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Reaction kinetics of hydrothermal carbonization of loblolly pine

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HIGHLIGHTS

- An innovative reactor was designed to measure hydrothermal reaction kinetics.
- At temperatures between 200 and 260 °C, weight loss kinetics are quite rapid.
- Reactions are modeled by parallel first-order degradation of hemicellulose and cellulose.
- Mass transfer and reaction kinetics may both be important.

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ABSTRACT

Hydrothermal carbonization (HTC) is a pretreatment process to convert diverse feedstocks to homogeneous energy-dense solid fuels. Understanding of reaction kinetics is necessary for reactor design and optimization. In this study, the reaction kinetics and effects of particle size on HTC were investigated. Experiments were conducted in a novel two-chamber reactor maintaining isothermal conditions for 15 s to 30 min reaction times. Loblolly pine was treated at 200, 230, and 260 °C. During the first few minutes of reaction, the solid-product mass yield decreases rapidly while the calorific value increases rapidly. A simple reaction mechanism is proposed and validated, in which both hemicellulose and cellulose degrade in parallel first-order reactions. Activation energy of hemicellulose and cellulose degradation were determined to be 30 and 73 kJ/mol, respectively. For short HTC times, both reaction and diffusion effects were observed.

1. Introduction

Because of the abundant renewable supply of lignocellulosic biomass, much research and development has been conducted to find economical means to utilize this feedstock for fuels, chemicals, and energy. More than a billion tons of dry lignocellulosic biomass is available in the US (Perlack and Stokes, 2011). Although lignocellulosic biomass is inexpensive, challenges, including diverse feedstocks, widely dispersed production, low calorific value, and seasonal availability, make biomass' handling and transportation expensive (Tester, 2005). Moreover, the chemical properties of lignocellulosic biomass make it even more unfavorable in traditional thermochemical applications. To overcome these challenges, there is a need for a process to homogenize the feedstocks and simultaneously produce a stable, energy-dense, solid fuel.

The major chemical fractions of lignocellulosic biomass are lignin, cellulose, hemicellulose, aqueous extractives, and ash (Goering and Van Soest, 1970). Monomeric sugars (mainly glucose and fructose) along with various alditols, aliphatic acids, oligomeric sugars, and phenolic glycosides are the main components of aqueous solubles in biomass (Minowa et al., 1998). Hemicellulose is a heteropolymer, composed of sugar monomers, including xylose, mannose, glucose, and galactose with β-(1–4) glucosidic bonds. The ratios of these monomers in hemicellulose vary dramatically within a given feedstock, but their cumulative content is almost identical in most types of wood (Garrote et al., 1999). Cellulose, a polysaccharide of glucose with β-(1–4) glucosidic bonds, is the most abundant chemical component of biomass (Cuiping et al., 2004). Lignin is a high molecular weight cross-linked polymer of phenyl propane derivatives (Peterson et al., 2008). Every biomass has these chemical components, however, their contents vary in each feedstock (Cuiping et al., 2004).

Hydrothermal carbonization (HTC) also known as wet torrefaction, is a prominent pretreatment process for biomass enhancement (Acharjee et al., 2011; Funke and Ziegler, 2010; Kobayashi et al., 2009; Yan et al., 2009). In HTC, biomass is treated with hot compressed water, resulting in three products: gases, aqueous products,

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and a solid product sometimes known as hydrochar, and referred to here as HTC biochar. Typical reaction temperatures are in the range of 200–275 °C, and pressures are maintained above the saturation pressure to ensure the liquid state of water. In this temperature range, the ionic constant of subcritical water increases nearly two orders of magnitude and liquid water behaves as a non-polar solvent (Bandura and Lvov, 2006). The gaseous products from HTC represent about 10% of the original biomass, depending on the temperature, consisting mainly of CO_2, while the aqueous soluble compounds are primarily sugars, acetic acid, and other organic acids (Hoekman et al., 2011). The solid product contains about 41–90% of the mass and 80–95% of the calorific value of the original feedstock (Garrote et al., 1999; Yan et al., 2010). HTC biochar is friable and more hydrophobic than the original biomass (Acharjee et al., 2011; Libra et al., 2011).

Aqueous extractives are readily extracted in hot compressed water. Hemicellulose, a non-crystalline polymer with a lack of repeating β-(1–4)-glycosidic bonds, has little resistance to hydrolysis or hydrothermal extraction in hot compressed water (Bobleter, 1994; Peterson et al., 2008). Mok and Antal (1992) found that an average of 90% of the hemicellulose degrades into monomeric sugars at 34.5 MPa and 200–230 °C (Mok and Antal, 1992). It is reported that the activation energy of hemicellulose degradation is 82–156 kJ/mol for various biomass materials in the temperature range of 145–190 °C assuming a first order reaction (Garrote et al., 1999; Grénman et al., 2011; Mittal et al., 2009).

Unlike hemicellulose, cellulose has repeating β-(1–4)-glycosidic bonds between glucose, which allows strong intra- and intermolecular hydrogen bonds to form, making cellulose crystalline, resistant to swelling in water, and resistant to attack by enzymes (Peterson et al., 2008). However, subcritical water at elevated temperatures (>230 °C) can disrupt the hydrogen bonds and crystalline structure, and thus hydrolyze the β-(1–4)-glycosidic bonds to form glucose monomers (Funke and Ziegler, 2010). The β-(1–4)-glycosidic bonds of both hemicellulose and cellulose can be broken using acidic liquid media at elevated temperatures (Lynam et al., 2011). Bobleter, (1994), showed first order reaction kinetics for cotton cellulose degradation with an activation energy of 129 kJ/mol in the temperature range of 215–274 °C (Bobleter, 1994). However, Peterson et al., (2008), plotted data from several literature sources using first order Arrhenius kinetics and found the activation energy of cellulose to be 215 kJ/mol in a temperature range of 210–370 °C (Peterson et al., 2008).

Lignin, with phenylpropane derivatives such as *p*-coumaryl alcohol, coniferal alcohol, and sinapyl alcohol, is a cross linked polymer which is stable in hot compressed water at temperatures below 260 °C (Zhang et al., 2008).

Owing to the molecular structure of lignocellulosic biomass, the complex reaction scheme in HTC could involve many different reactions. The main objective of the HTC is to economically convert raw biomass into a feedstock with improved physical and chemical properties for combustion and gasification. Hence, the solid char product after HTC is of the most interest. The kinetics of carbonization during HTC determine the required residence time and reactor volume, and are therefore of great importance for further process design and economic evaluation. The objective of this work is determination of the mass loss kinetics of HTC of wood by experiments in a specially-designed two-chamber reactor.

2. Methods

2.1. Biomass

Loblolly pine (*Pinus taeda* L.) (Alabama, USA) was used in all experiments reported here. A fiber analysis was measured according the Van Soest method (Goering and Van Soest, 1970). On a dry mass basis, the biomass consists of 11.9% hemicellulose, 54.0% cellulose, 25.0% lignin, 8.7% water-extractives and 0.4% ash (Reza, 2011). Pine samples were milled to a particle size range of 0.5 ± 0.2 mm, and dried at 105 °C for 24 h prior to the experiment.

2.2. Hydrothermal carbonization

HTC experiments are typically done in heavy steel reactors to hold the high pressure with long heating times (Funke and Ziegler, 2010; Yan et al., 2009). As the reactor is heated, it is likely that HTC reactions are initiated well before the desired reaction temperatures are reached. This makes the precise study of mass-loss kinetics difficult. To overcome this difficulty, a specially-designed two-chamber reactor was built, which allows very rapid heating of the biomass reactant during HTC.

2.2.1. Reactor set-up

Fig. 1a shows a schematic diagram of the reactor system, including a two-chamber reactor, a radiant heater, a temperature indicator, and a PID temperature controller. Two similar double-chamber reactors were designed and built for this kinetic study; they are referenced as reactor A and reactor B. The bottom chamber (volume: 20 mL for reactor A and 200 mL for reactor B) and the top chamber (volume: 10 mL for reactor A and 20 mL for reactor B) were connected with Swagelok ball valves (Sunnyvale, CA), which can handle high temperatures (up to 454 °C) and high pressures (up to 6.9 MPa). A ceramic radiant heater of 600 W (Omega Engineering, Stamford, CT) was used to heat the bottom chamber of the reactor, where the HTC reaction actually occurs. Two thermocouples (inside and outside the bottom chamber) were used, while only outside temperature was controlled by the controller. Since there was a constant temperature difference (typically 90 °C) between the chamber-wall temperature and the chamber-inner temperature, the controller set point input was set at 90 °C higher than the desired HTC temperature. A water cooling coil was placed on the top chamber to keep the biomass sample cool while heating the bottom chamber. While the valve is closed, the two chambers are thermally separated. For safety reasons, a pressure relieve valve was installed in the two-chamber reactor.

2.2.2. Experimental procedure

The procedure for HTC using the two chamber reactor is shown in Fig. 1b–d. For reactor A, 15 mL of de-ionized water was loaded into the bottom chamber (30 mL was used for reactor B), and the ball valve was closed to almost 90%. A biomass sample (0.2 g for reactor A and 1 g for reactor B) was wrapped into a close-ended cylindrical-shaped capsule (20 mm height and 10 mm diameter). Stainless steel screen (320 mesh), was used for making the sample holder. The biomass capsule was placed into the top chamber and the reactor was closed. After entering the bottom chamber, the sample holder allowed the liquid to rapidly wet the solid, and prevented the biomass from escaping. Nitrogen was charged for 2 min into the closed reactor at a rate of 80 mL (STP)/min, and then the pressure was released for 10–15 s. This process was repeated for five times to remove oxygen from the reactor. The ball valve was then fully closed.

The bottom chamber's external wall was heated to 115 °C above the reaction temperature, while the upper chamber was maintained at room temperature by cooling water. Once the wall temperature reached the desired value, the ball valve was fully opened, letting the capsule fall from the upper to the bottom chamber, which was then closed within 3–5 s. The rapid pressure drop experienced in the lower chamber, caused by opening the valve to the upper chamber, resulted in cooling by adiabatic expansion. This caused the water temperature to drop about 25 °C. Therefore, the water in the bottom chamber reached the desired