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ORIGINAL ARTICLE

Hydrothermal carbonization of loblolly pine: reaction chemistry and water balance

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Abstract Hydrothermal carbonization (HTC) is a thermochemical process to convert lignocellulosic biomass into lignite-like HTC biochar. In this study, chemical reactions occurring during a relatively short HTC reaction time are discussed (5–30 min), and reaction mechanisms are examined at temperatures between 200 and 260 °C. Solid HTC biochar products were analyzed by attenuated total reflectance (ATR)/Fourier transform infrared spectroscopy (FTIR), elemental analysis, and gas chromatography-mass spectrometry (GC-MS), while liquid products were analyzed with GC-MS and ion chromatography (IC) to predict the reaction schemes. HTC reactions for whole biomass (loblolly pine) were proposed in the context of HTC reactions for individual biomass fractions. Hydrolysis, dehydration, and decarboxylation reactions are the major reactions of HTC, though condensation, polymerization, and aromatization also occur. An experimental procedure was developed to determine the net water production, a balance between consumption by hydrolysis reactions and production by dehydration reactions. Net production of water is evaluated. At lower HTC temperature (200 °C), water was consumed. However, at higher HTC temperatures, water was produced and the production increases with increasing reaction time.

Keywords Hydrochar · Wet torrefaction · HTC biochar · Biomass pretreatment · Lignocellulosic biomass

1 Introduction

Although lignocellulosic biomass has four major constituents—lignin, cellulose, hemicellulose, 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 hydrothermal carbonization (HTC), at reaction temperatures of 220–230 °C for 4 h, very little or no change in cellulose was reported by Fuertes et al. and Falco et al. [1, 2]. At higher temperatures, cellulose undergoes hydrolysis, producing small chain polymers and monomers [3]. Following hydrolysis, reactions such as dehydration, decarboxylation, condensation, aromatization, and polymerization take place in solid and liquid phases simultaneously [4, 5]. Researchers have also proposed a mechanism for producing cross-linked hydrophobic polymer structures from cellulose during HTC [5, 6]. According to this mechanism, when the concentration of aromatic clusters, primarily a product of dehydration and decarboxylation, reaches critical supersaturation, a burst of nucleation takes place and reactive compounds with hydroxyl, carbonyl, or/and carboxylic groups form a cross-linked polymer [7, 8].

Hemicellulose consists mostly of linear heteropolymers composed of sugar monomers, including xylose, mannose, glucose, and galactose with β-(1,4)-glucosidic bonds [9]. Hemicellulose hydrolyzes more rapidly than cellulose [10], with the degradation of hemicellulose reported to start at temperatures as low as 180 °C [11]. Researchers have used

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xylan as a model compound for hemicellulose and have proposed HTC reaction mechanisms for it [12, 13]. Unlike cellulose, hydrolyzed products of hemicellulose do not undergo recondensation [14, 15]. Moreover, very low furfural yields have been reported for xylan hydrolysis [16], which implies that the degradation of hemicellulose yields only its monomers, such as xylose, glucose, and galactose, which do not further repolymerize, at least for short reaction times of <30 min [11].

Lignin, a high molecular weight cross-linked polymer of phenylpropane 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 the reaction mechanism may vary depending on feedstock [17]. Syringyl groups in lignin (mostly found in herbaceous biomass) are found to be susceptible to degradation in HTC [6]. A two-step reaction mechanism was proposed for lignin undergoing HTC at higher temperatures [18]. In the first stage, lignin fragments with low molecular weight and highly reactive fragments are solubilized by breaking lignin-carbohydrate bonds [19], followed by a slower repolymerization process, where the fragments during the first stage polymerize into an insoluble cross-linked polymer by condensation [20]. Moreover, the sugar and/or sugar products such as furfurals also react with the unhydrolyzed lignin fraction [21] to produce a type of lignin called pseudolignin, which increases the yield of Klason lignin (acid insoluble lignin) in the HTC solid biochar [22].

Other biomass components like extractives, which contain monomeric sugars (mainly glucose and fructose) along with various alditols, aliphatic acids, oligomeric sugars, and phenolic glycosides, are very reactive in hydrothermal media [23]. An instantaneous reaction mechanism proposes simple sugars being produced via hydrolysis, and degradation of sugar products via decarboxylation and dehydration. In addition, tannins, resins, and starch also undergo instantaneous degradation during HTC [8, 10]. Inorganic components are very stable and remain unchanged by HTC; thus, they contribute very little to HTC reactions [24].

Although detailed reaction chemistry has been studied for pure xylan, cellulose, and lignin, there is little published research on the chemistry of HTC applied to whole biomass. A few review articles have been published in recent years, where the reaction of individual components is described and it is speculated that the reaction of whole biomass might be similar to that of model compound components [7]. Reza et al. found that the reaction kinetics are much faster for lignocellulosic biomass than for the individual components, which is similar to the findings reported by Falco et al. and Knezevic et al. [1, 10, 25]. In whole biomass, activation energies of hemicellulose and cellulose degradation are reported as 30 and 73 kJ/mol, respectively, much lower than their individual activation energies [8]. HTC reaction dependency on biomass particle size was found, especially for short reaction times, implying a mass transfer effect during HTC. The solid phase and liquid phase reactions of biomass may be different from the reactions observed for individual biomass fractions. To more fully understand HTC, reaction chemistry for lignocellulosic biomass must be investigated.

The main objective of this article is to study the reaction chemistry of HTC when applied to loblolly pine. The primary reactions of hydrolysis, dehydration, decarboxylation, aromatization, and polymerization are examined. The effects of time and temperature on HTC reactions are discussed. Both solid and liquid phase reactions are considered. The water balance receives special consideration, as hydrolysis requires water, while dehydration, polymerization, and/or dewatering processes produce water.

2 Material and methods

2.1 Biomass and chemicals

Loblolly pine (*Pinus taeda*) was used for all experiments. Mature loblolly pine was harvested in Marengo County, Alabama, in May 2011. Wood stems were debarked and comminuted into wood chips. The material was dried in a warehouse by free air circulation for 4 weeks and further chopped into particles <15 mm by a Bliss model 4460 hammer mill (Ponca City, OK). These particles were kept in plastic containers in dry storage until further use. To promote a more homogeneous biomass reactant and provide effective subcritical water diffusion in the biomass, a blender was used to further reduce the raw biomass size. Samples were sieved to −1.18+0.60 mm, dried at 105 °C for 24 h, and stored in a sealed ziplock bag until treatment.

2.2 Hydrothermal carbonization

Hydrothermal carbonization of loblolly pine was performed in a 100-mL Parr bench top reactor (Moline, IL). Nitrogen of 80 cm^3 (STP) min^{-1} was first passed through the reactor for 10 min to purge oxygen. For each run, a 1:5 mass ratio mixture of loblolly pine to water was loaded into the reactor, while ensuring that biomass was completely submerged in water. The reactor was heated to the desired temperature and maintained at that temperature for either 5 or 30 min using a PID controller, after which it was cooled rapidly by immersion in an ice water bath. The HTC reaction takes 40–60 min to reach the HTC temperature (200, 230, or 260 °C) but takes less than 15 min to cool down to room temperature. The reactor pressure was not controlled but indicated by a pressure gauge and was always at or slightly above the water vapor pressure. After cooling, the gas was released to the atmosphere. The solid product was obtained by vacuum filtration (without rinsing,) using Whatman filter paper number 3, rinsed with DI water, and was dried at 105 °C for 24 h before further analysis. HTC 200, HTC 230, and HTC 260 refer to the dried solid products of hydrothermal carbonization at 200, 230, and 260 °C, respectively. The liquid product was stored in a refrigerator until further analyses were performed.

2.3 Fiber analysis

The van Soest method of NDF-ADF-ADL (neutral detergent fiber, acid detergent fiber, acid detergent lignin) dissolution was used to determine the content of water extractives, hemicellulose, cellulose, and lignin in solid samples [26]. Sample mass that is not assigned to one of those fractions consists of extractives. The samples were dried at 105 °C for 24 h prior to fiber analysis.

2.4 Elemental analysis

ASTM D 3176 was used to determine C, H, O, N, and S contents of HTC biochar samples along with raw loblolly pine. A Thermo Electron FlashEA 1112 (Pittsburgh, PA) elemental analyzer was used for ultimate analyses.

2.5 Attenuated total reflectance (ATR)-FTIR

A PerkinElmer Spectrum 2000 ATR-Fourier transform infrared (FTIR) with mid- and far-IR capabilities was used to characterize the raw and HTC-treated biomass. IR spectra of HTC 200, HTC 230, and HTC 260 as well as raw loblolly pine were recorded at 30 °C using ATR-FTIR. All samples were milled into a fine powder to homogenize them and then dried at 105 °C for 24 h prior to FTIR. A dry sample (5–10 mg) was placed in the FTIR for this analysis and pressed against the instrument's diamond surface with its metal rod. All spectra were obtained using 200 scans for the background (air) and 32 scans for the samples, which were scanned at 500–4,000 cm^{-1}.

2.6 Higher heating value

The higher heating value (HHV) of solid samples was measured in a Parr 1241 adiabatic oxygen bomb calorimeter (Moline, IL) fitted with continuous temperature recording. HTC biochar samples of 0.4–0.5 g were dried at 105 °C for 24 h prior to analysis. Results are reported on a dry, ash-free (daf) basis.

2.7 Gas chromatography-mass spectrometry (GC-MS)

Both solid HTC biochar and aqueous samples from the HTC experiments were analyzed by GC/MS. Prior to analysis, the HTC biochar samples were extracted sequentially with methylene chloride and acetone using a Dionex ASE 300 Accelerated Solvent Extractor (ASE). The extracts were combined and concentrated by rotary evaporation to obtain the organic components of interest. After drying, the extracted materials were derivatized with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), with 1 % trimethylchlorosilane (TMCS). Aqueous samples from HTC experiments were evaporated to dryness prior to derivatization with BSTFA. The derivatized samples were analyzed by an electron impact GC/MS technique using a Varian 4000 GC/MS with a model CP-8400 autosampler and a Saturn 2000 ion trap spectrometer (Varian, Inc., Walnut Creek, CA, USA). A 30-m DB-5ms capillary column (0.20 mm ID; 0.25-μm film thickness) was used (Agilent Technologies, Santa Clara, CA, USA). The initial column temperature was 70 °C (3-min hold) programmed to 180 °C (12 °C/min) then to 320 °C (8 °C/min). Ion source temperature was 220 °C and injector temperature was 260 °C. Additional details have been published elsewhere [27].

2.8 Ion chromatography (IC)

Organic acids present in the aqueous products from HTC processing were analyzed using IC following the method of Jaffrezo et al. [28] A Dionex ICS-3000 system was used, equipped with a Dionex IonPac AG11HC guard column (4× 50 mm) and AS11 HC analytical column (4×250 mm). The flow rate was maintained at 1.5 mL/min, and the temperature was held at 25 °C. A multistep gradient program of water and 100 mM NaOH was used to elute the organic acids. Detection of the eluted acids was accomplished using a DS3 conductivity cell. More analytical details have been published elsewhere [31].

3 Results and discussion

3.1 Fiber analysis and ultimate analysis of HTC biochar

In HTC, subcritical water at 180–260 °C is used. Under these conditions, the ionic constant of water is nearly two orders of magnitude higher than at room temperature; thus, liquid water behaves as a nonpolar solvent [29]. Water is sufficiently reactive in this condition to degrade extractives, hemicellulose, and, to a certain degree, cellulose. As a result, the mass yield of solid product (mass of HTC biochar per mass of biomass feedstock, dry basis) decreases with increasing HTC temperature (Table 1). The HHV of biochar increases with increasing HTC temperature. Since the degradation of hemicellulose and cellulose produces extractives, the net extractive concentration increases with HTC reaction temperature. Table 1 shows the fiber analysis of loblolly pine and HTC biochars.

Table 1 Mass yield, fiber analysis, energy value, and ultimate analysis of HTC biochar from loblolly pine for 5-min reaction time

Sample	Mass yield (%)	HHV (MJ/kg)	Liquid pH	Fiber analysis					Ultimate analysis				
				Water extractives (%)	Hemicellulose (%)	Cellulose (%)	Lignin (%)	Ash (%)	C (%)	H (%)	O (%)	N (%)	S (%)
Raw	100.0	19.5	–	8.7	11.9	54.0	25.0	0.4	50.3	6.0	43.3	0.0	0.0
HTC 200	88.5	20.3	5.2	24.3	0.0	47.4	27.8	0.5	54.7	5.9	39.1	0.1	0.0
HTC 230	70.6	21.5	3.8	25.3	0.0	44.1	30.2	0.4	56.1	5.8	37.8	0.1	0.0
HTC 260	61.0	24.5	3.0	31.8	0.0	33.9	33.8	0.5	72.1	4.9	23.1	0.2	0.0

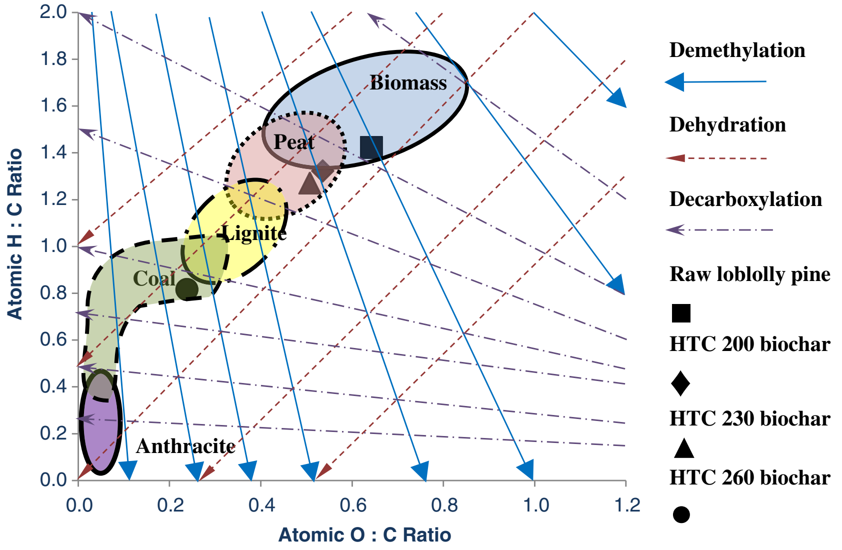
Table 1 also presents the ultimate analysis of raw loblolly pine and HTC biochars. The carbon mass fraction of the solid biochar increases with increasing HTC reaction temperature, while hydrogen and especially oxygen mass fractions decrease. A useful way to depict the effects of both HTC time and temperature is by means of a van Krevelen diagram, which is commonly used to evaluate the energy quality of solid fuels [30]. An example is presented in Fig. 1, which plots atomic H/C ratio versus atomic O/C ratio. Raw loblolly pine appears within the biomass region, whereas HTC 200 and HTC 230 are in the peat region and HTC 260 is in the coal region. The van Krevelen diagram also suggests that dehydration is the prominent reaction during HTC, as the HTC 200, HTC 230, and HTC 260 points lie almost on a straight line corresponding to dehydration reactions, consistent with previous reports [2, 5].

3.2 Reaction mechanisms

Water (liquid) at 200 °C breaks the β-(1,4)-glycosidic bonds of hemicellulose [11], causing it to degrade into sugar monomers, which further degrade into other compounds, including 2-furaldehyde (furfural) [25]. Cellulose can degrade into oligomers, a portion of which hydrolyzes into glucose with the remainder forming a cross-linked polymer [6]. Moreover, the degradation of hemicellulose, cellulose, and extractives leaves a porous HTC biochar solid product with concentrated sugars and organic acids dissolved in water. The porous structures provide significant surface area for deposition of dissolved sugars, acids, and furfurals during sample drying after HTC, so that the concentration of extractives increases in the solid HTC biochar [5]. The concentration of 5-HMF in the liquid product increases quite significantly with increasing HTC temperature [31].

Biomass components, under the reactive aqueous environment, are hydrolyzed to a large number of oligomers and monomers [7]. Due to their high solubility in water, much of these oligomers and monomers is extracted from the HTC biochar, depending on the feedstock and its particle size [8]. During HTC, the hydrolyzed products can subsequently undergo other reactions, including condensation, dehydration, and decarboxylation [5]. Some of the highly reactive oligomers can polymerize and/or aromatize to form a water-insoluble polymer, with properties similar to lignite [8]. Based

Fig. 1 van Krevelen diagram of HTC biochars for 5-min reaction time, with major reaction lines indicated



on the van Krevelen diagram, FTIR spectra, and previous studies of pure components, HTC can be represented using the following five major reactions [3, 5, 7, 8, 12].

3.2.1 *Hydrolysis*

Hydrolytic reactions are important solid surface reactions, where water initially reacts with glycosidic groups in cellulose and hemicellulose, beginning a cascade of reactions that result in the formation of a wide range of products including soluble oligomers, disaccharides, monosaccharides, furan derivatives, and others. A simplified reaction pathway is given in Fig. 2. The degradation product shown here, 5-HMF, can further degrade into levulinic acid, acetic acid, and formic acid [5].

Hemicellulose begins to hydrolyze at HTC temperatures near 180 °C [32], while cellulose hydrolysis requires higher temperatures of 230 °C and above [8]. This explains the lack of hemicellulose in any of the HTC biochar samples shown in Table 1. Under the experimental conditions used here, slight degradation of cellulose appeared to occur at 200 °C, with an increasing degree of degradation at 230 and 260 °C.

The effects of temperature upon degradation of hemicellulose and cellulose are also supported by the IR spectra obtained from raw pine and HTC biochars (Fig. 3). For example, the peak at 1,735 cm^{-1} observed in the spectrum of raw loblolly pine can be assigned to the ketone C=O functional group, which is often considered a signature peak for hemicellulose [33]. This peak is not present in the HTC biochar spectra, suggesting the absence of hemicellulose in these materials. Also, the peak near 900 cm^{-1}, which is characteristic of β-glycosidic linkages between the sugar units, especially for hemicellulose [33], is seen to disappear in the HTC 230 and HTC 260 spectra. A peak at 1,264 cm^{-1}, corresponding to the C–O–C bond of cellulose, remains quite consistent across all four samples, indicating that much of the cellulose remains unreacted over this temperature range.

The peaks at 1,440–1,500 cm^{-1} (O–CH_3 stretching of the ether linkage) are attributed to lignin and are found to sharpen with increasing temperature [2]. The absorption band at 1,176 cm^{-1} corresponds to C–O–C asymmetrical bridge stretching. This is a significant peak from softwood lignins and is attributed to coniferal dimers [8]. A strong peak near 1,050 cm^{-1} arises from the C–O–C pyranose ring of lignin; this peak becomes larger with increasing HTC temperature [5]. These IR spectral characteristics indicate the inert behavior of lignin during HTC treatment below 260 °C, which is consistent with literature [17].

The concentration of sugars, acids, and furfurals in solid HTC biochars and the corresponding liquid solutions are presented in Table 2. Monosaccharides are prevalent in both liquid and solid samples. Pentose (xylose, arabinose) concentrations in both liquid and solid are quite high at HTC temperature of 200 °C but decrease significantly with increasing HTC temperature. With the exception of mannose, hexose (glucose, fructose, and galactose) concentrations seem somewhat more stable with increasing temperature, although significant degradation is still observed at the highest temperature of 260 °C. Mannose behaves more like a pentose, with its concentration decreasing with increasing temperature. Xylose and mannose are degradation products from hemicellulose and extractives. Their higher concentrations at lower HTC temperatures indicate the degradation of hemicellulose and extractives at lower severity. Hydrolysis reactions occur at the surface of the biomass. After liquid water enters the pores and hydrolyzes the components, hydrolyzed products exit through the same pores. The rate of hydrolysis of biomass is primarily determined by diffusion within the biomass matrix [8]. This may explain why 5-HMF concentrations are found to be much higher in the solid HTC biochars than the liquid solutions. Another possibility is an affinity between 5-HMF and the carbonaceous surface of the resultant HTC biochar, which might act in a manner similar to that of activated carbon, used for removing organics from an aqueous stream.

3.2.2 *Dehydration*

Literature studies show that after initial hydrolysis, dehydration is the primary reaction process to occur in HTC. In this work, both qualitative and quantitative measures were used to understand dehydration during HTC. The qualitative behavior is analyzed here, based upon the van Krevelen diagram, IR spectra, and GC/MS analysis. Details of the quantitative approach are discussed in Section 3.3.

Dehydration during HTC can result from both chemical and physical processes. The physical process is well known as dewatering, where the bound water is ejected from the biomass during HTC due to the increased hydrophobicity of HTC biochar [34, 35]. Chemical dehydration may occur due to the elimination of hydroxyl groups [5]. During dehydration, biomass is significantly carbonized; consequently, the atomic

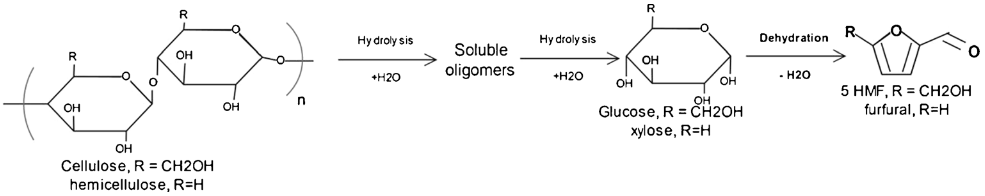


Fig. 2 Simplified reaction pathway of cellulose and hemicellulose degradation under hydrothermal conditions

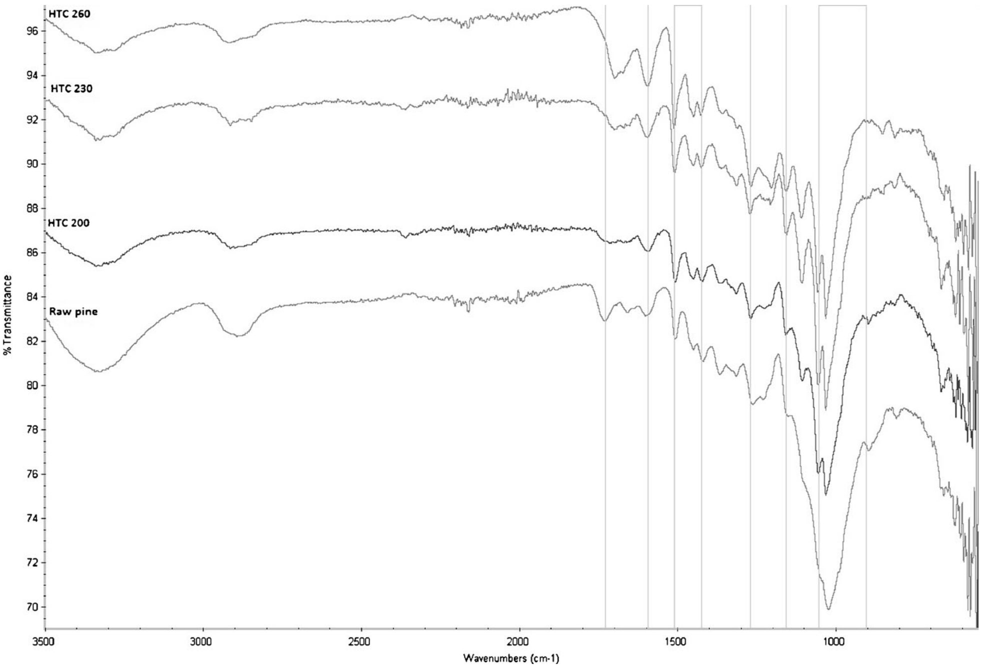


Fig. 3 ATR-FTIR spectra of raw loblolly pine and HTC-treated loblolly pine at 200, 230, and 260 °C. Common biomass peaks, along with the corresponding functional groups, are listed in Table 3. The *curves* correspond to HTC 260, HTC 230, HTC 200, and raw biomass, top to bottom, respectively

O/C ratio is reduced. As shown in Fig. 1, this reduction of O/C depends on the HTC temperature when a short reaction time is used (5 min). With increasing HTC temperature, both O/C and H/C ratios decrease. As a result, the characteristics of HTC biochar move from the biomass region to the coal region in the van Krevelen diagram as the HTC reaction temperature increases to 260 °C. The main reason for this significant decrease of O/C ratio is the removal of carboxyl groups from extractives, hemicellulose, and cellulose.

Dehydration and decarboxylation occur simultaneously. For example, 1 mol of glucose in an appropriate oxidizing environment can convert into 6 mol of CO_2 and 6 mol of H_2O. Thus, the ratio (r) of mol CO_2 to mol H_2O is 1 for glucose when fully oxidized. Similarly, r is reported as 0.2–1.0 for HTC of cellulose, depending on the reaction conditions [23]. From IR spectra as shown in Fig. 3, the absorption band attributable to O–H stretching at 3,000–3,600 cm^{-1} is weakened with increasing HTC temperature, meaning higher hydrophobicity or dehydration [33]. Bands attributed to carboxylic acids (1,410–1,435 cm^{-1}) remain constant with increasing HTC temperature, indicating that the biochar remains acidic during HTC reactions. There is evidence of increased carboxylic acid production with increased HTC temperature, for both the solid and liquid states. Table 3 shows that the production of lactic and levulinic acids increased more than four times when the HTC reaction temperature increased from 230 to 260 °C. Note that the dominant acid products (formic and acetic acids) are quite volatile and are lost to evaporation during the sample preparation process for GC-MS analysis. Thus, these volatile acids were not measured as part of the HTC experiments reported here. However, from other HTC experiments of loblolly pine conducted under similar temperature conditions, large increases in formic and acetic acids were observed with increasing temperature [30]. Results from these other experiments are included in Table 2 for comparison purposes.

Other reactions contributing to dehydration involve degradation of hydrolyzed products from biomass into furfurals, anhydrosugars, and aldehydes. For instance, each mole of 5-HMF produced from glucose yields 3 mol of water. As shown in Table 2, the amount of 5-HMF in both the liquid and solid samples increased significantly with reaction temperature. It is also seen that α-D-glucose and β-D-glucose concentrations in the liquid solutions decreased significantly when going from HTC 230 to HTC 260, while the concentrations in the HTC biochar solids remained approximately constant. This may indicate mass transfer limitations in the solid state or significant degradation in the liquid state. The production of 5-HMF serves as an indicator of the extent of dehydration. However, polymerization of hydrolyzed intermediates can also yield water. For instance, the retro-condensation of 5-HMF into aldol and/or keto-enol condensation yields 1 mol of water for each mole of monomer [5]. In addition, aromatization and polymerization also produce significant amounts of water [7].

3.2.3 Decarboxylation

Previous researchers have reported the major portion of HTC gas to be CO_2 [31, 36, 37]. From the van Krevelen diagram in Fig. 1, it can be seen that decarboxylation is a possible reaction during HTC. Carboxyl and carbonyl groups rapidly

Table 2 Analysis of solid and liquid products generated from HTC treatment of loblolly pine (microgram/gram raw dry biomass) at 5-min reaction time

	HTC biochar			Aqueous solution		
Temperature (°C)	200	230	260	200	230	260
Monosaccharides						
1,3-Dihydroxyacetone	319	36	78	13	11	11
D(+)Glyceraldehyde	263	178	418	93	195	359
α-D-Arabinose	2,417	281	44	1,915	391	6
β-D-Arabinose	2,221	270	107	2,151	891	491
α-D-Xylose	14,761	2,954	44	10,846	3,354	15
β-D-Xylose	12,751	2,409	3	11,573	3,514	285
α-L-Mannose	12,535	5,495	136	6,884	10,756	506
β-L-Mannose	4,031	4,048	38	7,272	1,586	122
α-D-Fructose	11,118	5,165	244	5,973	9,654	644
β-D-Fructose	4,184	2,433	1,190	3,511	4,934	1,051
D(+)-Galactose	4,432	1,248	229	6,271	3,540	2,048
α-D-Glucose	6,135	8,843	8,896	6,594	11,469	5,123
β-D-Glucose	5,000	7,211	7,114	7,309	10,846	4,666
α-D-Erythrose	1,318	1,470	1,664	1,015	2,400	1,791
β-D-Erythrose	2,387	2,943	1,381	1,224	2,231	2,262
Disaccharides						
Sucrose	2	1	8	–	0	0
α-Lactose	30	5	14	16	4	3
β-Lactose	63	11	30	72	11	2
Trehalose	221	32	7	158	10	1
Anhydrosugars						
Cellobiosan	43	123	232	397	31	15
Mannosan	1,743	1,386	16	371	330	3
Furan derivatives						
5-(Hydroxymethyl)furfural[a]	6,946	6,370	9,813	19,400	41,400	19,600
Furfural[a]	n/a	n/a	n/a	17,200	17,400	8,800
Organic acids						
Acetic acid	n/a	n/a	n/a	10,000	24,600	55,000
Formic acid	n/a	n/a	n/a	4,500	8,500	15,000
Lactic acid	2,085	2,925	12,272	1,700	2,600	7,800
Levulinic acid	247	769	1,307	51	92	198

n/a data that were not measured

[a] Results from larger-scale experiments with 30-min reaction time [30]

degrade at temperatures above 150 °C, yielding CO_2 and CO, respectively [6]. A peak at 1,735 cm^{-1}, assigned to the C=O functional group of hemicellulose, is not present in the IR spectra of any HTC biochar product, suggesting rapid degradation of hemicellulose [33].

A possible pathway for decarboxylation involves degradation of extractives, hemicellulose, and cellulose. Under hydrothermal conditions, these materials can degrade into monomers such as acetic acid, formic acid, and furfurals, which further degrade into CO_2 and H_2O [30, 38]. With increasing HTC temperature, most monosaccharides decrease substantially, degrading into carboxylic acids, such as acetic and formic acids [30, 31]. The presence of acids can be confirmed from the pH of the liquid solution after HTC. As shown in Table 1, the pH decreases with increasing HTC temperature, which is consistent with increased thermal degradation of monosaccharides. Other possible decarboxylation pathways involve condensation reactions, which result in formation of CO_2 [7].

3.2.4 Condensation polymerization

Some of the fragments (e.g., anhydroglucose, 5-HMF, aldehydes) formed from hydrolysis reactions in hydrothermal

Table 3 IR absorption corresponding to various functional groups [2, 33]

Wave number (cm^{-1})	Functional groups	Possible compounds
3,600–3,000	OH stretching	Acid, methanol, and water
2,860–2,970	$C–H_n$ stretching	Alkyl, aliphatic, and aromatic
1,735	C=O stretching	Ketone and hemicellulose
1,620–1,632	C=C	Aromatic and lignin
1,613 and 1,450	C=C stretching	Cellulose and lignin
1,440–1,500	$O–CH_3$	Lignin
1,435–1,410	OH bending	Carboxylic acid
1,402	CH bending	Carboxylic acid
1,264	C–O–C stretching	Cellulose
1,215	C–O stretching	Lignin
1,176 and 1,082	C–O–C stretching vibration	Cellulose and lignin
1,108	OH association	Alcohol and hemicellulose
1,060	C–O stretching and C–O deformation	Alcohol
910	C–H	Cellulose and hemicellulose
875	C–H	Aromatic and lignin
700–400	C–H	Hemicellulose

carbonization are highly reactive. These unsaturated compounds can polymerize easily by aldol condensation or/and intermolecular dehydration. By these dehydration and decarboxylation processes, water and CO_2 are created, respectively [2]. Furfural-like compounds can also generate acids, aldehydes, and phenols [5]. Data presented in Table 2 show that the production of lactic acid and levulinic acid increased significantly in both liquid and solid samples when HTC reaction temperature increased from 230 to 260 °C. The anhydrosugar, mannosan, also decreased with increasing temperature, in both liquid and solid samples. In contrast, cellobiosan decreased only in the HTC liquid with increasing reaction temperature.

The C=C functionality seen in the IR spectra may result from keto-enol tautomerism of dehydrated species or intramolecular dehydration [5], as well as from aldol condensation and aromatization reactions. Polymerization, which forms a solid precipitate, may also take place with further dehydration and decarboxylation. Polymerization may occur by condensation of such hydrolyzed products themselves or by condensation with lignin. A peak at 1,500 cm^{-1} (Fig. 3), indicative of a methoxyl group in lignin, appears to strengthen with increased reaction temperature. The peak at 1,440 cm^{-1}, indicative of C=C stretching in either cellulose or lignin, also appears to sharpen with increasing reaction temperature. The C–O–C ether bonds near 1,080 and 1,170 cm^{-1} also become more pronounced with increasing HTC temperature, indicating the increasing amounts of unreacted lignin, along with possible production of polysaccharides by condensation. Moreover, some of the monosaccharides (xylose, arabinose, mannose, and fructose) in Table 2 are seen to decrease with increasing HTC temperature. In this way, a linear polymer like cellulose can convert into a cross-linked polymer similar to lignin. Condensation reactions of monosaccharides are slower, since cross-linked polymerization competes with recondensation to oligosaccharides [7]. Condensation polymerization is likely governed by step-growth kinetics, which is enhanced by higher temperatures and longer reaction times [7]. Thus, it is likely that formation of HTC biochar during hydrothermal carbonization is mainly characterized by condensation polymerization, specifically aldol condensation [39]. Condensation of oligosaccharides within the biomass matrix could potentially “block” remaining transport of biomacromolecules, thus trapping hydrolysis products inside the pore, impeding access of water to the pore. This phenomenon could also contribute to increased hydrophobicity of HTC biochar [8].

3.2.5 *Aromatization*

Even though hemicellulose and cellulose are linear carbohydrate polymer chains, they can form aromatic structures under hydrothermal conditions [5]. The disappearance of the IR peak at 1,735 cm^{-1} (corresponding to hemicellulose), the appearance of a new peak near 875 cm^{-1} (corresponding to C–H aromatics), and the growth of a peak near 1,600 cm^{-1} (corresponding to C=C aromatic bond) in Fig. 3 may all be indications of aromatization for HTC 260. Aromatic structures exhibit high stability under hydrothermal conditions and may be considered a basic building block of the resulting HTC biochar. Cross-linking condensation of aromatic rings also comprises a major constituent of natural coal, which may explain the good agreement between natural coalification and hydrothermal carbonization [9]. On the basis of these considerations, it appears that HTC increases the production of aromatics from those intermediates produced during hydrolysis.

3.3 Water balance of hydrothermal carbonization

Figure 1 shows a strong trend of dehydration with increasing HTC temperature, while chemical analysis (Table 2) of the aqueous solutions shows the degradation of xylose and glucose, which are products of hydrolysis of hemicellulose and cellulose, respectively. In the ATR-FTIR spectra (Fig. 3), the peak for hydroxyl stretching at 3,000–3,500 cm^{-1} becomes flatter with increased HTC temperature, indicating a greater extent of dehydration. Further, polymerization of soluble monosaccharides can release water by means of condensation reactions. All of these factors indicate that dehydration and hydrolysis occur simultaneously and are both important reactions during HTC. Water production is positive if dehydration is greater than hydrolysis and negative otherwise. An experimental approach has been developed to quantify net water production, as described below.

3.3.1 Quantitative analysis

HTC reactions were conducted to quantify water production performed in a reactor configured specifically for this purpose. A glass liner was inserted in a 100-mL Parr reactor to make the measurements more convenient and reproducible while maintaining other parameters the same as described in the experimental Section 2.2. After quenching the reaction, followed by venting gases, the glass liner containing all its products, both liquid and solid, was weighed. Because the reactor was cooled to 10 °C before venting, we assume that the uncollected gases consist only of noncondensable species, primarily CO_2. The contents of the liner were then vacuum-filtered and subsequently dried at 105 °C for 24 h. The filter and contents were weighed before and after drying. The mass and pH of the filtrate were recorded. The nonvolatile residue (NVR) content of the filtrate was determined by evaporation of water and other volatiles at 105 °C for 24 h.

Because of the large mass of water used in the HTC process, it is challenging to use gravimetric methods alone to quantify water production [30]. However, use of the glass liner allows an accurate measurement of all condensed products and facilitates an accurate calculation, with the use of some simplifying assumptions. First, we assume that the contents of the glass liner M_{GL} may be divided into four categories:

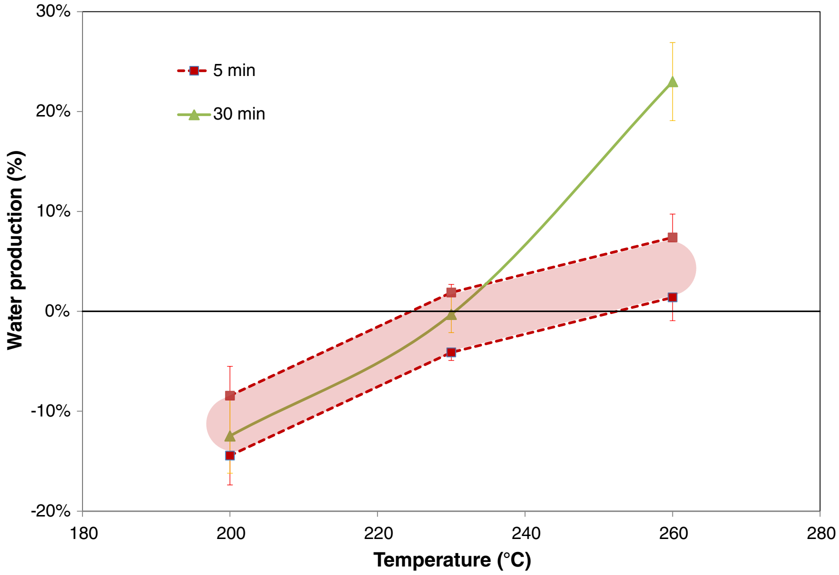
$$M_{GL} = M_{H_2O} + M_{Vol} + M_{bc} + M_{NVR} \quad (1)$$

The four terms on the right-hand side of Eq. (1) are mass of water, volatiles, biochar, and NVR, respectively. The mass of biochar (M_{bc}) and NVR (M_{NVR}) are found by drying the filtered solids and filtrate, respectively. For simplicity, we assume that the liquids lost by evaporation during drying of biochar and NVR (solids and filtrate) have identical compositions, and we assume that these liquids consist only of water, low boiling organic acids, and furan derivatives (5-HMF and furfural). Another work has shown a total carbon balance of greater than 95 % in the gaseous, aqueous, and solid products from HTC treatment of loblolly pine at temperatures of 175 to 275 °C, indicating that only very small amounts of volatiles are lost during product isolation [30]. We assume that only water, acetic acid, formic acid, lactic acid, 5-HMF, and furfural evaporate during drying, and we further assume that those species evaporate completely. With these assumptions, we can calculate the amount of volatiles present in the liquid (M_{Vol}) from the liquid phase analysis shown in Table 2. Thus, the mass of water in the glass liner, M_{H_2O} , can be calculated from Eq. (1). This water consists of water that was added to the reactor (W_{added}) and water that was produced during HTC (W_{HTC}):

$$M_{H_2O} = W_{added} + W_{HTC} \quad (2)$$

The amount of water added is known, so the net production of water W_{HTC} can be calculated from this approach. All measurements were done in triplicate, and error bars indicate standard errors.

Fig. 4 Variation in water production with temperature for 5-min and 30-min HTC reactions. A range of values is shown for a 5-min reaction time. *Error bars* are the standard error of three separate HTC experiments



The analysis of 5-HMF and furfural was done on products produced in a 2-L Parr reactor with a 30-min reaction time [30]. These reaction conditions were quite similar to those described in this paper, and quantitative analyses available (pH, mass and energy yield of biochar, etc.) indicate that the reactor products are similar. Those large-scale reactions were done at temperatures slightly different from those described here, but at a wider range (177, 201, 215, 239, 262, and 277 °C) [30]. Thus it was possible to interpolate those results from the recorded reaction temperature to the reaction temperature of interest herein to find the composition of volatiles in the vapor lost during drying. No analysis of 5-HMF or furfural production for the 5-min reaction time is available. Therefore, for the 5-min reaction time, the mass of volatiles computed (excluding 5-HMF and furfural) is too low, and so the water production calculated is an upper limit; the actual water production must be smaller (or more negative). For loblolly pine, the sum of furfural and 5-HMF is always below 6 % (based on solid dry biomass) at 30 min [30], and it is likely that the production of both is even smaller in 5 min. Thus, we estimate the content of 5-HMF and furfural to be between 0 and 6 %. For this case (5-min reaction time), the water production is presented as a range, rather than as a single number.

3.3.2 *Effect of reaction temperature*

Figure 4 shows the temperature and time effects on water production of loblolly pine during HTC reaction. Water production increases with increasing HTC temperature at a given reaction time. At 200 °C, water production is negative. Hydrolysis of hemicellulose or cellulose requires 1 mol of water to produce 1 mol of dissolved monomeric sugar. On the other hand, 2 mol of these monomers (e.g., glucose) can condense to form 1 mol of dimer (e.g., sucrose) and 1 mol of water. Alternatively, 1 mol of these monomers can further degrade into lower carbon components and water. As hydrolysis and dehydration occur simultaneously, water balance is the outcome of this competition. Thus, a net consumption of water at 200 °C indicates that hydrolysis is more prominent than dehydration at low temperature. Yan et al. reported that gas production increased with temperature for loblolly pine, but it was minimal at 200 °C [37], a result confirmed recently by others [30, 31]. As dehydration and decarboxylation are simultaneous reactions of monomer degradation, minimal gas production indicates that any water production is likely due to condensation reactions.

As discussed above, calculation of water production for a 5-min reaction time is limited by incomplete analysis of volatiles. Although presented as a range, some general observations can be made. Water production for 5-min HTC experiments increased modestly upon increasing reaction temperature from 200 to 230 °C. This results from a change in the balance between hydrolysis of hemicellulose and cellulose polymers and decomposition of sugar monomers. A further increase in water production was observed upon increasing the temperature from 230 to 260 °C, to the extent that now water production is positive at both reaction time studies. Sevilla and Fuertes proposed a reaction model for pure cellulose under subcritical conditions where dehydration (C–O bond splitting) and retro-aldol condensation (C–C bond breaking) were found to be the key reactions [5]. 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) [2].

3.3.3 *Effect of reaction time*

As previously discussed, sugar monomers degrade rapidly at temperatures above 230 °C, and the degradation continues with time. As shown in Fig. 4, at a temperature of 260 °C, water production increased greatly when reaction time increased from 5 to 30 min. At a reaction temperature of 260 °C and a reaction time of 30 min, the net water production was found to be 23.0± 3.9 % of solid biomass feedstock. The corresponding solid mass yields at 5 and 30 min were 62±1 % and 54±1 %, respectively. Extending the reaction time beyond this has a minimal effect on mass yield and biochar fuel value [10, 31]. The increase of produced water with extended reaction time indicates a continuation of liquid-phase reactions, while the relatively constant solid mass suggests an end of solid phase reactions.

4 Conclusions

Hydrolysis, dehydration, decarboxylation, condensation polymerization, and aromatization are the primary reactions in HTC. Dehydration is the dominant reaction, especially in the liquid phase, but its extent depends on HTC reaction time and temperature. Reactions in the liquid phase are dominant for longer reaction times, while HTC solid biochar yields remain relatively constant after 5 min. Water production changes from negative at 200 °C to positive at 260 °C and can be as much as nearly 25 % of biomass feedstock at 30 min of reaction time.

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