Behavior of selected hydrolyzed and dehydrated products during hydrothermal carbonization of biomass

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HIGHLIGHTS

- An innovative slurry sampling system was designed for hydrothermal reaction system.
- Elemental carbon increases rapidly after 90 min for HTC cellulose at 230 °C.
- The liquid state reactions continued for hours for HTC of poplar and straw.
- Selective hydrolyzed compounds' degradation follow first-order reaction kinetics.

ARTICLE INFO

ABSTRACT

In this study, effects of reaction temperature and reaction time on both solid hydrochar and HTC process liquid products were studied for hydrothermal carbonization (HTC) of cellulose, wheat straw, and poplar. A novel slurry sampling system was designed and used with an 18.6 L Parr reactor for 0–480 min in 200, 230, and 260 °C. Sugars (sucrose, glucose, and fructose), HMF, and furfural were found maximum in lower HTC temperature and time. However, they degrade following first order degradation kinetics. Activation energies of total sugars (glucose, fructose, sucrose, and xylose), furfural, and HMF for straw and poplar were 95–127, 130–135, and 74–90 kJ mol^{-1}, respectively and individuals were lower for HTC of cellulose than others. Organic acids (acetic acid, formic acid, and lactic acid) and phenolic compounds (phenol, catechol, and guaiacol) were increasing with higher HTC severity.

1. Introduction

In current practice, hydrothermal carbonization (HTC) is considered as one of the most effective thermochemical pretreatment processes, where biomass is treated with hot compressed water (180–280 °C) for 5 min to 8 h (Reza et al., 2013a, 2014a,b,c,d). During HTC, volatile oxygen-rich compounds of biomass are removed from the structure, leaving behind stable carbon-rich micro–nano particles (hydrochar) (Jin, 2014). Subcritical water has maximum ionic product in temperature range of 200–280 °C (Bandura and Lvov, 2006). Hydrolysis of the extractives, hemicellulose, and cellulose probably occur first, followed by dehydration, decarboxylation, condensation, polymerization, and aromatization in the liquid phase (Funke and Ziegler, 2010; Reza et al., 2014a). Although overall reaction chemistry follows mainly the stated reaction paths, each of the individual HTC reaction has their own reaction kinetics and is probably catalyzed by one another (Reza et al.,

2013b). Moreover, liquid phase HTC reactions are responsible for the production of so-called liquid biocrude (Reza et al., 2014a,d), which is considered as the primary precursor of solid hydrochar. Thus, quality of hydrochar heavily depends on the composition of HTC process liquor (Libra et al., 2011).

Hydrolyzed and dehydrated products during HTC like HMF, furfural, phenol, and their derivatives are potentially toxic and hazardous products, which make HTC process liquor as waste water and thus, requires proper treatment prior to discharge into the environment, even after successive recycling (Uddin et al., 2013). Such toxic volatile organic compounds (VOCs) are reported in the solid hydrochar especially for lower HTC temperatures (e.g., 200–230 °C) (Becker et al., 2013). Presence of selective VOCs in hydrochar prohibits its use for soil amendment (Libra et al., 2011). It is also reported in previous studies that with the increase of HTC temperature (e.g., 250–270 °C) and a prolonged reaction time (6–8 h) many of the VOCs were not observed in hydrochar (Becker et al., 2013). This might be one possible reason for practicing HTC at higher temperature for a prolonged time, which unfortunately also makes HTC economically less viable. Recently, Wirth

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and Mumme (2013) reported on anaerobic digestion of high strength HTC process liquor for biogas production, which can potentially contribute to the overall economics besides treating waste water. However, high capital cost and proof-of-concept (for HTC process liquid) are hindering anaerobic digestion of such high strength process liquid.

In contrary, many researchers reported HMF, furfural, lactic acid, levulinic acid, levoglucosan, and other hydrolyzed products as platform chemicals or building blocks (Bozell et al., 2000; Jin, 2014; Reza et al., 2014d; Yan et al., 2013). HMF can be dehydrogenated into DHMF and then liquid alkanes in presence of catalysts (Olcay et al., 2013). Furfurals can be used for perfumes and preservatives, while levulinic acid and levoglucosan can be converted into liquid fuels as well (Win, 2005). Lactic acid can be converted into poly-lactic acid (PLA), which is well known as biodegradable plastic (Oda et al., 1997). Thus, hydrolyzed and dehydrated products have market value at their semi-pure to pure form (>70%). Hoekman et al. (2013) reported that up to 4–10% of the dry feedstock can be found in HTC process liquid as valuable hydrolyzed intermediates after 30 min of reaction time for 215–255 °C for various feedstocks. Reza et al. (2014c) also reported that up to 18% of dry maize silage can be found as furfural, HMF, lactic acid in HTC process liquid treated at 200 °C for 20 min. Both literatures also reported that many of the valuable hydrolyzed products degrade with higher HTC temperature and longer reaction time. So, knowledge about degradation chemistry and kinetics of hydrolyzed intermediates within the liquid phase of specific feedstock are necessary for a comprehensive HTC process and product optimization.

The objective of this work was to study HTC process liquid obtained by varying HTC reaction conditions. One of the main problems of such study is the lack of sampling scope, which allows taking samples during the HTC reaction. Most of the researchers used 100–2000 ml batch pressurized reactors (Becker et al., 2013, 2014; Hoekman et al., 2011, 2013; Reza et al., 2014a,b,c), where it is difficult to install such high pressure high temperature sampling system and justify with the overall HTC reaction. Thus, the first objective of this work was to design a high pressure high temperature slurry sampling system on an 18.6 L (5 gal) Parr reactor. Therefore, several different reaction conditions were implied in this study by changing biomass feedstock, reaction time, and reaction temperature, and both solid and liquid phase were studied. Further objective of this work was to prepare a degradation model for selective hydrolyzed products and validate for various lignocellulosic feedstocks.

2. Methods

2.1. Biomass preparation

A grassy biomass (wheat straw), a woody biomass (poplar), and a model compound (micro-crystalline cellulose) were studied in this work. Wheat straw and poplar chips were acquired from a locally grown test site at Leibniz Institute for Agricultural Engineering (ATB), Potsdam, Germany. Wheat straw and debarked poplar chips of 1 ± 0.5 cm were washed and dried prior to the final grinding to minimize loose dirt presence in the biomass. Both biomass were grinded using a cutting mill (SM 100, sieve size: trapezoid holes 0.25 mm; Retsch, Haan, Germany) into 0.3 ± 0.2 mm to facilitate slurry sampling as well as minimize the mass diffusion effect during HTC. The industrial microcrystalline cellulose (MCC) was purchased from Avicel PH 101 (Sigma Aldrich, Switzerland). Avicel PH 101 MCC is a microcrystalline, powdery material with an average particle size of 50 μm and a bulk density of 0.28 g cm^{-3}.

2.2. Parr reactor and slurry sampling system

An 18.6 L Parr stirred pressure reactor (model 4555) was used for HTC experiments in this study. A high pressure high temperature slurry sampling system was designed and equipped with the batch reactor as shown in Fig. S1. For sampling, a hollow dip-tube (model 316TI-T10M-S-1.0M2ME, Swagelok, Leipzig, Germany) was installed in the reactor from the top and extended till the lower third of the reactor. Two high pressure high temperature ball valves (valve 1 and valve 2) were inserted in the long horizontal tube outside of the reactor. A single ended 100 ml sample cylinder (model 316L-HDF4-150, Swagelok, Leipzig, Germany) was connected at the end of the sampling line. The sample cylinder was immersed in a cooling bath (maintaining 4 °C). The HTC reaction temperature and stirring were controlled with SpecView 32849 data acquisition software via Parr controller (model 4848, IL, USA). The accuracy of the controller was set at ±1 °C. Reaction times, pressure, heating jacket temperature, and cooling water temperature were recorded every 2 s throughout the reaction. Four thermocouples were used to monitor and control HTC reaction temperatures. One thermocouple was inserted on the heating jacket and three others were inserted into the Parr reactor in different depths. The average of the three inside temperatures was reported as the reaction temperature throughout this study and hence was controlled.

For a typical HTC experiment, around 1 kg of dry feedstock was weighed and transferred into the reactor. Eight liters of de-ionized (DI) water was weighed by same balance (maintain 1:8, biomass: water ratio) and poured into the reactor. To evaluate the effects of reaction time and reaction temperature, two sets of reactions were carried out, i.e., three isotherms at 200, 230, and 260 °C and one dynamic run from 160 to 260 °C with 10 °C interval for each feedstock. In all cases, the heating rate of the reactor was maintained at 2 °C.min^{-1} and the reactor content was stirred at 90 rpm throughout HTC reaction. Eleven different slurry samples were collected from each isotherm at various times (0, 10, 20, 40, 60, 90, 120, 180, 240, 360, and 480 min) and eleven different ones from dynamic runs at different temperatures (every 10 °C interval). It is important to be noted that although it took 87.5–117.5 min to reach the isotherms, reported reaction time counts from zero, when it reached the isotherm for the very first time.

For sampling, valve 1 and then valve 2 were opened and let the slurry to collect in the sample cylinder (Fig. S1). Pressure difference was the driving force for this sampling system. After 1 min of sampling, valve 2 and then valve 1 were closed, respectively. The sample cylinder was immersed for 4 min, slurry was collected afterwards, and slurry was vacuum filtered using a round filter paper (type 113A, Carl ROTH, Karlsruhe, Germany). The sample cylinder was cleaned and sample line was purged with nitrogen prior to the next sampling. After the end of reaction period (480 min or 260 °C for isotherms or dynamic runs, respectively), the heater was turned off and let the reactor cool down naturally for overnight. The process liquids were stored into a 4 °C refrigerator for further analyses. The solid products were dried in a heating oven for overnight at 105 °C. Dried hydrochar was weighed, placed into a ziplock bag, and stored for further use.

2.3. Product characterization

Elemental carbon, hydrogen, nitrogen, and sulfur (CHNS) were measured using a Vario El elemental analyzer (Elementar Analysesysteme Hanau, Germany). Sulphonic acid was used in this elemental analysis as reference and two ovens were set at 1150, and 850 °C, respectively. Each sample was analyzed three times, and the oxygen content was calculated by the difference method (O% = 100 − (C% + H% + N% + S%) − ash%). Dry matter (DM) was