelleting), liquefaction, supercritical fluid liquefaction, destructive carbonization, pyrolysis, gasification, hydrothermal liquefaction and hydrothermal upgrading, Fischer–Tropsch synthesis, anaerobic digestion, hydrolysis, and fermentation.

1.7 Pretreatment of Lignocellulosic Biomass

U.S. agriculture and forestry resources have alone the capability to produce at least one billion dry tons of sustainable biomass annually, which has the potential to displace 30% or more of the nation's present petroleum consumption [6]. Unfortunately, diverse biomass feedstocks exhibit diverse handling characteristics, complicating their usage. Furthermore, the seasonal availability of agricultural residues and the wide distribution of forest wastes make the handling and storage more difficult. These difficulties lead to the necessity of pretreatment techniques [33].

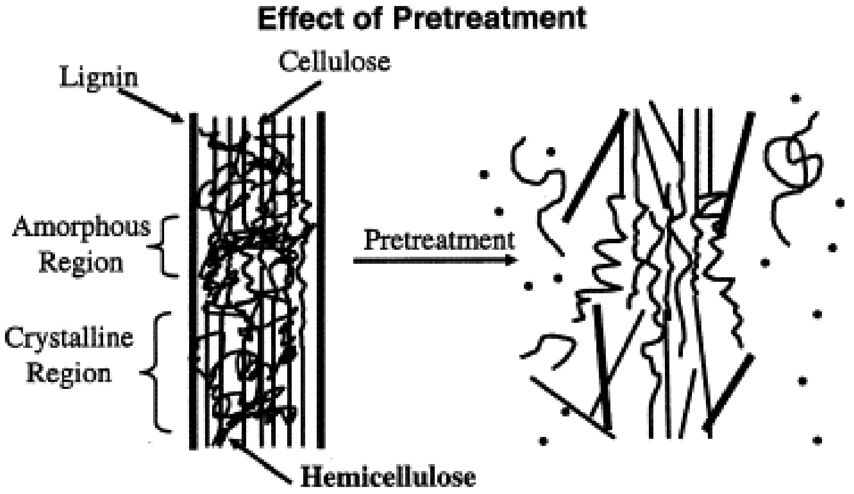

Figure 1.6 Schematic of goals of pretreatment on lignocellulosic material [34].

Hsu et al., proposed the conversion mechanism of lignocellulosic biomass under pretreatment condition to extract alcohol from cellulose. They explained that pretreatment breaks the protective outer layer of biomass materials to access and degrade sugar polymers (Figure 1.6). Besides, pretreatment is an important tool for practical biomass conversion processes. Much literature has been published that investigates effective pretreatment criteria where results must be balanced against their impact on the cost of the downstream processing steps and the trade-off between operating costs, capital costs, and biomass costs [35-38]. Economic analysis helps to direct research and development efforts by identifying process parameters that have the greatest impact on overall economics. For those various benefits, it creates a large scope of pretreatment of lignocellulosic.

1.8 Hydrothermal Carbonization

Hydrothermal carbonization (HTC) is one of the most promising technologies to convert the diverse lignocellulosic feedstocks into homogeneous, energy rich solid products that are readily available for further thermochemical conversion. This technology has been used in coal petrology for many years to simulate natural coalification [39-40]. To measure the potential oil source rocks, geochemists apply HTC to substantially higher temperatures (300–360 ^{0}C) for artificial maturation of organic material [41-42]. HTC has also been practiced in the field of biochemical process engineering for years to produce organic acids, furfural and furanoid derivatives where the solid is considered as a byproduct [43].

As with the diverse nature of biomass, HTC has also not been defined by any specific set of conditions. Subcritical water pretreatment is the most common one where the pressure is maintained to keep the water in liquid state in an inert atmosphere at a temperature range of about 180~350 ^{0}C, substantial hydrolysis temperature [44]. Hydrolysis can be enhanced by adding acids or bases to produce different liquid fraction [45-46]. The residence time in the reactor cannot be limited to a meaningful range because reaction rates are largely unknown. However, reaction times have been reported from 1 minute to several hours, although most of the reactions seem to occur within the first 20 minutes [47-48].

1.9 Properties of hot compressed water

In the water phase diagram, the triple point is 273.16 K (0.01 °C) at a pressure of 0.61 kPa, and the critical point is at 374°C and 22.1 MPa. However, the properties of hot compressed water (HCW) change with temperature and density continuously between those two temperatures. These unique properties of water offer the opportunity to use it for chemical reactions [49–51]. With increasing temperature, the ionic product increases up to three orders of magnitude higher than under ambient conditions at high pressure and subcritical conditions. This facilitates water to act as a bipolar solvent, which means that water is an acid/base catalyst precursor. HCW provides either free radical or polar and ionic reactions depending on the conditions of temperature and pressure. This indicates that HCW is an “adjustable” solvent or “tuning solvent” of different applications [52]. The ionic product increases slightly with temperatures up to around 10^{-11} in the range of 200~300 °C [53-54].

Under supercritical conditions, the thermophysical properties of water, such as viscosity, ionic product, density, and heat capacity, also change dramatically with only a small change in the temperature or pressure, resulting in a substantial increase in the rates of chemical reactions.

1.9.1 Cellulose under HCW

About 50-90% of the cellulose in lignocellulosic materials is bound laterally by hydrogen bonds that form crystalline structures. The remaining portion is less ordered and is often called amorphous cellulose [55]. The major challenge lies in the crystalline structure of cellulose in effective hydrolysis. Another significant challenge in cellulose hydrolysis is the physical barrier of cellulose provided by hemicellulose and lignin [55].

Hydrolytic reactions lead to the cleavage of mainly ester and ether bonds of the bio-macromolecules by addition of one mole of water. A detailed reaction network has been summarized by Petersen et al., in which cellulose was hydrolyzed significantly under hydrothermal conditions above approximately 200 ^{0}C, [56]. The activation energy studied in literature for pure cellulose under subcritical water conditions is in the range of 129~215 kJ/mol [57-59].

The breakdown of cellulose crystalline structures was extensively studied by temperature scanning techniques. When scanning at 11 to 14 ^{0}C/min at 25 MPa, Deguchi et al. observed a loss of birefringence, a term use to describe the gelatinization at around 320 ^{0}C, indicating that the cellulose crystallinity disappeared at these conditions [60].

They observed a breakup of the cellulose fibers very shortly after the loss of crystallinity, suggesting that the crystallinity was preventing the breakdown of the cellulose.

1.9.2 Hemicellulose under HCW

Hemicelluloses are connected to lignin and cellulose within biomass by covalent bonds and have less hydrogen bonding, which lack of repeating β-(1→4)-glycosidic bonds and the random nature of polymer, hemicelluloses do not form as crystalline and resistant of a structure as cellulose. It is much more easily broken down than crystalline cellulose and susceptible to hydrothermal extraction and hydrolysis. The heterogeneity of hemicellulose and the resulting variety of hydrolysis reaction mechanisms involve the challenges of understanding the hydrolysis process [55]. In general, hemicellulose hydrolysis models are based on acid-catalyzed breakdown of long chains of hemicellulose to form shorter oligomers that continue to break down to monomeric sugars.

Hemicelluloses are readily hydrolyzed at around 180 ^{0}C and higher, but detailed reaction pathways are less well understood. According to Bobleter, hemicellulose is easily dissolved in water at temperatures above about 180 ^{0}C [61]. A number of other studies show that an average of 95% of hemicellulose can extract as monomeric sugars at 200 to 230 ^{0}C over a span of just a few minutes [62-64]. Garrote et al. also reviewed reaction kinetics for hemicellulose degradation into sugars and subsequent degradation of the sugars into furfurals and other degradation compounds, and found that most studies reported hemicellulose extraction and recovery as sugars or oligomers at yields of 65 to 82% [65].

1.9.3 Lignin under HCW

Lignin is cross-lined with cellulose and hemicelluloses, and they have to degrade to make accessible hydrolysis of lignin. van Parijs et al., developed a mathematical model to predict the frequency of the different bond types, the number of different polymers, their lengths, and the relative abundance of the different length of polymers under varying parameters to understand the influence of lignin degradation in processes such as alkaline pulping or biomass pretreatment methods used in biofuel production [66].

Hydrothermal degradation of lignin is most likely realizable at around 200 °C due to its high amount of ether bonds [43]. Some of the researchers assumed that lignin does not degrade below 250 °C [65]. However, this discrepancy in degradation temperature may arises from the characteristics of lignin, its source, maturity, etc.

1.9.4 Extractives under HCW

Since extractives are not an integral part of the cellular structure, they can be removed by solution in hot or cold water, ether, benzene, or other solvents that do not react chemically with biomass components. Reza assumed that extractive reactions are instantaneous and solubilize at the start of the HTC process [65].

1.10 Project Objectives

The objective of this thesis is to understand the hydrothermal carbonization (HTC) of lignocellulosic biomass, namely loblolly pine, under different sets of conditions. This includes the finding of important variables and their effect on the HTC process. Recycling of process water, an important parameter for the continuous operation of HTC in large scale applications has been investigated thoroughly by analyzing the solid product mass yield, energy/calorific value, and equilibrium moisture content.

1.11 Organization of Thesis

Chapter 2 shows the effect of process water recycling effects on loblolly pine under hydrothermal process at a temperature range of 200-260 ^{0}C. Effects on mass yield of solid biochar/biocoal, higher heating value (HHV), and equilibrium moisture contents, are discussed in this chapter. Liquid products are characterized by measuring total organic carbon content and also discussed here.

In the first part of Chapter 3, rigorous stochastic error analysis is applied to previously measured reaction data, allowing for prediction of rate constants and activation energy. The Monte Carlo simulation method applied to analyze the reaction kinetic parameters of loblolly pine is also presented. Effects of particle size on HTC accounting simultaneous mass and heat transfer are discussed in the second part of this chapter.

In Chapter 4, the detailed procedure to measure the water production during HTC process is presented. The temperature effect on dehydration reactions along with residence time has been discussed in this chapter. The error analysis tool discussed in the previous chapter is applied here to understand the experimental uncertainty to account for the water balance technique

In Chapter 5 summarizes some conclusions drawn from the previous chapters of this thesis and contains recommendations for further research.

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Chapter 2

Recycle process water effect on hydrothermal carbonization

Hydrothermal carbonization process requires at least 3 times as much water as biomass feed for pretreatment [6]. This water requirement needs to be assessed to determine the feasibility of this growing technology. This chapter is focused on the recyclability of the process water to improve process efficiencies. Loblolly pine was treated hydrothermally (hot compressed water at 200 °C, 230 °C, and 260 °C) for 5 minutes with a 5:1 water :biomass mass ratio. The solid products (bio-carbon) were characterized by their mass yields, higher heating values (HHV), and equilibrium moisture content (EMC), while the liquid samples' total organic carbon content (TOC) and pH were determined. With increasing successive recycles, bio-coal mass yield increases by 5±1% for each temperature investigated. The higher heating values remain almost unchanged with increasing number of recycles at reaction temperatures of 200, 230 and 260 °C. The water soluble carbonaceous substances are concentrated with the number of recycles. The EMC results suggest unchanged hydrophobicity of the bio-coal despite the increased mass yield, which is thought due to the sugar deposition on the biochar surface, and sugar is highly hydrophilic to reduce the char hydrophobicity.

2.1 Introduction

The carbon dioxide concentration in the atmosphere has clearly increased over the few past decades as a result of depending on fossil fuels for energy production. The global atmospheric concentration of CO_2 increased from a pre-industrial value of about 280 ppm to 390 ppm in 2010 [1]. Today biomass is seen as a promising energy source to mitigate greenhouse gas (GHG) emissions [2]. It appears to have strongly positive environmental properties, such as reduced GHG emissions and possibly reduced NO_x and SO_x emissions, depending on the fossil fuels displaced. Half of the total energy demand in developing countries is projected by 2050 to come from modernized biomass energy [3, 4]. However, since biomass usually contains high moisture content and has low density, there are challenges in transportation, storage and usage of raw biomass. Biomass thermochemical conversion technologies such as pyrolysis and gasification are frequently used, and such combustion is responsible for over 97% of the world's bioenergy production [5]. In both cases, feedstock handling is complex due to the diverse nature of feedstocks, which include hardwood, softwood, agricultural residues like rice hulls, corn stover, and wheat chaff, and energy crops such as switch grass and miscanthus [6].

Hydrothermal pretreatment is a promising technology for converting diverse sources of lignocellulosic biomass into energy dense solid fuel. Such fuel may be referred to as hydrochar, biochar, biocarbon or bio-coal. From soil amendment to carbon sequestration, alkali metal-free feedstock for bio-refinery to low-hazard bio-coal for gasification [7], hydrothermal carbonization (HTC) is getting more and more attention from around the world.

In the HTC process, lignocellulosic biomass is pretreated in hot compressed water at a temperature range of 200 °C to300 °C under subcritical conditions. Typical practice for this process is to add about four times more water than biomass by weight [8 - 12]. In an intensive bio-energy production scenario, the supply of process water will be one of the key factors in industrial practice. For example, to produce one metric ton of dry bio-coal from loblolly pine at 260 °C assuming a 60% mass yield in a batch process, would require 8.34 metric ton of demineralized water per batch [10]. This large demand for process water can be minimized by recycling it after filtration for a batch or continuous processing system. Other advantages of recycling exist. Process heat could be recovered, significantly reducing external heating costs and wastewater treatment costs could be reduced since less waste water would be generated per kg of feedstock. For both batch and continuous processes, optimization of process water recycling is very important because biomass pretreatment could be affected by the presence of sugars and inorganic materials remaining in the liquid solution. It is expected that the increase of sugar concentration in the liquid would increase mass transfer resistance for sugar monomers produced from hemicelluloses and cellulose degradation. This hindering of sugar monomer movement to the liquid phase could impede the energy densification aspect of the HTC process.

There is limited literature available on HTC water recycling. Stemann et al., first addressed the prospect of water reuse by investigating the recyclability of process water for poplar wood HTC [13]. For large scale application of HTC to produce bio-coal, a continuous pretreatment method where hot compressed process water is reused in successive cycles is preferable. For this reason, the effect of recycled water on pretreatment parameters is important to understand. In this study, the effect of process water recycling on mass yield, higher heating value (HHV), equilibrium moisture content (EMC), and total organic carbon content (TOC) in liquid phase was investigated for loblolly pine, a representative lignocellulosic biomass, at three different temperatures.

2.2 Experimental Section

2.2.1 Biomass

Loblolly pine, native to the Southeastern United States and obtained from Desert Research Institute, Reno, NV, was used in this study. On a mass basis, it consists of 11.9% hemicelluloses, 54.0% cellulose, 25.0% lignin, 8.7% extractives, and 0.4% ash [14]. The pine samples were crushed, ground, meshed to be in a 0.6-1.2 mm particle size range using a regular fruit blender, and dried at 105°C for 24 h before undergoing the hydrothermal pretreatment (HTC) process.

2.2.2 Recycle experiments

Liquid recycle experiments of loblolly pine were done in a 100 mL Parr Series 4560 bench-top reactor (Moline, IL) with a glass liner fitted inside the reactor at temperatures ranging from 200 °C to 260 °C. For each of the control runs, a mixture of loblolly pine and demineralized water was loaded into the glass liner with a mass ratio of

1:5 pine: water. The mixture was stirred manually to ensure complete wetting. Nitrogen was passed through the reactor for 5 min to purge oxygen from the reactor (80 cm^3 (STP).min^{-1}). The temperature of the reactor was controlled using a single display proportional-integral-derivative (PID) controller. The reactor pressure was not controlled, and was approximately in accordance with the water vapor pressure. A TEMPCO ceramic band heater (500W, 120V) (Wood Dale, IL) was used to heat the reactor, which took 20-35 min depending on temperature, and maintained it at the desired temperature for a chosen period of time (~ 5 min). In the final step, the reactor was cooled to room temperature rapidly by immersion in an ice bath. When the reactor temperature cooled off to ≤ 25 ºC, the gaseous products were released into the atmosphere. The solid and the liquid were separated by vacuum filtration using a Buchner funnel with Whatman filter paper (grade 3, 0.6 µm). The wet pretreated solid product was dried at 105°C for 24 h before further analysis. The liquid collected from the initial control run was used for the next pretreatment experiment along with makeup water following the similar procedure described above, and this was repeated for successive recycle experiments. In general, the amount of water recycled from one run to the next constituted about 60-70% of the water needed. The pH of the liquid sample was recorded after every run.

2.2.3 Higher Heating Value (HHV)

HHV's of solid samples were measured in a Parr 1241 adiabatic oxygen bomb calorimeter (Moline, IL) using pellets of weight 0.6 ~ 1.0 g made from pretreated solid samples, which were dried at 105°C for 24 h prior to analysis.

2.2.4 Total Organic Carbon (TOC)

The liquid products were filtered through a 0.45 micron syringe filter then diluted 200 times with ultra-pure water. TOC was measured by a Shimadzu Total Organic Carbon Analyser, model TOC-V.

2.2.5 Equilibrium Moisture Content (EMC)

The static desiccator technique [15] was used to measure the EMC by exposing the solid samples, which were dried at 105°C for 24 h prior to use, to constant relative humidities maintained by saturated salt solutions and water. Biomass samples weighing about 0.3~ 0.5 g were placed in Petri dishes and then into transparent jars containing salt solution. Each dish was placed on top of a plastic stand inside the jar to keep it separated from the saturated aqueous salt solutions at the bottom of the jars, and a canning lid sealed the jars. Three different humidities [100% (water), 11.3% (LiCl) and 53% ($Mg(NO_3)_2$)] were used to measure the EMC of the samples. Equilibrium humidities of saturated salt solutions are available in the literature [16]. The salt solutions were prepared by dissolving the salt crystals in distilled water at room temperature. Excess salt was added to saturate the solutions to ensure constant relative humidity conditions [14]. The jars were placed in a water bath at a constant temperature of 30 °C. The time for the samples to reach equilibrium varied from 9–21 days, depending on pretreatment conditions and on the relative humidity in the jar. A sample was assumed to be in equilibrium when three consecutive weight measurements showed a difference of less than 1 mg. Weight measurements were recorded on every day. The opening and weight measuring time difference were kept at minimal level to avoid any moisture gain or loss.

2.3 Results and Discussions

2.3.1 Mass yield

The mass yields of loblolly pine for reaction temperatures 200 °C, 230 °C, and 260 °C obtained from the liquid recycle experiments are reported in Figure 2.1 on a dry mass basis.

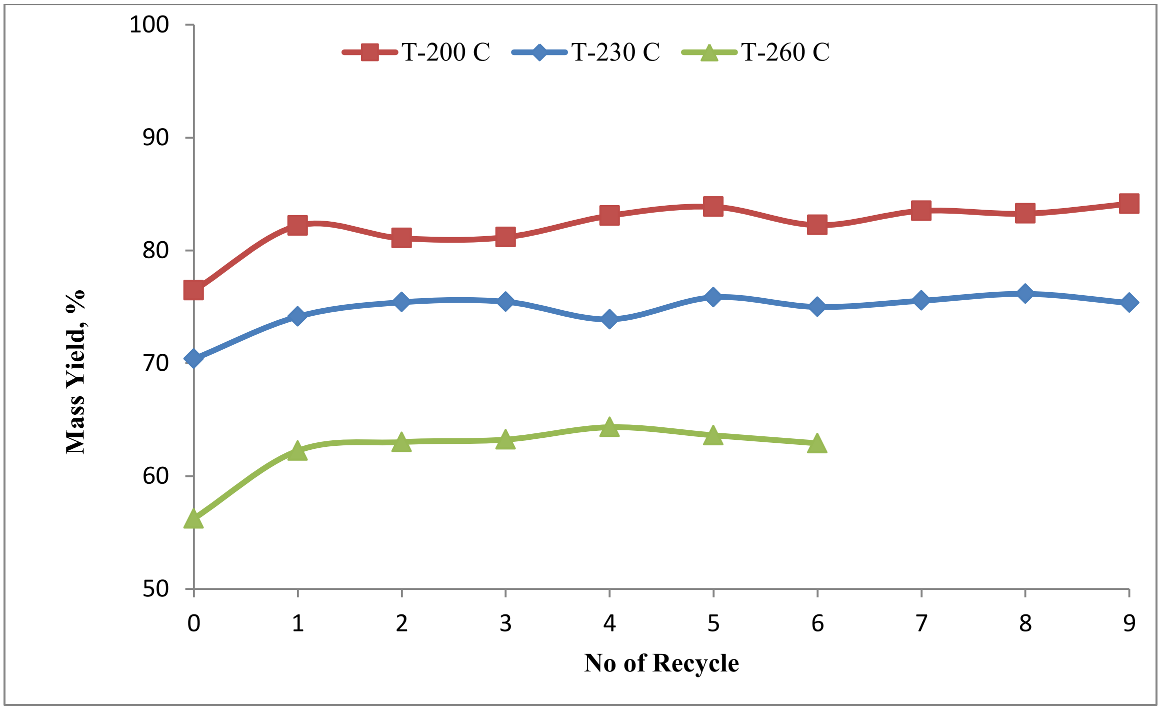


Figure 2.1 Mass yield of loblolly pine obtained from the liquid recycle experiments (number of recycle ‘0’ indicates the control run in all cases).

There were 10 recycle experiments for 200 and 230 °C and 7 for 260 °C. It shows about a 5~6% mass yield increase after the first liquid recycle experiment for all three temperatures compared to their respective control run mass yield. The increased mass yield may result from the deposition of sugar molecules, produced from the decomposition of hemicelluloses and cellulose during the control run, on the surface of loblolly particles. The scanning electron microscope (SEM) image of raw and pretreated loblolly pine shown by Reza (2011) was porous in structure, which is likely to be clogged if sugar molecules deposit on the pore surface [17]. Or the recycled liquid solution offers a resistance to diffuse the degraded sugar monomers from the particle surface to the bulk solution and, therefore, an increased mass yield may occur. Stemann et al., (2012) similarly found about a 3% increased mass yield for poplar wood at a reaction temperature of 220 °C and a 4 hr reaction time [13].

The mass yields remain almost nearly similar for the rest of the liquid recycle experiments compared to the first recycle run. It is possible to have an increased amount of sugar loss due to filtration with increasing recycle number. This effect may facilitate to have a nearly constant sugar concentration throughout the rest of the recycling offering a same degree of mass transfer resistance in each recycle.

Apart from that, the small amounts of organic acids (e.g. acetic acid, the main acid, and formic acid,) present in the liquid may inhibit some of the decomposition reactions and others may reach equilibrium. The relatively unchanged mass yield indicates that the reactions of the complex lignocellulosic systems have attained equilibrium. The measured pH values shown in Table 2.1 indicate that at a reaction temperature of 200 °C the liquid solution is less acidic than at other temperatures. Bobleter reported that cleavage of glycosidic bonds in lignocellulosic biomass is assumed to be independent in a pH range of 3-7 [18]. No catalytic behavior of the organic acid produced during cellulose decomposition was detected [19]. However, Lynam et al., showed that an addition of greater amounts of acetic acid suggested a catalytic mechanism in the biomass degradation reactions [20]. Bobleter et al., also found a catalytic effect with acetic acid on ester hydrolysis [19]. Another confirmation of this idea appears in a study by Li et al., where it was shown that a mixture of formic and acetic acid had a catalytic effect on fructose decomposition [21].

Table 2.1 pH data of liquid recycle experiments.

Temperature, (°C)	Control run	Recycle number								
		1	2	3	4	5	6	7	8	9
	pH									
200	3.41	3.38	3.30	3.30	3.27	3.27	3.25	3.25	3.24	3.24
230	2.96	2.96	2.97	2.97	2.97	3.01	2.99	3.00	3.01	3.01
260	2.85	2.89	2.93	2.94	2.93	2.92	2.92	NM	NM	NM

NM: not measured

The small change in mass yields after the1st recycle, therefore, cannot be explained with the acidic nature of the liquid. The reaction severity doesn't change with this small change in pH the way it does with temperature change. The change in mass yield of loblolly pine with increasing temperature is predominant compared to pH.

2.3.2 Higher Heating Value (HHV)

Figure 2.2 shows the change in HHV of loblolly pine at three different temperatures with liquid recycle number. Each of these HHV measurements is, at least, duplicated and data presented in the chart is their mean values. The variances of measured HHV are within 0.4~1.5%. One of the main purposes of hydrothermal carbonization of lignocellulosic biomass is to produce energy dense high quality solid fuel, and HHV is the measure of bio-coal's fuel quality.

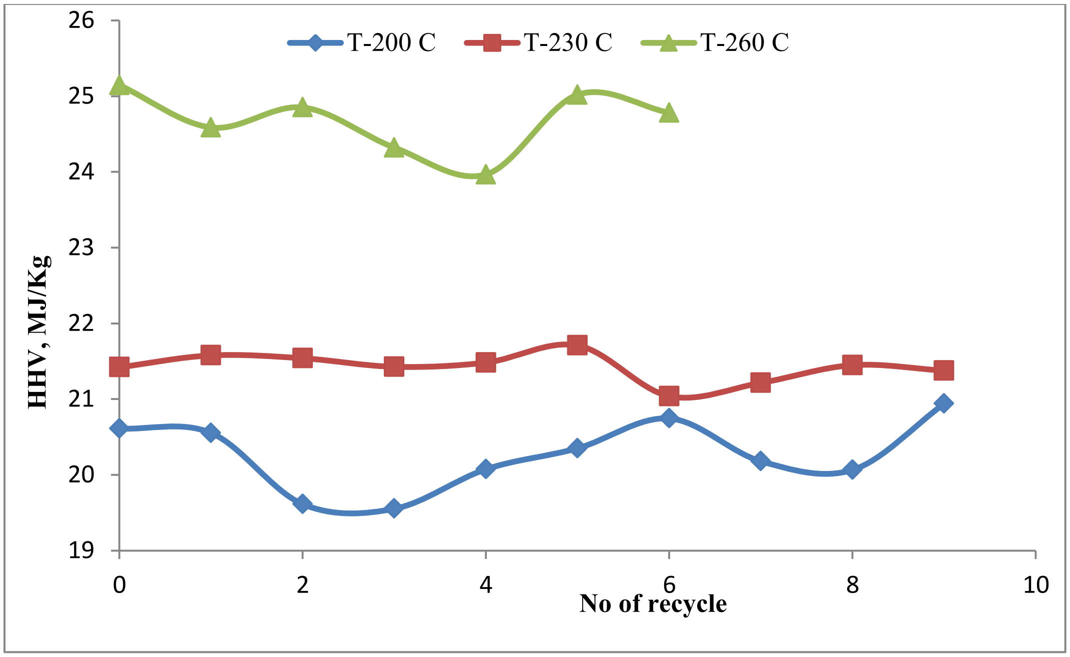


Figure 2.2 Higher Heating Values (HHV) of loblolly pine obtained from the liquid recycles experiments.

It has been shown in various works that HHV of lignocellulosic biomass increases with increasing reaction temperature, and this evidence is shown in Figure 2.2. However, for 200 °C and 260 °C, the value of HHV does change with successive recycles. At temperatures 200 and 260 °C, the HHV values show a decreasing trend up to the fourth recycle. Acetic acid which is a key representative of organic acids [22] produced during hydrothermal carbonization, has a HHV of 14.6 MJ/Kg while glucose, another main sugar component of liquid [12], has a HHV of 15.6 MJ/Kg. Both of these two compounds have a lower HHV than pretreated solid loblolly pine's HHV. Any deposition of those acids or sugars on pretreated particles surface would be expected to decrease the HHV of the solid char. However, for recycles above 4 these values level off compared to the control. The small increase for a 200 °C reaction temperature in the later cycles may result from the dehydration of hexose sugars to pentose sugars and some retro-aldol condensation of pentose sugars. These pentose sugars and aldehydes have a greater HHV than glucose as they have less oxygen content.

Table 2.2 Amount of organic acids as represented by acetic acid in the liquid solution calculated applying the Henderson-Hasselbalch equation for dilute weak acid.

Temperature, °C	Control run	Recycle number								
		1	2	3	4	5	6	7	8	9
	Acetic acid, g/g loblolly									
200	0.002	0.002	0.003	0.003	0.003	0.003	0.004	0.004	0.004	0.004
230	0.016	0.015	0.015	0.014	0.017	0.012	0.014	0.013	0.013	0.013
260	0.030	0.024	0.020	0.019	0.020	0.021	0.021	NM	NM	NM

NM: not measured

At 260 °C, cellulose decomposes to glucose that subsequently forms 5-hydroxymethylfurfural (5-HMF) [23]. With successive recycling, the concentration of 5-

HMF in the solution may increase, and this increased concentration may compete with pentose sugar deposition on the particles' surface. The HHV of 5-HMF is about 22.2 MJ/Kg and any deposition of this molecule rather than pentose will increase the HHV. Although 5-HMF's HHV is lower than that of the pretreated solid, it is higher than that of the sugars competing to deposit in the pores. Deposition of 5-HMF and other high HHV dehydration products, which concentrate in the recycled liquid, may cause an increase in the biocoal's HHV at the 6th recycle. A steady value of HHV is obtained throughout the recycle experiments for a reaction temperature of 230 °C. It is seen from Figure 2.3 that for 230 °C HTC the changes in mass yields are minimal and mass yield remains nearly constant, just as HHV does with successive recycling. Stemann et al., reported a 5±1% increase of HHV for poplar wood pretreated at 220 °C for 4 hr after 19 recycles of process water [13]. However, Lynam et al., showed that the addition of 0.4 g acetic acid along with 1 g LiCl per g loblolly pine in liquid during HTC could increase the HHV by 30% for a fresh sample [20]. A simple calculation is performed to calculate the concentrations of acetic acid, assumed as representative of all organic acids formed, in the liquid solutions, which are shown in Table 2.2.

$$pH = pK_a + \log(\frac{[A^-]}{[HA]}) \qquad (1)$$

Where $[A^-]$ represents the acetate ion concentration and [HA] represents acetic acid concentration. For dilute weak acid dissociation, it is assumed that concentration of acetate ion and hydrogen ion are equivalent. The amount of acetic acid was calculated using its standard dissociation constant (1.6E-05 at 298K) and molecular weight reported in literature. These values suggest that the liquid solution alone is unlikely to change the HHV of the bio-coal produced. Although the pH values of liquid samples did not vary much, from the HHV chart it can be inferred that a pH near 3.0favors the reaction chemistry for hydrothermal carbonization using recycled liquid solution.

2.3.3 Total Organic Carbon (TOC)

Figure 2.3 shows the change in TOC in the liquid phase with recycle number. TOC measurements were done for the liquid samples for HTC temperatures of 200 °C and 230 °C. A sudden increase of TOC in liquid sample is noticed up to second recycle, but for the rest of the recycles the change is very small.

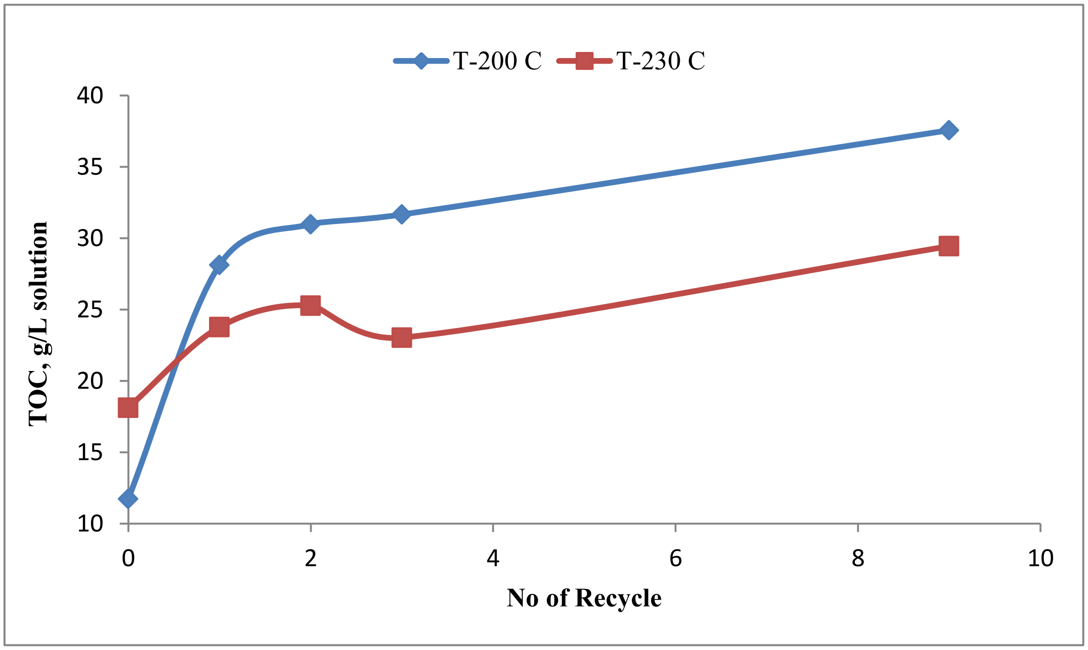


Figure 2.3 Total Organic Carbon (TOC) content of liquid phase of pretreated loblolly pine.

It was expected that the TOC would increase with recycle number but the results indicate a change in liquid and solid reaction chemistry for later recycles. Stemann et al., (2012) described this as an unidentified polymerization of substances [13]. The nearly constant mass yield at later recycles can be explained with the help of TOC measurement. Loblolly pine has collectively about 20% hemicellulose and extractives that will nearly completely hydrolyze at or above 200 °C [6]. Sevilla et al., reported that there is no chemical transformation for cellulose when treated below 220 °C [24].

Both cellulose and lignin are partially reacted with HTC, and the extent of reaction increases with temperature. As cellulose sugars start degrading 230 °C, the initial TOC is greater than that of 230 °C. However, sugar present in the liquid shows more dehydration/polymerization tendency at 230 °C [25] and as a result, TOC value does not increase as it does at 200 °C after 1st recycle. Hoekman et al., reported a not measureable gas quantity released at 200 °C for HTC of Tahoe mix [12] and it was also true in the case of loblolly. That evidences may further claim higher increase of TOC at 200 °C.

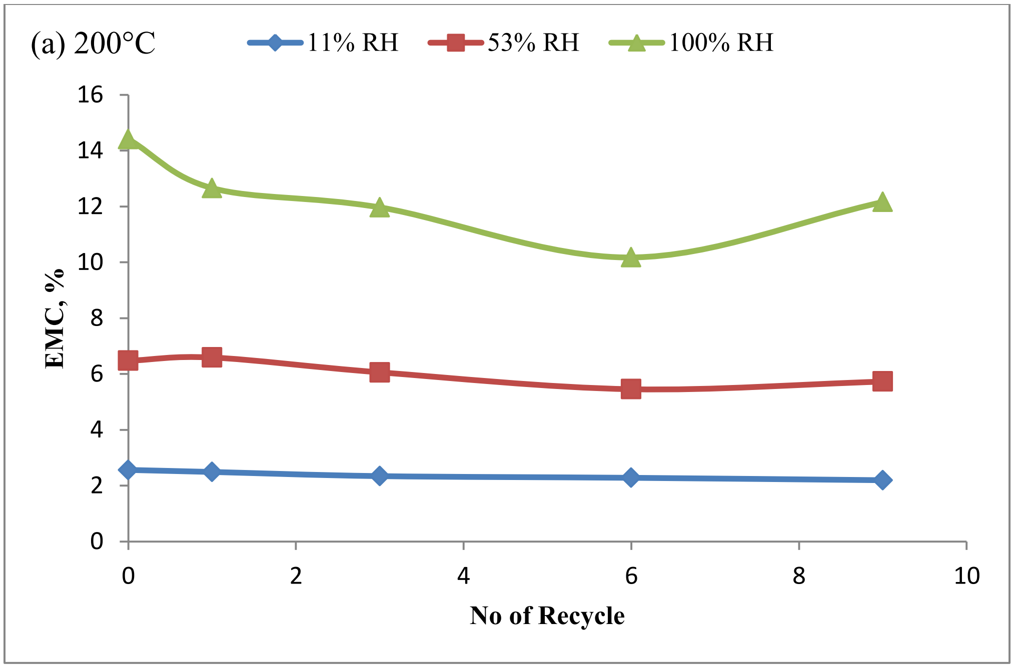
2.3.4 Equilibrium Moisture Content (EMC)

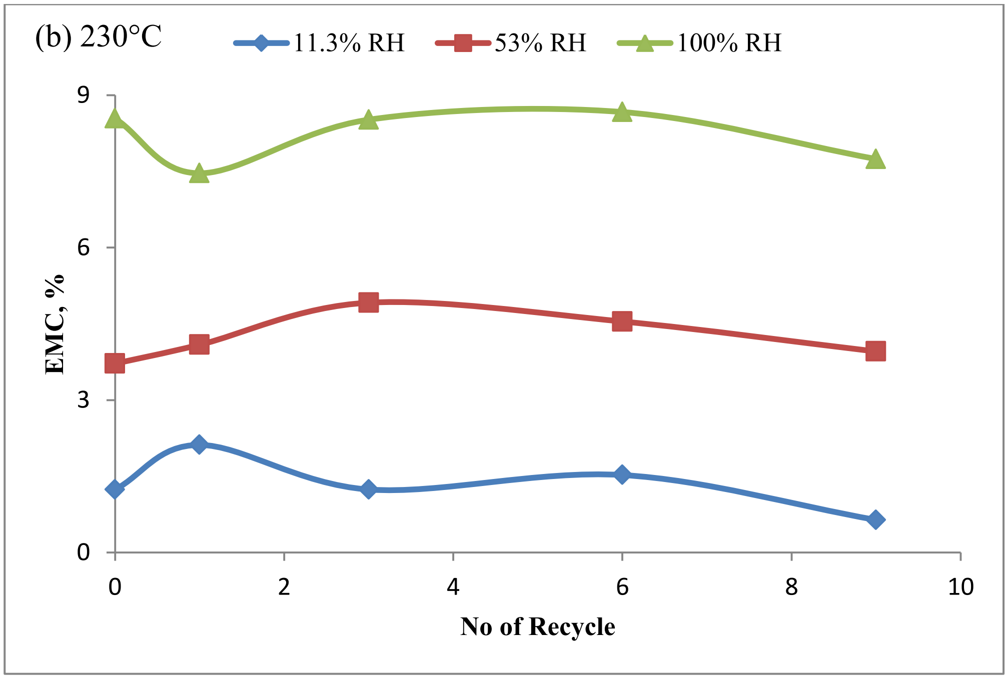
The EMC of a sample at a particular relative humidity was calculated as follows:

$$EMC\ (\%) = \frac{M_{EMC} - M_{bone\ dry}}{M_{bone\ dry}} \times 100 \qquad (2)$$

where M_{EMC} is the weight of the sample at equilibrium moisture content and $M_{bone\ dry}$ is the weight of a bone dry sample. In this study, equilibrium was attained in 9–15 days. Figure 2.4 shows the change of EMC on liquid recycle at three different temperatures. The EMC of pretreated samples would be expected to increase with recycle number because mass yield data give an increasing trend from sugar deposition on the particle's surface. Sugar molecules are highly hydrophilic and their deposition on particles means an increase of water absorption under controlled relative humidity conditions. But all of the EMC curves show different behavior than expected.

For Figure 2.4 (a) with hydrothermal pretreatment at 200 °C, the EMC values decrease slowly with recycle number for the three relative humidity conditions, while the pH of the liquid phase similarly decreases with recycling (Table 2.1), although the changes are very small and it is hard to claim a real discrepancy in values if experimental errors are accounted. Due to the degradation tendency of sugars at 230 °C and 260 °C, there is slight increase of pH values in these liquid samples, and also a slight change of EMC is observed at those temperatures (Figures 2.4 (b) & (c)). At 53% relative humidity, found using a ($Mg(NO_3)_2$ solution, the increasing trend of humidity is closely followed by the pH values in Table 2.1. however, the EMC of bio-coal with HTC pretreatment decreases with increasing reaction temperatures. From Figure 2.4, it can be seen that EMC values decreases from 14% at 200 °C to ~8% at 230 °C in 100% relative humidity (RH) condition and a similar trend can be seen for the other RH conditions.


(a) 200°C
11% RH
53% RH
100% RH
EMC, %
16
14
12
10
8
6
4
2
0
0
2
4
6
8
10
No of Recycle


(b) 230°C
11.3% RH
53% RH
100% RH
EMC, %
9
6
3
0
0
2
4
6
8
10
No of Recycle

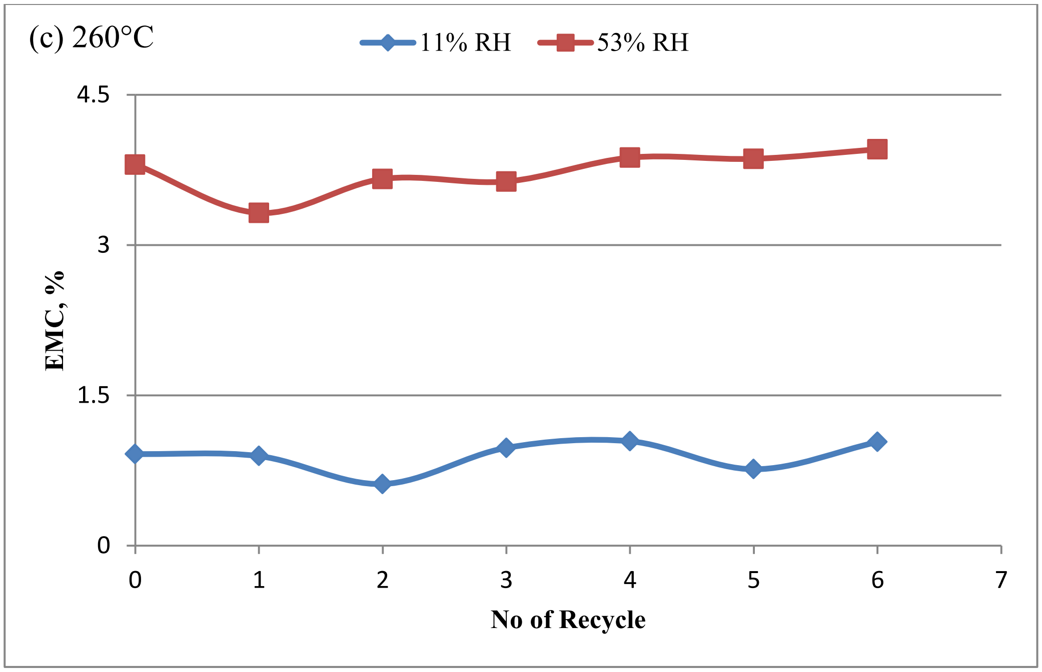


Figure 2.4 Equilibrium Moisture Content (EMC) of pretreated loblolly pine in three different constant relative humidity solutions. Biomass pretreated three reactions at three reactions at temperatures: (a) 200 °C; (b) 230 °C and (c) 260 °C. At 30 °C, relative humidities (RH) for saturated solutions of LiCl and $Mg(NO_3)_2$ are 11.3% and 53% respectively. Water is used as 100% relative humidity solution.

Of the three primary components of lignocellulosic biomass, hemicelluloses have the greatest capacity for water sorption, while lignin has very little capacity for water sorption. At the optimal pH, the HTC process maximizes solubilization of the hemicellulose fraction as liquid soluble. The analysis shows that sugar deposition on particle surface is not significant as the EMC values of recycled samples remain nearly similar compared to control run. However, more study is required to understand the unchanged characteristics of pretreated biomass in recycle experiment.

2.4 Discussion

In general, all lignocellulosic biomass have constituents like hemicelluloses, cellulose, lignin, extractives, and inorganic materials or ash. Their amounts differ by biomass type, but building blocks for hemicelluloses and cellulose are either pentose or hexose sugars. With HTC of lignocellulosic biomass, part of these sugar monomers will dissolve in the liquid phase along with the extractives, depending on pretreatment condition and type of biomass. The inorganic content is as low as below 1% for woody biomass to as high as above 20% for agricultural residues, and most of this inorganic component is silica. HTC alone is not capable of removing inorganics. Loblolly pine, a representative woody biomass, is studied in this research work, but the findings of this study can be generalized for similar kinds of lignocellulosic biomass. The mass yield analysis shows a predictable trend over the temperature range investigated in process water recycling. The slight variation of HHV with increasing recycle number cannot limit the recycling of process water as, from a statistical point of view; the change will be insignificant if a regression analysis is done for those data sets. At low temperature, the change in synergic value is not significant and, on the other hand, with high temperature HTC, e.g. at 260 °C, the subcritical water pressure is 4.6 MPa, which requires a higher pressure system and more tar formation is likely to happen at this temperature. Those may limit the aspects of pretreatment and recycling of process water.

Reza et al., (2013) showed that the HTC process can leach out some of the heavy metals along with alkali and alkali earth metals from biomass structure [7]. In the successive recycling of process water, there may build up of those metals inside the reactor. It requires study to identify such effects if it applies in a continuous process. However, more study is needed to make a general statement about process water recycling.

2.5 Conclusion

HTC, a promising technology for making energy dense, homogeneous bio-coal, is increasing in popularity enough to consider optimizing its different process parameters. Recycling of process water in successive experiments shows many positive results. There is about 5% increase of mass yield at all temperatures investigated after the 1st recycle. HHV values show nearly constant trend with increasing recycle numbers with some small variation. The water soluble carbonaceous substances are concentrated with successive recycles, but not as much as would be expected to increase after first recycle. The EMC results indicate unchanged hydrophobicity of the bio-coal with recycling process water. Although recycling process water results show good characteristics, further study requires choosing appropriate operating conditions. It has been done 10 recycle experiments for loblolly pine and based on these results, recycling of process water can be repeated for 10 successive run. However, more investigation is required to avoid heavy metal accumulation inside the reactor based on the biomass types. Furthermore, replication and change in recycle water need to be analyzed for continuous process application.

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Chapter 3

3.1 Error analysis of kinetic model of loblolly pine

3.1.1 Introduction

Uncertainty means lack of sureness about something. Uncertainty may range from a falling short of certainty to an almost complete lack of conviction or knowledge, especially about an outcome or result. It applies to predictions of future events, to physical measurements already made, or to the unknown. On the other hand, an error is defined as a difference between the desired and actual performance, and behavior of a system or object. This definition is the basis of operation for many types of control systems, in which error is defined as the difference between a set point and the process value.

In science and engineering, there are numerous experimental measurements made to predict or to conclude about something. And there is no absolute technique to take those measurements without error. This error may come from deviations and inaccuracies caused by the measuring apparatus or from the inaccurate reading of the displaying device, but also with optimal instruments and digital displays there are always fluctuations in the measured data. However, thermal experiments possess more error range than other physical parameter measurement techniques [1]. Such kinds of errors make it difficult to obtain same result from successive experiments. This indicates that there is a wide range of set of data that can be generated from the same piece of equipment that can be termed the uncertainty of the process or the lack of complete knowledge of the data sets. So the knowledge of the experimental uncertainties is essential to assess the reliability of the conclusion made from the experimental data.

3.1.2 Monte Carlo simulation

The Monte Carlo method is just one of many methods for analyzing uncertainty propagation, where the goal is to determine how random variation, lack of knowledge, or error affects the sensitivity, performance, or reliability of the system that is being modeled [2]. Monte Carlo simulation is categorized as a statistical sampling method because the inputs are randomly generated from probability distributions to simulate the process of sampling from an actual population. The first step is to select a distribution for the inputs that most closely matches the experimental data recorded, or best represents the current state of knowledge. The data generated from the simulation can be represented as probability distributions (or histograms) or converted to error bars, reliability predictions, tolerance zones, and confidence intervals for the purpose of statistically characterizing the level of confidence in the computed output.

Monte Carlo methods vary, but tend to follow a particular pattern [3]:

- Define a domain of possible inputs;
- Generate inputs randomly from a probability distribution over the domain;
- Perform a deterministic computation on the inputs; and
- Aggregate the results.

3.1.3 Kinetic Model for Hydrothermal Carbonization

The reaction of lignocellulosic biomass fractions namely lignin, cellulose, and hemicellulose follows distinct path in the presence of a specific hydrothermal condition [4]. In literature, the reaction path and their corresponding activation energy for those pure components are available. However, lignocellulosic biomass consisting of all compounds together, may experience different activation energies. One reaction can affect the other, resulting in a change of activation energy for the individual components. Reza et al., proposed a simple kinetic model, consisting of two parallel first-order reactions, to calculate the activation energies of cellulose and hemicellulose of loblolly pine assuming the water extractive reactions are instantaneous [5].

Extractives → Soluble + Gas (1)

Hemicellulose → Soluble sugars + Gas (2)

Cellulose → β B_c + $(1 - \beta)$ (Soluble sugar + Gas) (3)

where B_c, represents solid products from cellulose decomposition. Cellulose does not decompose completely and the mass yield of biochar from cellulose is denoted by the parameter β in the third reaction. The rates of decomposition of both hemicellulose (H(t)) and cellulose (C(t)) are both described by the first order reaction kinetics, where k_1 and k_2 are the rate constants for the two reactions.

$$\frac{d\mathrm{H}(t)}{dt} = -k_1 \mathrm{H}(t) \tag{4}$$

$$\frac{dC(t)}{dt} = -k_2 C(t) \tag{5}$$

The solution of these equations is shown below, with the initial mass at time zero. The expression for the functions of H(t), C(t), and $B_c(t)$ are function of reaction time but the function of L(t) is expressed as a constant as lignin is considered to be an inert component.

$$H(t) = H_0 e^{-k_1 t} \tag{6}$$

$$C(t) = C_0 e^{-k_2 t} \tag{7}$$

$$B_c(t) = \beta C_0 (1 - e^{-k_2 t}) \tag{8}$$

$$L(t) = L_0 \tag{9}$$

where H_0, C_0, and L_0 represent the initial mass of hemicellulose, cellulose, and lignin in loblolly pine, respectively. If M(t) represents the mass of unreacted biomass plus solid-phase reaction products at time t, M(t) can be written by

$$M(t) = H(t) + C(t) + B_c(t) + L(t) \tag{10}$$

To express the mass yield of biomass Y(t), Eq. (10) can be rewritten as Eq.(11)

$$Y(t) = \frac{M(t)}{M_0} = Y_{H0} e^{-k_1 t} + Y_{C0} e^{-k_2 t} + \beta Y_{C0} (1 - e^{-k_2 t}) + Y_{L0} \tag{11}$$

To calculate the rate constants k_1 and k_2, the mass yield of loblolly pine is measured experimentally for various reaction times at a specific HTC temperature. The experimental data for Y(t) are plotted as a function of time; k_1 and k_2 are adjusted according to a nonlinear optimization algorithm to minimize the difference between predicted yield, and measured yield. An Arrhenius plot of these rate constants will finally generate the degradation activation energies of hemicellulose and cellulose under HTC process of loblolly pine.

3.1.4 Error in experimental mass yield of loblolly pine

HTC of loblolly pine was performed in subcritical water at temperatures of 200, 230, and 260 °C. The experimental data were collected at eleven intervals: 15 s, 30 s, 45 s, 1 min, 2 min, 3 min, 4 min, 5 min, 10 min, 20 min, and 30 min [6]. Each experiment (mass yield at a specific time and temperature) was repeated in triplicate. The error involved in the measurement of loblolly pine's mass yield is seen from the sample data in Table 3.1, where the experiment was repeated three times under the same condition of 200 °C and reaction time of 1minute and mass yield was calculated using the following equation:

$$Mass\ yield, \% = \frac{w_3 - w_1}{w_2} \times 100 \qquad (12)$$

There were three direct weight measurements taken for calculating each mass yields of solid product and three sets of data show different mass yields. This indicates that there are systematic, random, and round-off or truncation error associated with the final prediction of rate constants and hence, the activation energies of cellulose and hemicellulose. Systematic errors are external effects which can change the results of the experiment, but for which the corrections are not well known. This is why several independent confirmations of experimental results are often required to make conclusion from experimental data. Random errors are errors which fluctuate from one measurement to the next. They yield results distributed about some mean value. They can occur for a variety of reasons. The round-off error is a kind of propagated error, which is repeated throughout the calculation using finitely many digits to represent real numbers (which in theory have infinitely many digits).

Table 3.1 Example of mass yield calculations from experimental measurement.

HTC temperature 200 °C and reaction time 1minute (Data from [6])				
	Recorded weight, g			
Run	Steel mesh, w_1	Biomass sample, w_2	Steel mesh + dried HTC biomass, w_3	Mass Yield, %
1	0.2652	0.2060	0.4278	78.93
2	0.3012	0.2062	0.4727	83.17
3	0.2601	0.1708	0.4005	82.20

3.2 Data analysis

The data of weight measurements shown in Table 3.1 were taken in a scale (manufacturer-Denver Instrument, model - S-234), with precision of 0.1mg. The recorded weight is assumed to be close to the actual weight, and it is assumed that the sample weight can be represented by a normal distribution of weights, with mean equal to the recorded value, and standard deviation equal to the instrument precision.

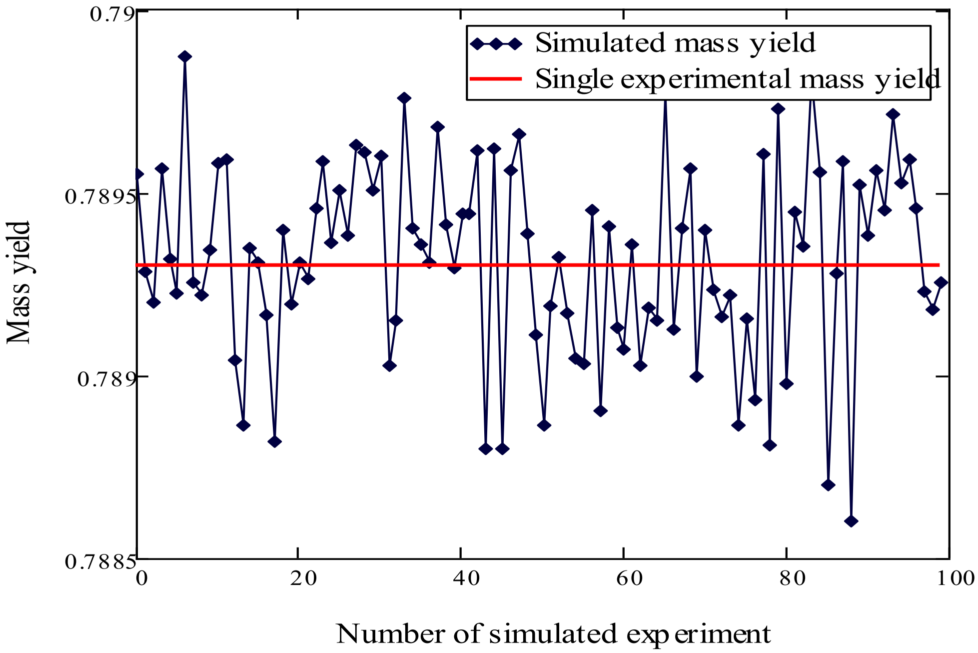


Figure 3.1 (a) Probable mass yields of solid char from loblolly pine according to random distribution of run 1 data from Table 3.1.

This allows generating a distribution of many values, each equally likely to be the real value. Following the Monte Carlo method of generating random distribution of probable data, there has been 100 randomly selected values of weights for steel mesh, 100 random values for biomass sample weight, and 100 values for steel mesh and dried

HTC biomass, all for run 1 of Table 3.1. For run 1 alone, the mass yield can be calculated 100 times, each an equally valid measure of the real mass yield. Figure 3.1 shows the equally likely experimental outcome of the mass yield if done 100 times for run 1 and 3, which are predicted from the single real experiment. So, the three repeated experimental results at the same condition provide 300 equally valid values of the mass yield. That distribution can be characterized with a mean and standard deviation, which might be used to statistically characterize the mass yield at 1 minute, 200 ˚C.

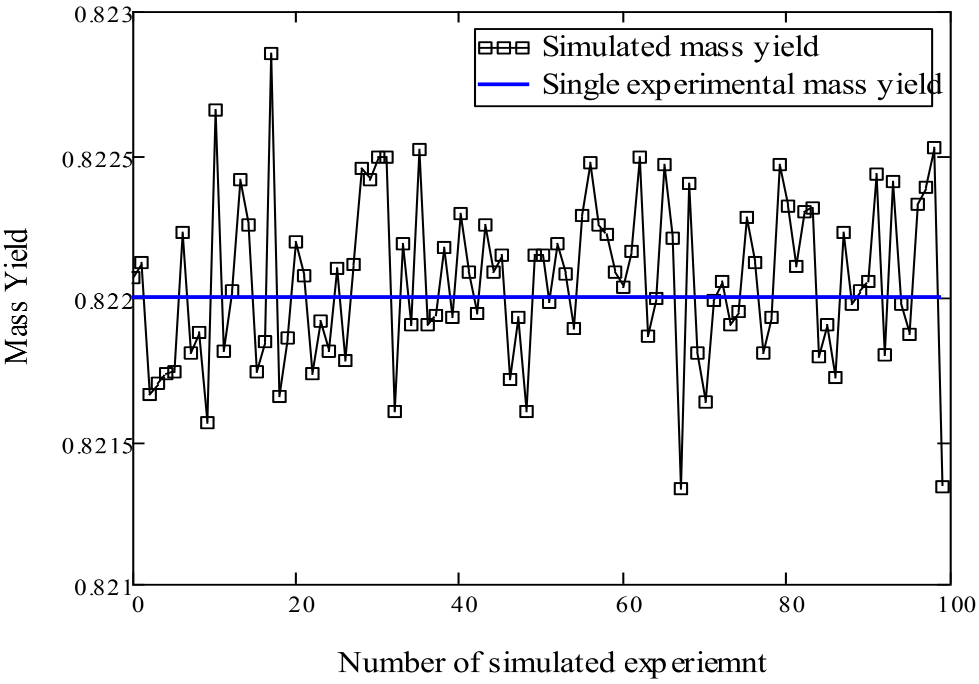


Figure 3.1 (b) Probable mass yields of loblolly pine according to random distribution of run 3 data from Table 3.1.

Subsequently, when the mass yield is required 100 new values of mass yields are generated randomly from a normal distribution generated with that mean and standard deviation. This analysis leads to a statistically characterized value of the mass yield. The mean and standard deviation of mass yield calculated from the three values for mass yield shown in Table 3.1 are 81.44% and 2.2%, while the mean and distribution of the three hundred values generated stochastically are 81.40% and 1.8%, respectively. The similar procedure has been followed to generate a mean and standard deviation for the rest of the 10 time intervals at 200 ˚C.

$$Residual(k_1, k_2) = \sum_{t=0}^{\infty}(Y(t)_{experimental} - Y(k_1, k_2, t)_{model})^2 \qquad (13)$$

Using the Nonlinear Quasi-Newton solution method in MathCAD-15, the best fit values for rate constants k_1 and k_2 from Eq. (11) and (13) are determined for each set of data minimizing the residual function with a tolerance 10^{-7} at a single temperature for each randomly generated time series, 100 times.

As result, there are 100 paired values for rate constants k_1 and k_2 at 200 °C. In fact, the objective function F(k_1, k_2) is minimized at each reaction temperate (200 °C, 230 °C, 260 °C) 100 times, providing a distribution of both rate constants at each temperature. At 200 ˚C, the mean values of k_1 and k_2 are 0.0153 s^{-1}, and 0.00282 s^{-1}, with standard deviations of 0.0059 s^{-1} and 0.00044 s^{-1}, respectively. Table 3.2 gives the mass yields found at all temperatures and times using the stochastic method described above, and Figure 3.2 shows the rate constants for degradation of hemicellulose and cellulose calculated at three different temperatures found by minimizing the objective function given in equation 13. The small change in mass yields allows for the generation a wide range of rate constants that are randomly distributed at a specific reaction temperature. Cellulose rate constants have less random characteristics than hemicellulose.

Table 3.2 Mass yields of loblolly pine. Values calculated from the mean mass yield from deterministic measurements are labeled “Experimental”, while those calculated from the Monte Carlo error analysis are labeled “stochastic”.

Temperature (^oC)	**Time (s)**	**Mass yield (Experimental) (%)**	**Mass yield (Stochastic) (%)**
200	15	90.13 ± 1.8	90.10 ± 1.4
	30	85.02 ± 1.7	85.00 ± 1.4
	45	82.45 ± 1.7	82.40 ± 1.4
	60	81.44 ± 2.2	81.40 ± 1.8
	120	76.80 ± 2.1	76.80 ± 1.7
	180	74.45 ± 1.8	74.50 ± 1.4
	240	69.59 ± 0.9	69.60 ± 0.7
	300	63.88 ± 0.1	63.9 ± 0.1
230	15	85.47 ± 2.2	85.5 ± 1.8
	30	76.50 ± 0.9	76.10 ± 0.3
	45	70.19 ± 0.8	69.9 ± 0.1
	60	66.48 ± 0.9	66.50 ± 0.1
	120	63.65 ± 0.5	63.5 ± 0.1
	180	62.70 ± 1.5	62.10 ± 1.0
	240	59.51 ± 1.0	59.50 ± 1.0
	300	58.04 ± 1.1	58.2 ± 1.0
260	15	85.83 ± 1.9	85.80 ± 1.6
	30	73.79 ± 0.9	73.80 ± 0.7
	45	63.69± 1.1	63.70± 0.9
	60	55.90± 1.4	54.90± 1.1
	120	54.94± 4.2	55.90± 3.5
	180	54.70± 4.9	54.30± 4.0
	240	54.60± 3.4	54.70± 2.8
	300	54.30± 4.5	54.60± 3.7

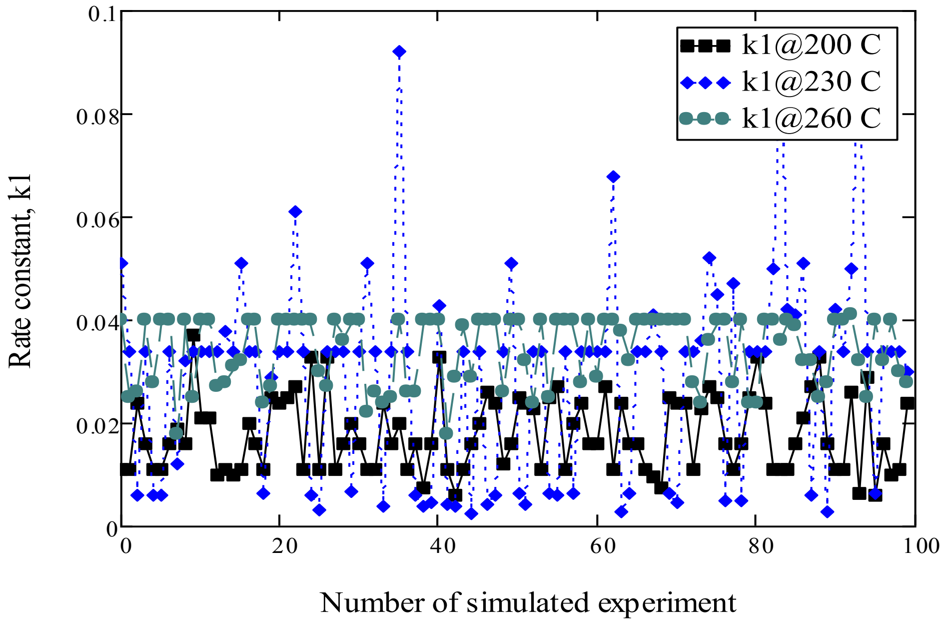


Figure 3.2 (a) Simulated rate constants for hemicellulose

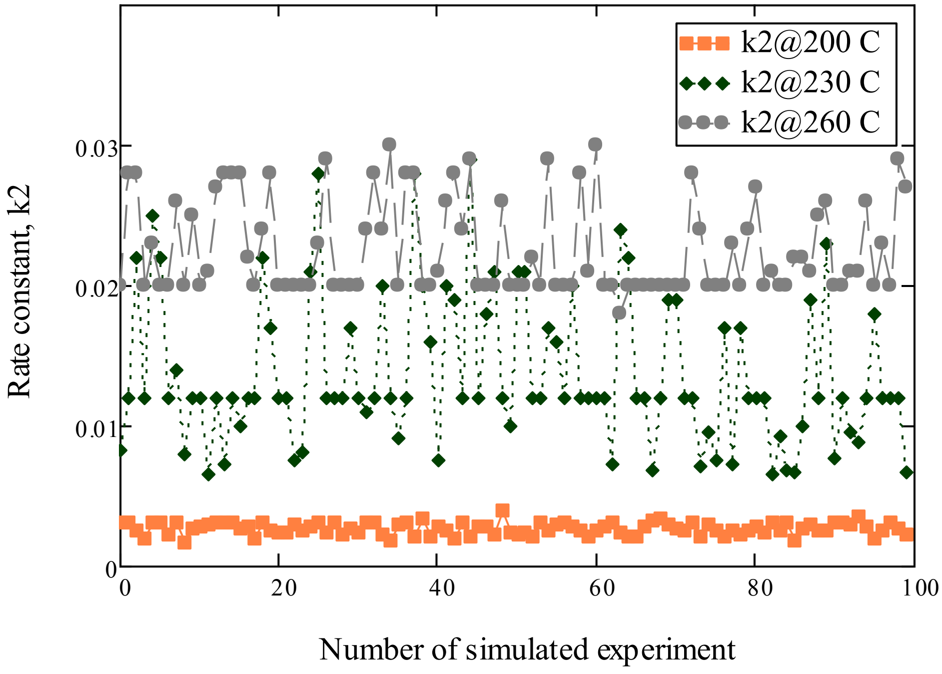


Figure 3.2 (b) Simulated rate constants for cellulose

By minimizing the objective function F(k_1, k_2) only once using the average mass yields at 200 ˚C, the average values of k_1 and k_2 are 0.04 s^{-1} and 0.0022 s^{-1}. Table 3.3 data are calculated using the Generalized Reduced Gradient (GRD2) linear optimization of Microsoft Excel to minimize the residual function for the experimental average data. The values of rate constants calculated in both methods are listed in Table 3.3 and Table 3.4. The value of k_2 calculated both ways is pretty close at all three temperatures. The same cannot be said about calculation of k_1, where the standard deviation of the Monte Carlo sample is relatively high at all temperatures.

Table 3.3 Kinetic parameters of hydrothermal carbonization of loblolly pine. k_{01} and k_{02} are pre-exponential factors. All are calculated using the experimental results deterministic values, as described by Reza (2011).

T (°C)	k_1 (s^{-1})	**E₁** (kJ·mol⁻¹)	k_{01} (s^{-1})	k_2 (s^{-1})	**E₂** (kJ·mol⁻¹)	k_{02} (s^{-1})
200	0.04			0.0022		
230	0.07	28.56	58.58	0.0085	77.42	824.06×10^3
260	0.09			0.0200		

Table 3.4 Results of Monte-Carlo simulation of kinetic parameters. Shown in the 90% confidence interval, and in all cases, 1st value is the mean and 2nd is standard deviation.

T **(° C)**	***k_1*** **(s^{-1})**	**E_1** **($kJ \cdot mol^{-1}$)**	***k_{01}*** **(s^{-1})**	***k_2*** **(s^{-1})**	**E_2** **($kJ \cdot mol^{-1}$)**	***k_{02}*** **(s^{-1})**
200	0.015±0.0059			0.0028±0.0004		
230	0.030±0.02	30.15±12.14	331±573	0.0140±0.0053	73.04±6.1	$1\times10^6\pm2\times10^6$
260	0.034±0.0067			0.0230±0.0034		

A linear Arrhenius plot is generated using those rate constants, giving 100 values of slope which are the activation energies for thermal decomposition of hemicellulose and cellulose, and also100 values of intercepts which are pre-exponential factors of Arrhenius equation. Both activation energies are calculated as a statistical distribution, and each may be characterized with a mean and corresponding standard deviation. Figure 3.3 shows the overall distribution of activation energies and Figure 3.4 represents the relative frequency distribution of activation energies with 90% confidence interval along with cumulative distribution.

That reaction rate is quite fast, and the reaction is essentially completed before one minute. It is possible that the rate of degradation of hemicellulose is limited by mass transfer, not considered by this analysis. (The topic of mass transfer limitation is taken up in detail in section 3.2) The Monte Carlo simulation has identified a possible weakness in the experimental method that is not apparent from the straightforward analysis.

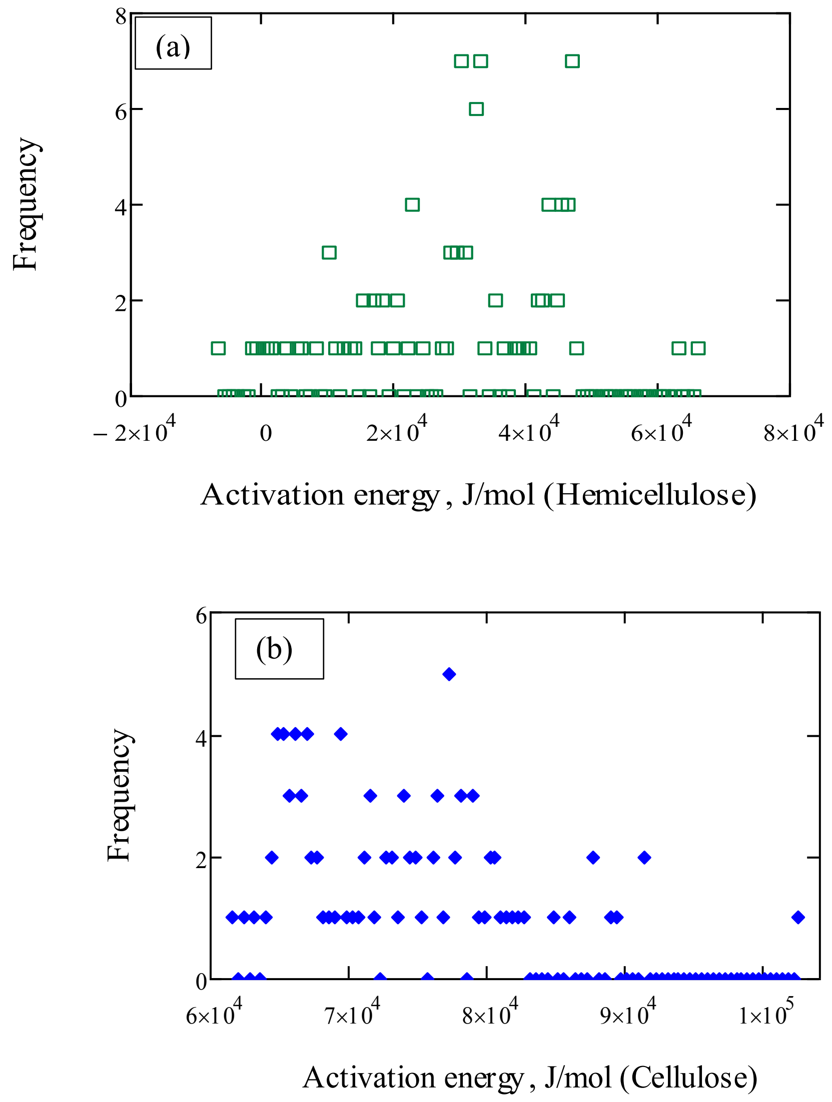


Figure 3.3 (a) & (b) Activation energy distribution of hemicellulose and cellulose

It shows that the deterministic values of kinetic parameter have large degree of uncertainty, especially for hemicellulose. The higher activation energy for cellulose compared to that of hemicellulose is consistent with data reported elsewhere [4, 6], indicating the greater recalcitrance of cellulose.

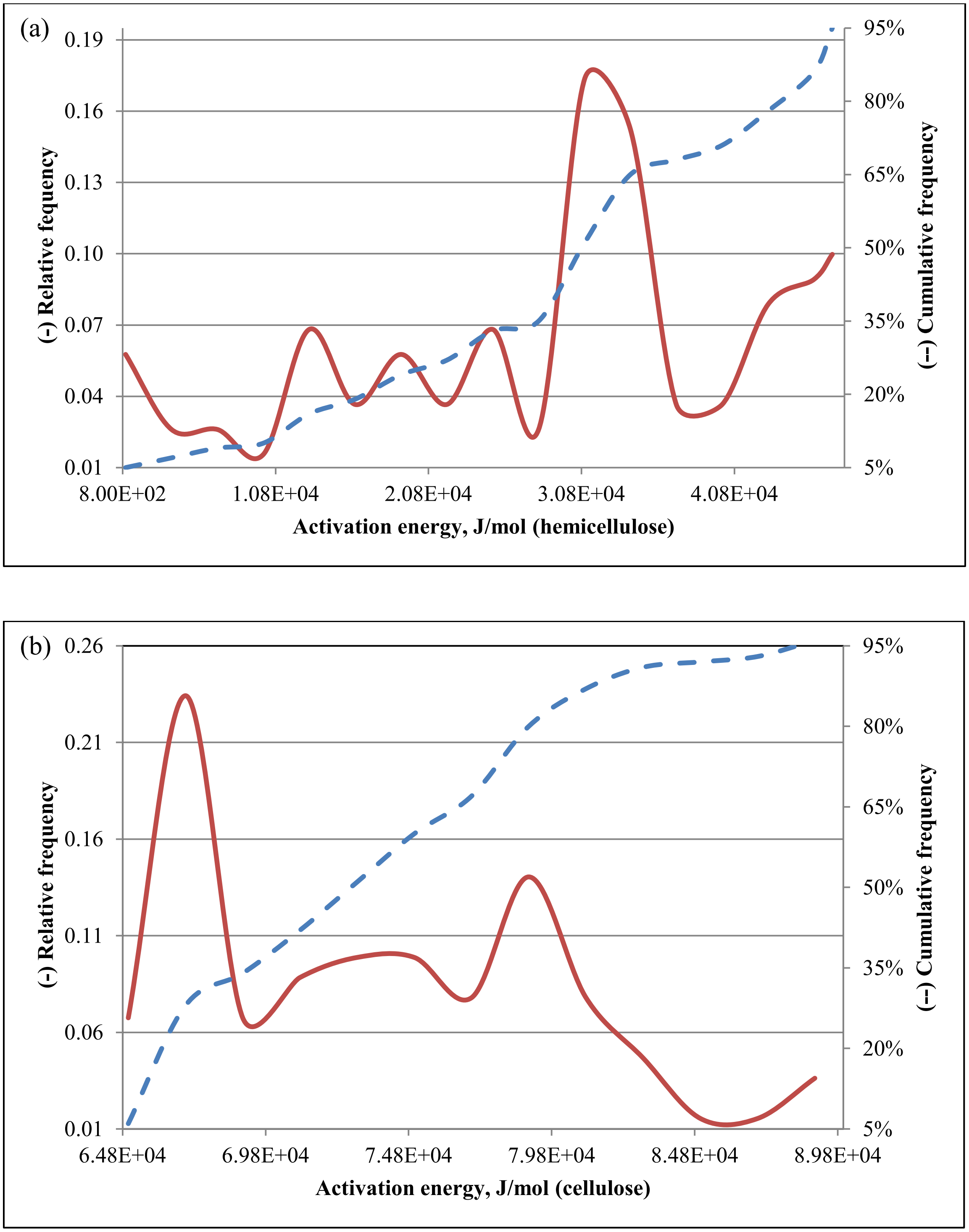


Figure 3.4 (a) & (b) Distribution of values for activation energy of hemicellulose and cellulose degradation. Shown is the 90% confidence interval.

The numerical values for activation energies are smaller than those of the pure hemicellulose and cellulose (129-215 kJ/mol) in this temperature range [4, 7]. Instantaneous degradation of aqueous extractives likely reduces the pH of the solution and thus enhances degradation of hemicelluloses and cellulose [8], while hemicellulose degradation results in even greater acid production, further catalyzing cellulose reactions. As a result, the individual activation energies for both hemicellulose and cellulose are lower than those for the pure forms not encased in a lignocellulosic biomass package.

3.2Mass transfer effects

3.2.1 Particle size effect on hydrothermal carbonization

Both mass transfer and intrinsic reaction kinetics may play a role in determining the overall rate of the mass degradation reactions of lignocellulosic biomass in hydrothermal media. The HTC reactions occur within the pores of the biomass and thus, hot water must enter the pores while at the same time the aqueous products must leave the pores. Mass transfer of reaction products from the pores could be a rate limiting step, since the reaction kinetics seems to be fast, as discussed above. Below, the effects of mass transfer are evaluated by measuring reaction rates with different particle size for short contact times.

Table 3.5 shows the experimental conditions, and a summary of the relevant results. For an identical time, temperature, and biomass, the mass yield is increasing with increasing particle size, which implies that mass transfer effects may be rate limiting. A simple model has been developed to account for simultaneous mass and heat transfer effects for HTC reactions. In this model, cellulose degradation was assumed to represent all HTC reactions, since hemicellulose can be assumed to be essentially degraded after 1 minute at 230 ˚C, while lignin is relatively inert. Other key assumptions for the mass transfer analysis were the following:

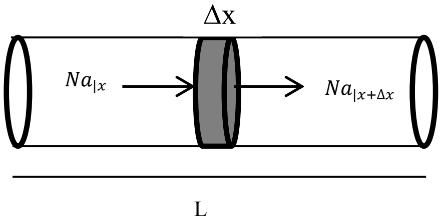
a) Reaction is said to occur on the surface of a cylindrical pore extending through the particle to the particle surface, with length equal to the particle length.

b) Mass diffusion and reaction occur on the pore surface and there is no radial mass transfer; mass transport is modeled to occur only in the axial direction of the pore.

c) Glucose is the only fluid product of cellulose degradation, and glucose alone is transported out of the pore during reaction.

d) The system is modeled as steady state. Strictly speaking, this is incorrect, since the solid reactant is being continuously consumed, and the rate of reaction decreases continuously. However, this is a pseudo-steady state assumption, in which it is assumed that the pore geometry and rate of reaction change only slowly relative to the time required for diffusion through a pore.

A steady-state material balance on glucose in a differential volume in a single cylindrical pore gives:



Rate of mass in – Rate of mass out + Rate of production = 0 (13)

$$A\,Na_{|x} - A\,Na_{|x+\Delta x} + r_{rxn}(A\,\Delta x) = 0 \tag{14}$$

Where A is the cross sectional area, r_{rxn} is the rate of glucose production per unit volume, Δx is the differential length, and L is the pore length. After dividing by volume on each side of Eq. 14 and approximating the differential length to zero, Eq.14 becomes

$$\frac{Na_{|x}-Na_{|x+\Delta x}}{\Delta x}+r_{rxn}=0 \quad (15)$$

$$-\frac{dNa}{dx}+r_{rxn}=0 \quad (16)$$

Applying Fick’s law of diffusion for glucose and considering the rate of glucose production according to Eq. 5 and 7and substituting all this parameters in Eq.16 gives

$$Na=-D_{eff}\frac{dC_{gl}}{dx} \quad (17)$$

$$D_{eff}\frac{d^2C_{gl}}{dx^2}+k_2\,C_{gl0}e^{-k_2t}=0 \quad (18)$$

Where C_{gl} is glucose production at time t, C_{gl0} is the initial glucose in cellulose. Eq.18 can be written in the following dimensionless form, assuming constant diffusivity and dilute concentration.

$$\frac{d^2\psi}{d\lambda^2}+\Phi^2=0 \quad (19)$$

$$\Phi=\sqrt{\frac{L^2\alpha k_2e^{-k_2t}}{D_{eff}}} \quad (20)$$

Eq.20 can be expressed as

$$\Phi^2=\frac{surface\ reaction\ rate}{diffusion\ rate} \quad (21)$$

ψ is the dimensionless glucose concentration, and λ is the dimensionless axial position. D_{eff} is the effective diffusivity, L is the particle/pore length reported in Table 3.5, k2 is the rate of cellulose degradation, and α is the stoichiometric production of glucose from cellulose. Note that the glucose is a product of reaction, not a reactant, and its rate of production is first order in cellulose; that is, the rate is independent of glucose concentration. This is mathematically similar to a zero order reaction, from the perspective of glucose, concentration of glucose does not affect the reaction rate. Next, the dimensionless Thiele modulus φ is evaluated to identify the rate limiting step [8].

The temperature effect on diffusivity (D_{eff}) is taken into account by applying the Stokes-Einstein equation for liquid diffusion, as follows:

$$D_{eff} = D(T_o)_{eff}[\frac{T}{T_o}\frac{\mu(T)}{\mu(T_o)}] \tag{16}$$

Here T and T_o represent the reaction temperature and a reference temperature at which the viscosity $\mu(T_o)$ and diffusivity $D_{eff}(T_o)$ are known. Numerical values needed to evaluate D_{eff} and φ are provided in Table 3.6, and the computed values of φ are given in Table 3.5.

Table 3.5 Effect of particle size on Hydrothermal Carbonization at 230 °C and 1 minute reaction time

Tyler Mesh	Average Particle diameter, mm	Average Particle length, mm	Mass Yield, %		Thiele modulus
			Experimental	Model	
14-28	0.88	3.5	68.6	66.8	2.0
10-14	1.41	4.2	69.9	72.6	2.4
8-10	2.1	5.1	71.4	76.3	2.9

Table 3.6 Physical properties used for calculation of Thiele modulus.

Variable	Description	Value	Reference
T_0	Reference Temperature	25 °C	
μ (T_0)	Viscosity of water at reference temperature	8.89 E-4 Pa.s	
D_{eff} (T_0)	Effective diffusivity of glucose at reference temperature	6.735E-10 m^2/s	[11]
α	Stoichiometric production of glucose from degradation of cellulose	0.4	This work
t	Time	60 s	
T	Reaction temperature	230 ˚C	

This is similar to the Thiele Modulus for a zero-order order porous catalyst reactive system [9]. For φ <0.4, the concentration of reactant does not drop appreciably within the pore; thus pore diffusion offers negligible resistance and the rate of reaction is limited by intrinsic kinetics. This means that a short pore, a slow reaction, or rapid diffusion exists, with all three factors tending to lower the resistance to diffusion. For φ >4, the concentration of reactant drops rapidly to zero on moving into the pore; hence diffusion strongly influences the r ate of reaction [9]. The effects of both reaction and diffusion are prominent in HTC, as they are in the range of 2-2.9. As temperature increases, both mass transfer and reaction increase; since the Thiele modulus is increasing with particle size, it is concluded that the overall reaction rate is more dominated by mass transfer considerations at larger particle size. From the analogy of Thiele Modulus it can be said that mass diffusion and cellulose reaction rate both play important roles in HTC reaction rate in the temperature range considered here.

3.3 Conclusion

The final result of this exercise was a distribution of values for rate constants for both k_1 and k_2, shown in Figure 3.2. Mean values and standard deviations for both reaction constants were calculated from those distributions. The mean activation energy for hemicellulose degradation (E1) was 30 kJ/mol with a standard deviation of 12 kJ/mol, and for cellulose (E2) was 73 kJ/mol with a standard deviation of 6 kJ/mol. The variance for the activation energy for E1 (hemicellulose) was relatively high (40%), while that for E2 was about 8%. Hemicellulose degradation is very rapid and the effect can be observed only during the first 1-2 minutes at lower temperatures; mass transfer may indeed be rate limiting. It is possible that the experiments done in such short times involved more errors than those done in longer time periods because it is difficult to satisfy all the conditions in 15 s reaction time. Thus, numerical evaluation of the first-order rate constant of hemicellulose degradation is subject to a high degree of uncertainty. The mean values found from this Monte Carlo simulation were close to those found by deterministic calculations, as shown in Table 3.3, and were compared in Table 3.4. In both cases, the mean values found from deterministic calculations (using only mean mass yields) were within a single standard deviation of the mean found from the Monte Carlo simulation. The particle size effect on HTC process can play an important role for degradation and the simple analogy with the Thiele Modulus can be insightful for further study of it kinetics.

3.4 References

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Chapter 4

Water production during HTC of loblolly pine

Lignocellulosic components are large, straight, and cross-linked polymers that can be degraded into multiple of components in the HTC process resulting in a large number of chemical reactions between different components in the reaction mixture, which makes it difficult to model the degradation kinetics. Although literature studies show that hydrolysis, dehydration, decarboxylation, condensation/polymerization, and polymerization reactions occur in parallel in the HTC process, dehydration reactions are found as the primary after initial hydrolysis. To simplify the degradation model and understand the primary reactions, an experimental and theoretical approach has been developed for the quantification of dehydration. A detailed water balances were performed on HTC reactions at 200 °C, 230 °C, and 260 °C for 5, 15, and 30 min reaction times. The results suggest that it is possible to consume water at lower temperature pretreatment with short residence time. However, dehydration/water production increases with the HTC temperature.

4.1 Introduction

Nature has been converting carbonaceous plant materials to valuable fossil fuels for millions of years using geothermal conditions of high pressure and temperature. In the last century, researchers have begun to suspect that coal's natural formation is mainly a chemical process, rather than a biological process [1]. Scientists, such as Bergius, Berl, Schmidth, Leibnitz, and van Krevelen, tried to mimic the natural coal formation process in their laboratories [1]. This artificial coalification process has been called hydrothermal carbonization (HTC) [2]. Wet biomass, agricultural waste, or municipal wastes are treated in hot compressed water at subcritical temperatures. The concept of using hot compressed water for HTC was first explained by Leibniz in 1958 [3], who demonstrated the necessity of H_2O (either steam or water) in the mechanism of the reaction. van Krevelen proved that certain plant species could give specific recognizable lithotypes in the coal product and that the medium also affects the result [4], and suggested the dominant reactions during HTC and introduced the atomic H:C and O:C diagram known as van Krevelen diagram. Other researchers in the 1960s found that several complex chains of chemical reactions are involved, each with their own intermediate products [5, 6]. Nevertheless, the extremely challenging reaction mechanism and kinetics leave synthetic coalification still a mystery. Although lignocellulosic biomass has four major constituents, lignin, cellulose, hemicelluloses, and extractives, most major studies of reaction mechanism have been carried out using cellulose as a model compound. Cellulose is a polysaccharide of glucose with β-(1-4) glucosidic bonds. During HTC at reaction temperatures of 220-230 $^{\circ}$C, very little or no change in cellulose was reported by Sevila (2009) [7]. Hemicelluloses are mostly linear heteropolymers composed of sugar monomers, including xylose, mannose, glucose, and galactose with β-(1-4) glucosidic bonds [8]. Hemicelluloses hydrolyze more rapidly than cellulose, with the degradation of hemicellulose reported to start at temperatures as low as 180 °C. Lignin, a high molecular weight cross-linked polymer of phenyl propane derivatives, is the most stable component of lignocellulosic biomass when undergoing HTC. The degradation of lignin likely starts at temperatures higher than 250 °C, although lignin composition can vary from biomass to biomass so that reaction mechanism may vary depending on feedstock [9].

However, the production of water during hydrothermal carbonization of lignocellulosic biomass has not been investigated fully as a separate topic, although there are a number of supporting materials that provide insight into water production. Dinjus et al. found the stoichiometric equations (Eq. 1), from the elemental compositions of beech wood after carbonization at 220 °C for a reaction time of 4 h and the corresponding HTC coal, which give 14% water production [10].

$$4\ C_{41}H_{56}O_{29} \leftrightarrow 3\ C_{51}H_{54}O_{21} + 31\ H_2O + 11\ CO_2 \qquad (1)$$

A detailed pathway (Figure 4.1) of cellulose degradation was proposed by Ehara et al. [11]. They proposed that cellulose decomposition started through hydrolysis, dehydration, and fragmentation. First, cellulose is hydrolyzed to polysaccharides and oligosaccharides. The decomposition to polysaccharides gives a range between 13 and 100 monosaccharide units, while oligosaccharides' are between 2 and 12 units. The reducing end of glucose is dehydrated and fragmented to levoglucosan, erythrose, and glycolaldehyde.

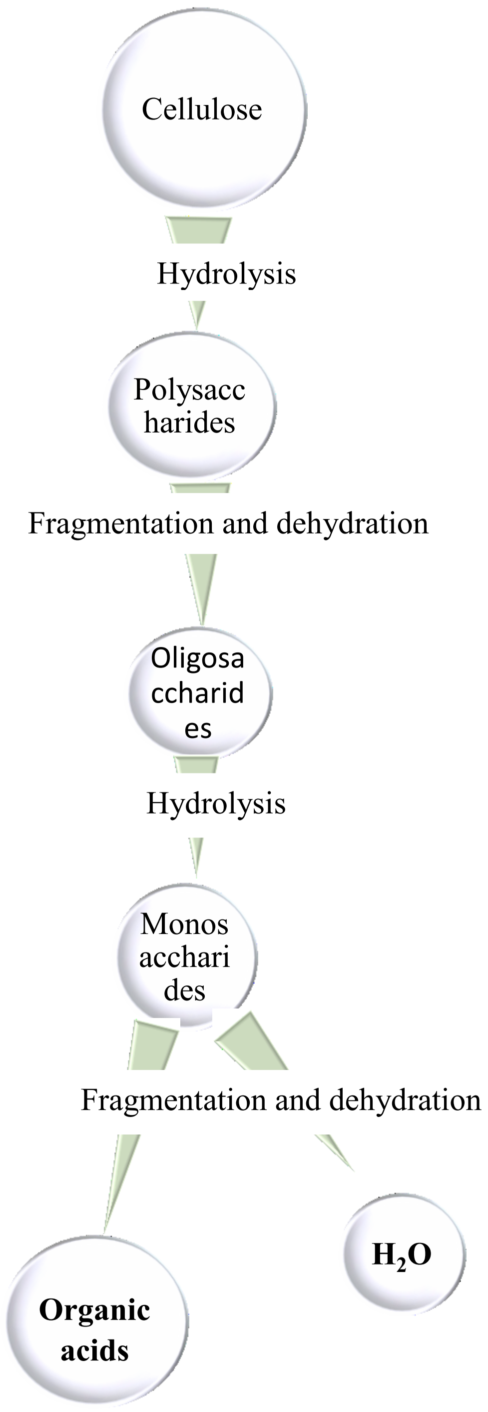

Figure 4.1 Cellulose decomposition pathways [11]

These dehydrated and fragmented oligosaccharides are further hydrolyzed in the oligosaccharide portion to glucose, which is isomerized to fructose. The resultant hexoses are then further decomposed, if treatment is prolonged, to levoglucosan, 5-hydroxymethyl furfural, erythrose, glycolaldehyde, methylglyoxal, and dihydroxyacetone by way of dehydration and fragmentation. These literature studies show that hydrolysis, dehydration, decarboxylation, condensation/polymerization, and polymerization reactions occur in parallel in the HTC process of pure component.

Although such detailed reaction chemistry have been studied and reported for pure individual components and model compounds of lignocellulosic biomass, little study on biomass itself is found in the literature. It is assumed that dehydration reactions are the primary after initial hydrolysis in the HTC process of lignocellulosic biomass. Hence, this study on water production of loblolly pine will provide some useful information on hydrolysis and dehydration characteristics of lignocellulosic biomass.

4.2 Experimental procedure

4.2.1 Biomass

Loblolly pine (*Pinus taeda*) (Alabama, USA) was investigated for these experiments. On a mass basis, it consists of 11.9% hemicellulose, 54.0% cellulose, 25.0% lignin, 8.7% extractives, and 0.4% ash [12]. A commercial food blender was used to reduce the size of the biomass to between 1.4 mm and 0.75 mm diameter and dried at 105 ºC for 24 h before undergoing the HTC process.

4.2.2 Hydrothermal Carbonization

HTC of loblolly pine was performed in a 100 mL Parr Series 4560 bench-top reactor (Moline, IL) with a glass liner fitted inside the reactor. The temperature of the reactor was controlled using a proportional-integral-derivative (PID) controller. The reactor pressure was not controlled, and was approximately in accordance with the water vapor pressure. For each run, a mixture of loblolly pine and water in a mass ratio of 1:8 was loaded into the glass liner. The mixture was stirred manually to ensure complete wetting. Nitrogen was passed through the reactor for 5~ 10 min to purge oxygen from the reactor. The reactor was heated to the desired HTC temperature and maintained at that temperature for the desired time using a PID controller. After the reaction time, the reactor was rapidly cooled off by immersion in an ice bath. All experiments were performed at least 3 times.

4.2.3 Quantitative measurement of products

When the reactor temperature cooled off at or below 10 ºC, the gaseous products were released into the atmosphere. Immediately after opening the reactor, the glass liner along with the liquid and wet solid product was weighted and then the solid and the liquid were separated by vacuum filtration using a Buchner funnel with Whatman filter paper (grade 3, 0.6 µm). The wet pretreated solid product was dried at 105 ºC for 24 h. The amount of nonvolatile organic residue was determined by drying off the liquid product at 105 ºC for 24 h. The amount of volatile acids was estimated from the measured pH of the liquid after filtration.

4.3 Results and discussions

As discussed before, the complex chemical structure and composition of hemicelluloses, celluloses, and lignin, and their variation with maturity, geographic location, and environmental conditions has made difficult to predict the dehydration behavior of lignocellulosic biomass from a common point of view. The variation of water production with reaction temperature during hydrothermal carbonization is expected from what is found in the literature. However, with a long reaction time at specific temperature, the conversion of biomass from low carbon to high carbon content may reach a saturation level within 5~10 min, with aqueous-phase reactions occurring during the rest of the reaction time. The overall results are summarized in Table 4.1.

There are several parameters that have been measured to quantify the produced water through experimental measurements. The definition of those parameters is given below:

$$\boldsymbol{W_d = \frac{W_2}{W_1} \times W_{ws}} \tag{2}$$

$W_d = Total\ mass\ of\ dry\ HTC\ biomass\ from\ reaction$

$W_1 = Mass\ of\ wet\ solid\ biomass\ put\ in\ oven$

$W_2 = Mass\ of\ solid\ after\ drying$

$W_{ws} = Total\ mass\ of\ wet\ solid\ after\ filtration$

$$\boldsymbol{M_p = (\frac{M_2}{M_1} \times M_f)} \tag{3}$$

$M_p = Total\ mass\ of\ precipitate\ produced\ by\ reaction$

$M_1 = Mass\ of\ filtrate\ put\ in\ oven$

$M_2 = Mass\ of\ precipitate\ after\ drying$

$M_f\ = Total\ mass\ of\ filtrate$

$$\boldsymbol{M_a = \left(10^{pK_{eq}-2pH} + 10^{-pH}\right) \times MW \times V_f} \tag{4}$$

M_a = Mass of volatile acids (acetic acid)

K_{eq} = A*cid dissociation constant*

$pH = -log_{10}[H^+]$

$pK_{eq} = -log_{10}[K_{eq}]$

MW = Molecular weight of acid

V_f *= Volume of filtrate*

The gaseous product was released at or below 10 °C, which was small enough to neglect water vapor. The following equation is used to calculate the amount of water produced during reaction:

$$\boldsymbol{W_{\mathrm{H_2O}} = W_{\mathrm{t}} - W_{\mathrm{i}} - W_{\mathrm{d}} - M_{\mathrm{p}} - M_{\mathrm{a}}} \tag{5}$$

$W_{H_2O}\ = Mass\ of\ produced/consumed\ water$

W_t *= Total mass of products before filtration*

W_i = Mass of input water

Table 4.1 Product distribution of loblolly pine, as a function of reaction time and temperature. Values are reported with standard deviations.

Temperature, °C	Time, min	Char, %	Precipitate, %	Acid, %	Gas, %	H2O, %
200	5	79.2±1.1	21.0±1.9	1.6±0.1	6.7±5.9	-8.4±3.6
	30	78.3±0.3	19.0±1.4	1.6±0.1	9.4±5.9	-8.3±4.5
230	5	75.9±0.5	12.4±0.5	1.9±0.2	6.1±2.3	3.7±1.2
	30	72.2±1.5	8.6±1.0	1.6±0.3	9.3±0.7	8.3±1.0
260	5	63.3±0.6	10.6±1.4	3.4±1.0	8.9±3.1	13.8±1.8
	15	56.0±1.0	12.5±1.6	2.3±1.8	12.4±5.0	16.9±5.2
	30	56.0±1.2	7.0±1.0	2.7±0.2	11.3±2.0	23.0±1.0

4.3.1 Effect of temperature

Figure 4.2 shows the temperature effect on water production of loblolly pine during HTC reaction for 5 and 30 min residence time. Since each of these experiment is, at least, triplicated and data are presented as average with error bars. The graph shows that the amount of produced water increases almost linearly with increasing reaction temperature over the temperature range considered. However, the average water production for 5 and 30 min reaction time at 200 °C is negative. Hydrolysis of hemicellulose and cellulose requires one mole of water to produce one mole of dissolved monomeric sugar. On the other hand, two moles of those monomers (e.g. glucose) in the liquid can form one mole of dimer (e.g. sucrose) and one mole of water, or one mole of those monomers can further degrade into lower carbon component and water.

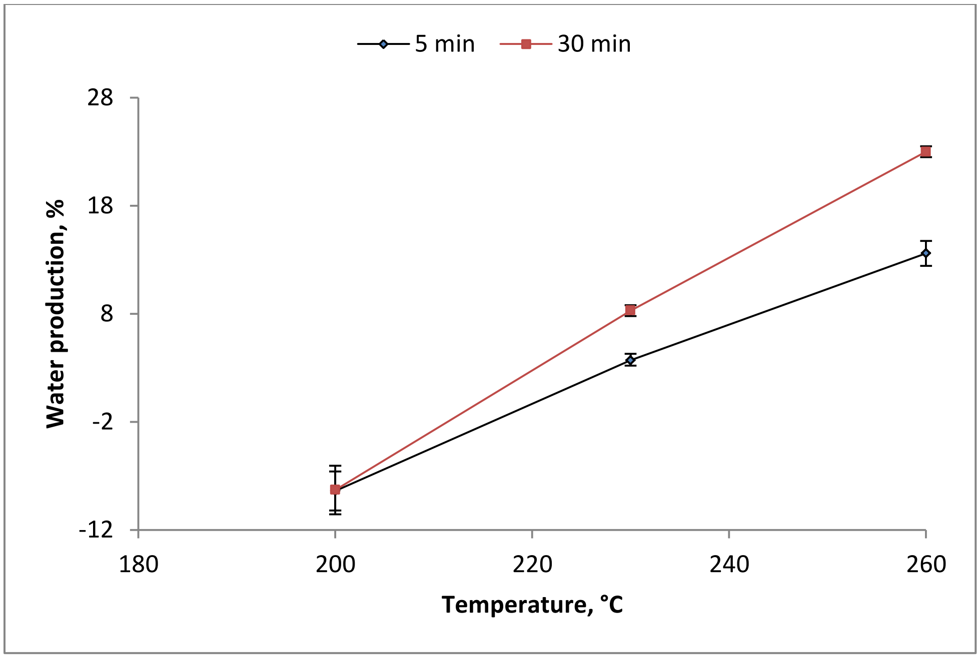

Figure 4.2 Water production variations with temperature. This curve is generated using the experimental mean and standard deviation data.

If there is no other means of water production in the process then only dehydration or polymerization or degradation to lower carbon component of those dissolved sugars can balance the water input. Thus, the possible explanation for a negative water production at 200 °C is that the dehydration reactions are not significant in this case and the further degradation/polymerization of monomers is slow. Furthermore, Yan et al., (2011) reported that the gas production increased with temperature for loblolly pine and it was minimal at 200 °C [12]. CO_2, primary in the gas stream, can be produced either from the breakage of sugar monomers where 5 or 6 moles of H_2O can be produced based on sugar monomer reaction stoichiometry or decarboxylation of the monomers/polymers. Hoekman et al., (2011) even found no measureable amount of gas for 30 min residence time of Tahoe mix (a mix of Jeffrey Pine and White Fir) at 215 °C. Those also suggest that at 200 °C the amount of sugar breakage is not enough to balance the consumed water during initial hydrolysis [13], which would result in minimal water production.

In general, the following simplified reaction pathways are known for the main constituents of biomass [9, 11, 14]: 1. Cellulose hydrolysis forms glucose and fructose which then can form HMF. These sugar monomers subsequently is assumed to polymerize to form char or may also form levulinic acid and formic acid; 2. Hemicellulose forms xylose which then forms furfural and/or subsequently polymerizes. Many studies showed that the HTC decomposition behavior of hemicellulose in plant biomass commences at 180 °C, while cellulose decomposition would not start until the temperature is over 230 °C. Because the decomposition of hemicellulose starts at a lower temperature (180 °C) than that of cellulose (230 °C) and the degradation of glucose rapidly increases at temperatures >230 °C, the degradation of glucose would be unavoidable if hemicellulose and cellulose are hydrolyzed together [15-18]. For instance, the water production increases from -8% to ~4% from 200 °C to 230 °C for 5 min reaction time. This might be the result of simultaneous hydrolysis of hemicellulose and cellulose polymers and decomposition of sugar monomers. A further increase of temperature from 230 °C to 260 °C increases the dehydration rate, and there is about two times more water production from ~4% to 13.6% at 260 °C for 5 min residence time. Sevila et al., (2009) proposed a reaction model for pure cellulose under subcritical condition where dehydration (C–O bond splitting) and retro-aldol condensation (C–C bond breaking) were found to be the key reactions [7]. Other researchers report that the contribution of retro-aldol condensation is dominant at higher temperatures (400–500 °C), while that of the dehydration reaction is dominant at lower temperatures (250–350 °C) [14].

4.3.2 Effect of reaction time

The residence time effect on HTC reaction for loblolly pine is shown is Figure 4.3. Water production or dehydration rate at 200 °C remains unchanged with extent of time, which may indicate that the activation energy required for monomer degradation or polymerization may not sufficient enough at this temperature to produce water. As discussed in the previous section, cellulose degradation starts after 220 °C and continues increasing with extent of reaction temperature. The water production curve for 230 °C shifts from negative to positive region. Sugar monomers degradation in the liquid phase rapidly increases at temperatures above 230 °C and continues increasing with extent of time. In Figure 4.3, almost two times of water was produced for 30 min compared to 5 min residence time at 260 °C. It has been reported in several studies that the removal of extractable oxygen-rich compounds (e.g., fragrances and oils) and/or hydrolysis of hemicellulose, take place within minutes instead of hours [19-21].

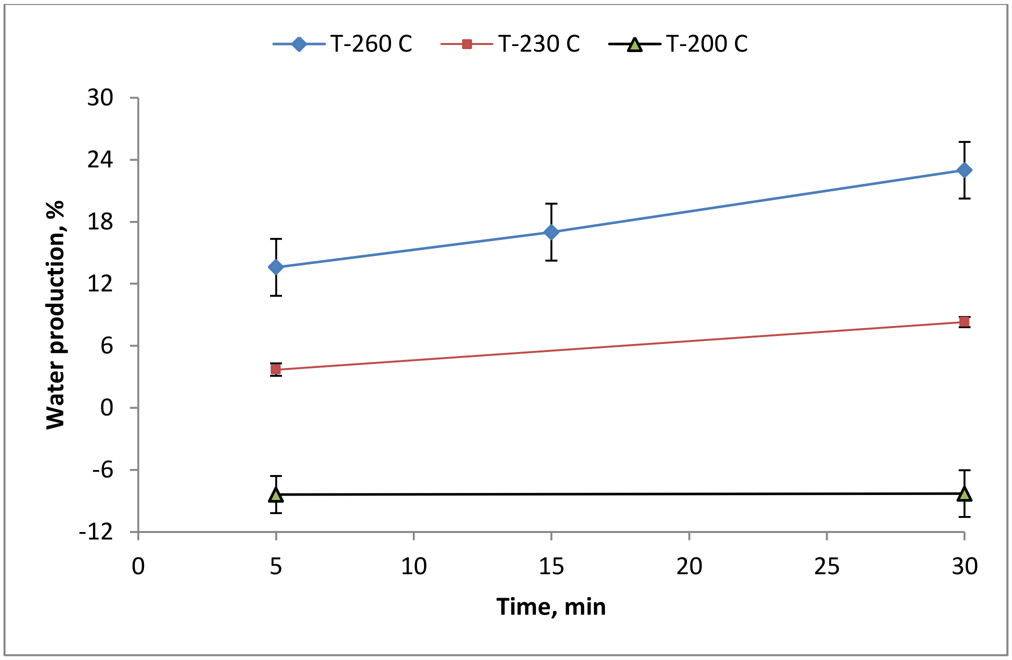

Figure 4.3 Water production variations with time. This curve is generated using the experimental mean and standard deviation data.

With a long reaction time, the conversion of biomass from low carbon to high carbon content may slow down within 5~10 min, with side reactions occurring in the liquid phase during the rest of the reaction time. As evidence to this claim, the mass yield of the solids at 5 and 30 min HTC reaction were 62±1% and 54±1% respectively and it is assumed that the further extent of residence time will not affect the biochar fuel value. Hoekman et al., (2011) reported similar results for Tahoe Mix, where they found that after 30 min of reaction time the carbon content at 260 °C is constant. They also found about 50% increased water production for 1hr residence time than 5 min at that temperature [13].

The amount of nonvolatile organic residue was calculated for 5 min and 30 min liquid solution according to Eq.3. The result showed 21% decreased residue in the liquid product with a 30 min residence time compared to a 5 min residence time (Table 4.1). The breakage of sugar monomers, where 5 or 6 moles of H_2O can be produced based on sugar monomer reaction stoichiometry or decarboxylation of the monomers/polymers, may increase the amount of water production with a longer reaction time.

4.4 Dehydration as van Krevelen diagram

As discussed above, dehydration reactions depend on both residence time and temperature. The ultimate analysis of raw and pretreated loblolly pine shows that the HTC process produces a solid fuel with increased carbon content and decreased oxygen content. This is consistent with an increase in energy density of thermal pretreated solids [22-23]. The increased fuel value results from dehydration, which as shown above depends on time and temperature of the HTC process. A useful way to depict the effects of both HTC time and temperature is by means of a van Krevelen diagram. This diagram is presented as Figure 4.4, which plots atomic H:C ratio vs. atomic O:C ratio, as commonly used to evaluate the energy quality of solid fuels [4]. Raw loblolly pine can be found in the biomass region, whereas HTC 200 and HTC 230 are in the peat area and HTC 260 is in the lignite region according to the van Krevelen diagram. It can also be noticed that dehydration is probably the primary reaction during HTC according to the van Krevelen diagram.

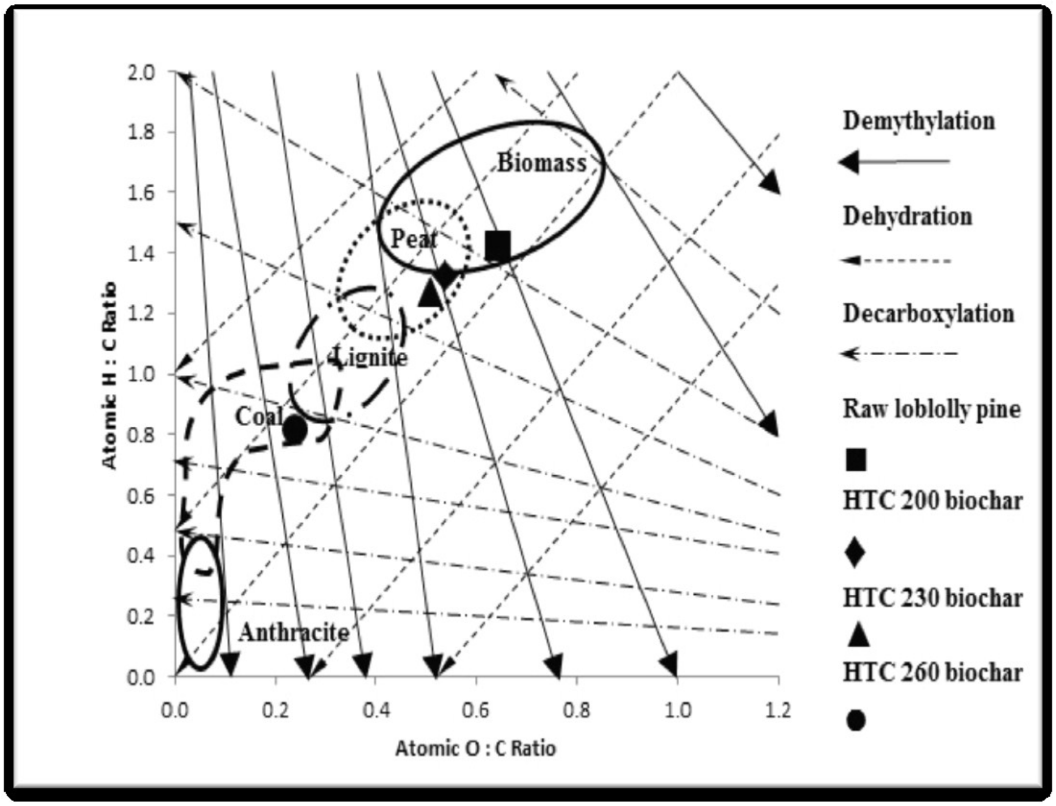

Figure 4.4 van-Krevelen diagram of HTC biochars for 5 min reaction time with major reaction lines [25].

HTC 200, HTC 230, and HTC 260 are in a straight line corresponding to the dehydration reactions. But from raw loblolly pine to any HTC biochar, both decarboxylation and dehydration are probable, consistent with the previous literature [7, 24].

4.5 Validation of water production calculation using oxygen balance

The detailed laboratory analysis of raw and pretreated (260 °C, 30 min) loblolly pine samples are reported in US DOE report 2012 [26]. An elemental oxygen balance is performed on both feedstock and pretreated products to calculate the amount of produced water during the HTC process of loblolly pine at 260 °C for a 30 min residence time. The calculation procedures are given below.

Theoretical amount of oxygen before reaction is:

$$Total\ oxygen\ (in) = O_2(raw\ biomass) + O_2(moisture\ in\ biomass) + O_2(added\ water) \tag{6}$$

Amount of oxygen that can be theoretically obtained from the product streams is:

$$Total\ oxygen\ (out) = O_2(HTC\ char) + O_2(sugars) + O_2(acids) + O_2(gases) + O_2(water\ produced) \tag{7}$$

Oxygen in output can be obtained by setting equal Eq.6 and 7.

$$Total\ oxygen\ (output\ water) = Total\ oxygen\ (in) - [O_2(HTC\ char) + O_2(sugars) + O_2(acids) + O_2(gases)] \tag{8}$$

The oxygen equivalent amount of water in the output is:

$$Total\ output\ water = \frac{Total\ oxygen\ (\ output\ water) \times MW_{water}}{16} \tag{9}$$

The amount of produced water is:

$$Water\ (produced) = Total\ output - Added\ water - Moisture \tag{10}$$

The data reported in the following tables is based on per gram dry feedstock.

Table 4.2 Ultimate analysis of raw and pretreated loblolly pine [26].

	Raw loblolly pine	HTC biochar
Carbon (F/S) %	49.3	70.7
Hydrogen (F/S) %	5.8	7.2
Nitrogen (F/S) %	0.0	0.0
Sulfur (F/S)%	Undetectable	Undetectable
Oxygen %	44.9	21.3

Table 4.3 GC-MS analysis of gas products loblolly pine pretreated at 260 °C, 30 min [26].

CO_2	7.96%
CO	0.30%
CH_4	0.00%
H_2	0.00%

Table 4.4 HPLC analysis of liquid products loblolly pine pretreated at 260 °C, 30 min [26].

5-HMF	1.71%
2-Furaldehyde	0.81%
Levoglucosan	0.43%
Sorbitol	0.01%
Mannosan	0.01%
Fructose-Inositol-Arabinose	0.20%
Glycerol	0.03%
Erythritol	0.60%
Glucose-Pinitol	0.01%
Arabitol	0.01%
Sucrose-Trehalose	0.06%
Lactic Acid	1.17%
Acetic Acid	3.61%
Formic Acid	0.70%
Glutaric Acid	0.18%
Succinic Acid	0.14%
Malonic Acid	0.01%
Maleic Acid	0.04%
Oxalic Acid	0.01%

Using the data provided in the above tables (Table 4.2-4) and plugging those numbers in the previously described equations, the amount of produced water is 26.34%, and the experimental water production according to the procedure described in section 4.3 is 23% with a standard deviation of 1%. This analysis provides a useful conformation of the experimental calculations developed for the dehydration reactions of loblolly pine.

4.6 Error analysis of the water production data

The water production calculation involves several steps that include use of measured and calculated variables containing various experimental errors and uncertainties. A simple Monte Carlo simulation method was applied here to understand how each calculation step could influence the overall results and allows quantifying the error in calculated water production reported below. The method followed here is identical to that described in Chapter 3. Monte Carlo simulation is categorized as a statistical sampling method because the inputs are randomly generated from probability distributions to simulate the process of sampling from an actual population, where the goal is to determine how random variation, lack of knowledge, or error affects the sensitivity, performance, or reliability of the system that is being modeled [23]. There were eighteen direct weight measurements taken for calculating water production, and each experiment was repeated, at least three times. These weight measurements were taken using a weight scale (S-234, Denver Instrument) with precision of 0.1mg. The recorded weight is assumed to be close to the actual weight, and it is assumed that the sample weight can be represented by a normal distribution of weights, with the mean equal to the recorded value, and the standard deviation equal to the instrument precision. This allows generation of a distribution of many values, each equally likely to be the real value. A Monte Carlo simulation was performed 1350 times for each independent experimental run and presented with 90% confidence in Table 4.5.

Table 4.5 Water production from HTC of loblolly pine, as a function of reaction time and temperature. Values are reported with standard deviations.

Temperature, °C	Average water production, % (5 min)		Average water production, % (30 min)	
	Experimental	Stochastic	Experimental	Stochastic
200	-8.4±3.6	-9.0±3.0	-8.3±4.5	-9.3±3.9
230	3.7±1.2	1.6±1.2	8.3±1.0	6.6±1.7
260	13.8±1.8	12.0±2.0	23.0±1.0	25.0±2.0

The experimental uncertainty involved in each of the temperature investigated is also analyzed though graphical presentation. As an example, simulation results for water production at 260 °C and 30 min reaction time is shown in Figure 4.5, where the percentage of water production shows a wide range variation starting from 21% to 30%. This graph helps to understand the uncertainty and randomness involved in the experiments.

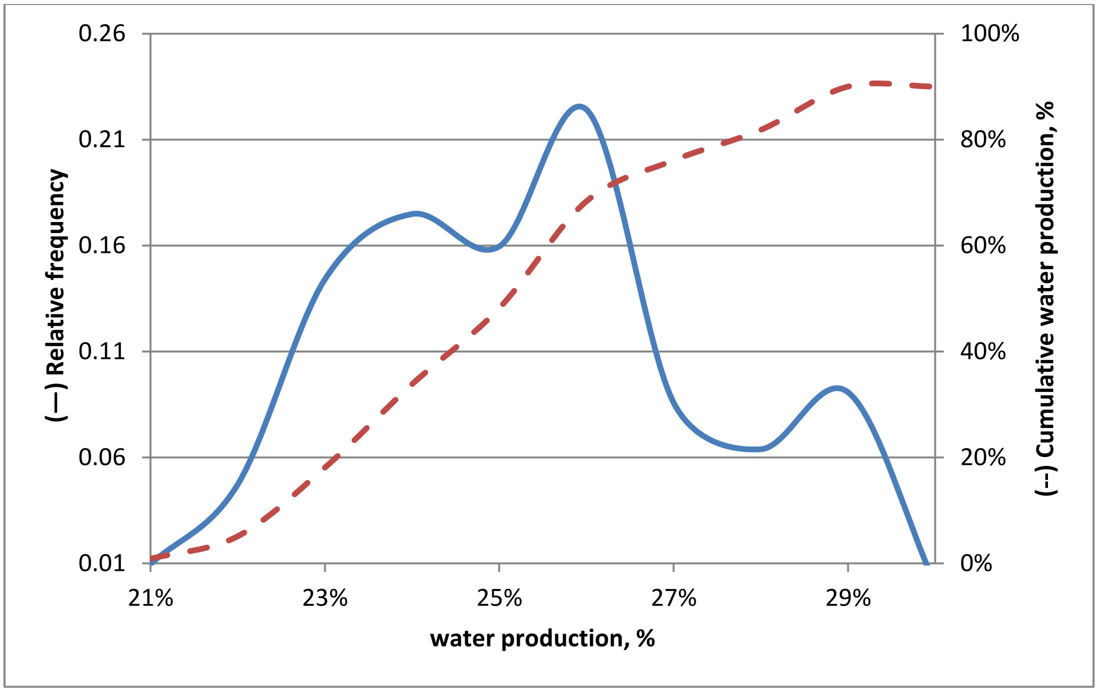

Figure 4.5 Simulation results for water production at 260 °C and 30 min reaction time.

4.7 Conclusion

All the possible reactions during HTC, namely hydrolysis, dehydration, decarboxylation, condensation-polymerization, and aromatization, may continue simultaneously but dehydration plays the dominant role, especially in the liquid phase. However, its extent depends on HTC reaction time and temperature. Reactions in the liquid phase are dominant for longer reaction times, while HTC solid biochar yield remains similar for 5 or 30 min. The amount of water consumed in hydrolysis may be higher than that of produced by dehydration for HTC at 200 °C for any reaction time. Water production increases with increasing of HTC temperature, and with increasing reaction time.

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Chapter 5

Conclusions and Recommendations for Future Research

5.1 Conclusions

In this section, conclusions are drawn regarding the work reported in previous chapters.

5.1.1 Recycling of process water

Hydrothermal carbonization shows great potential as a thermochemical conversion technology to handle the diverse biomass feedstocks. Water necessary for the HTC process is an inherent component, and recycling of the process water increases the process sustainability and benefits environmentally. For loblolly pine, a woody biomass, the effect of recycled water has major effect at higher temperature pretreatment where reduction of higher heating value of the solid biocarbon limits the reuse. However, low temperature pretreatment does not increase the fuel value appreciably, and so 230 °C is found a potential temperature for the recycling process water. The storage property, hydrophobicity, and fuel value at this temperature show stable nature for loblolly pine.

5.1.2 Error analysis of reaction kinetics

It is impossible to reproduce the exact same data from the same pieces of equipment because of many factors, and these kinds of uncertainty need to be considered before making conclusion from experimental results. The Monte Carlo, a basic tool for uncertainty analysis, simulation results of the reaction kinetic parameters underscores the necessity of application of extensive data analysis tools.

The reaction kinetics of biomass components (i.e. hemicelluloses, cellulose and lignin) vary from each other depending on their constituent biomass structure.

5.1.3 Mass transfer effect

The degradation of biomass in the HTC process may limit by particle size. The particle size of the biomass can alter the kinetics due to the mass transfer effect in case of larger particles. It was shown that under the conditions studied, both reaction kinetics and mass transfer considerations are important to determine overall reaction rates.

5.1.4 Water production

The study of reaction chemistry of lignocellulosic biomass is as complex as its structure. The analysis of model compounds reveals the possible reactions during HTC, namely hydrolysis, dehydration, decarboxylation, condensation-polymerization, and aromatization. The quantitative analysis of the loblolly pine products shows that dehydration reactions are dominant, while decarboxylation reactions occur in parallel with small extent. However, these reactions are also time dependent in the liquid phase along with rates strongly dependent on reaction temperature. A rigorous error analysis of the experimental results shows that the low temperature pretreatment even takes some water to hydrolyze the biomass components and is not able to balance the input water. The extent of dehydration reactions increases with the increase of reaction time and temperature.

5.2 Recommendations for future research

Lignocellulosic biomass shows wide varieties in compositions depending on their maturity, geographic location, and environmental conditions. Throughout this study, loblolly pine was considered as a soft wood biomass representative for hydrothermal carbonization and investigated in limited scope which needs to be explored for other woody biomass like poplar wood, pinyon-juniper, etc. to make a general conclusion about woody biomass products' characteristics after pretreatment. There are other kinds of biomass like hard wood, grassy biomass, agricultural wastes, and energy crops, needed to analyze to optimize the HTC process parameters.

About 60~70% of the process water was recycled and found that 230 °C was a promising temperature for water reuse, but higher temperature pretreatment substantially increases the higher heating value and hydrophobicity. This needs further study varying the percentage of recycle water to find a suitable ratio of fresh and reuse water so that recycling can apply at high temperature. The similar investigations need for other woody biomass of consideration.

No generalized reaction kinetics is available for lignocellulosic biomass conversion, and for designing continuous process, it is important to find the rate parameters to design and fabricate the HTC reactor. Only three temperatures were considered in this kinetics study but the use of more temperatures will verify the accuracy of the kinetic values found.

The effects of particle size on reaction kinetics were studied in a very simplified manner, but this demands more investigation. Nevertheless, other variables, such as pressure, environment, and water to biomass ratio, are not negligible. To design the HTC process and commercialize it, all the variables need to be considered and optimized.

The liquid product has some potential to derive high-end value products, especially 5-HMF which is not neglected throughout this work and needs further study. The use of liquid as feed for liquid biofuel production is an area of study.

So far, the process parameters are studied for a batch reactor only, and for commercialization of this technology, further studies are required to optimize the process variables. The HTC process requires extra heat to make HTC biochar and it will be extremely useful to study the techno-economic analysis of the HTC process to prove the utility of this process.

The study of the process integration (i.e. collection of feedstocks, pretreatment of feed stocks, gasification of solid biocoal, and generation of electricity) is necessary prior wide scale application of HTC process.

It will be very insightful to develop a general model for lignocellulosic biomass pretreatment from where the mass yield and energy densification can predict based on the relative amount of hemicelluloses, cellulose, lignin, extractives, and inorganic contents of the biomass.

Since the HTC process can take any kind of wet biomass as feed, this can be explored for other wet feedstocks like municipal waste stream, paper and pulp waste stream, waste from food and liquor processing industries, poultry wastes, etc.