Hydrothermal conversion of woody biomass with disodium octaborate tetrahydrate and boric acid

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ABSTRACT

In this study, Scotch pine (*Pinus sylvestris* L.) was used as a woody biomass in the form of sawdust. Hydrothermal conversion of the biomass was carried out in the absence and presence of disodium octaborate tetrahydrate and boric acid at the temperatures of 250, 300 and 350 °C. The effects of temperature and catalysts on the product distributions and bio-oil compositions were investigated. The highest total bio-oil yield obtained at 300 °C with disodium octaborate tetrahydrate was 34.9 wt%, whereas the total bio-oil yields from the non-catalytic run and the run with H_3BO_3 at 300 °C were 24.6 wt% and 19.1 wt%, respectively. Although the composition of bio-oils was similar in all runs, some compounds such as furfural and furfural derivatives were not observed in the light and heavy bio-oils produced from the non-catalytic run and the run with disodium octaborate tetrahydrate at 300 °C. The light bio-oils from all runs contained mainly oxygenated hydrocarbons. The major compounds in HBOs were the following: 4-methyl-3-penten-2-one and 4-hydroxy-4-methyl-2-pentanone for disodium octaborate tetrahydrate, 4-hydroxy-4-methyl-2-pentanone and (Z,Z)-9,12-octadecadienoic acid for the non-catalytic run and (Z,Z)-9,12-octadecadienoic acid for the run with boric acid. The maximum heating values for the LBO and HBO were estimated to be about 25 and 28 MJ/kg, respectively, and they were obtained with disodium octaborate tetrahydrate. SEM analysis of the bio-char obtained from the non-catalytic run at 250 °C showed a semi-char formation. An increase in temperature from 250 to 300 °C led to the formation of regular channels on the surface of the bio-char. These open channels closed when the temperature was increased from 300 to 350 °C.

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1. Introduction

Research on the conversion of biomass to valuable products has been gaining worldwide momentum. The effective use of biomass is of great importance with respect to environmental concerns that contribute to both economic and ecological sustainability. As such, there have been a number of studies to develop new biomass conversion technologies which will increase the yields of valuable products (Huber et al., 2006; Effendi et al., 2008; Conde et al., 2011; Haykir et al., 2013; Odetoye et al., 2013; Matsushita et al., 2013).

Biomass, one of the most renewable sources of energy, is a natural material that is constituted primarily of lignin, cellulose and hemicellulose. There are various forms of biomass (i.e., agricultural crops, forestry products and wastes, animal wastes, municipal solid wastes, and fruit processing) which can be considered as potential feedstock of biomass for conversion into bio-fuels and/or value added products (Knezevic et al., 2007; Jin and Enomoto, 2009; Ingram et al., 2009; Wormeyer et al., 2011).

The current water-based hydrothermal conversion process of biomass is important, as water is a unique and environmentally safe solvent (Savage, 2009). In addition, the process has distinct advantages: hydrothermal biomass conversion requires lower temperatures than processes such as pyrolysis, and the conversion has a high de-oxygenation ability; also, there is no need to dry wet biomass (Tekin and Karagoz, 2013a).

The physicochemical properties of water at high temperatures are quite different from those of ambient water. For instance, the relative permittivity (dielectric constant), ε_r, of water decreases quickly when the temperature increases. When the thermal energy increases, the electronegativity of the oxygen molecule becomes reduced and this converts water molecules from very polar to fairly

non-polar. This polarity change makes water more affinitive to the lignocellulosic materials that consist of oxygenated hydrocarbons. Another distinct change is the drastic dissociation of water to H^+ and OH^- ions at high temperatures. These properties make water a perfect reaction medium in which water acts as a catalyst in the conversion of biomass (Zhang, 2010; Oomori et al., 2004; Onwudili and Williams, 2008).

A great number of investigations have been carried out pertaining to the hydrothermal conversion of biomass (Schutt et al., 2002; Ramsurn and Gupta, 2012; Valdez et al., 2011; Moller et al., 2011; Jin and Enomoto, 2011). Wood is one of the most difficult biomass types to liquefy without any catalysts. Thus, there have been great efforts to use catalysts in hydrothermal conversion of biomass (Li et al., 2011; Zhou et al., 2011).

Most of the studies related to hydrothermal conversion of biomass have been conducted using alkaline catalysts as additives. This has been done because the use of alkaline catalysts in the hydrothermal conversion of biomass hinders the formation of bio-char and increases bio-oil yields (Karagoz et al., 2005).

Bio-oils from the hydrothermal conversion of biomass, which are mostly oxygenated hydrocarbons, can be used as fuel oil after upgrading or can be used as chemicals after separation and purification.

Another important product of hydrothermal conversion of biomass is bio-char. Bio-chars are valuable in agriculture as they are used to improve soil fertility and reduce pollution in rivers and underground water sources (Marris, 2006; Barrow, 2012).

Disodium octaborate tetrahydrate ($Na_2B_8O_3 \cdot 4H_2O$), an alkaline salt, is often used as an insecticide and fungicide. Boric acid (H_3BO_3), a weak acid of boron, is often used as a fireproofing agent for wood, as a preservative, as an antiseptic, and is also used as a fungicide and as an insecticide powder (Wahl, 2005).

In this study, the hydrothermal conversion of Scotch pine (*Pinus sylvestris* L.) was carried out without and with either disodium octaborate tetrahydrate ($Na_2B_8O_{13} \cdot 4H_2O$) or boric acid ($H_3BO_3$) at the temperatures of 250, 300 and 350 °C. The effects of temperatures, as well as the types of catalysts on bio-oil and bio-char yields were investigated under identical conditions. The bio-oil compositions from non-catalytic and catalytic runs were identified and compared. The elemental compositions and heating values of bio-chars were determined. In addition, the surface morphology of bio-chars from the non-catalytic runs was observed in relation to hydrothermal conversion temperatures.

2. Materials and methods

2.1. Material

As wood is a relatively well-known biomass, not too heterogeneous and containing low levels of impurities, it was selected as a biomass and used for the hydrothermal processing. The biomass used in this study was Scotch pine (*P. sylvestris* L.) in the form of sawdust. The biomass contained 5.3 wt% moisture, 0.16 wt% ash, and 88.51 wt% volatile matter. The composition of biomass was determined according to the previously described method (Li et al., 2004). It contained 27.70 wt% lignin, 47.30 wt% cellulose, 20.54 wt% hemicellulose, and 4.30 wt% extractives.

Disodium octaborate tetrahydrate ($Na_2B_8O_3 \cdot 4H_2O$) was obtained from Eti Mine Works, Turkey, and was not altered. The chemical properties of $Na_2B_8O_3 \cdot 4H_2O$ are as follows: 67% B_2O_3, 14% Na_2O; 0.38 g/cm^3 bulk density; 9.5% water solubility at 20 °C; pH 8.51 (1% solution at 20 °C); 99.90% purity. Boric acid (H_3BO_3) was obtained from Merck AG (Darmstadt, Germany). The chemical properties of H_3BO_3 are as follows: 0.45 g/cm^3 bulk density; 4.72% water solubility at 20 °C; pH 5.1 (1% solution at 20 °C); 99.90%

purity. BET surface areas of $Na_2B_8O_3 \cdot 4H_2O$ and H_3BO_3 are 1.44 and 1.25 m^2/g, respectively.

2.2. Hydrothermal conversion procedure

The equipment was the same as previously used (Tekin and Karagoz, 2013b). A brief description is provided here. The reactor is a batch stainless steel reactor with a volume capacity of 500 mL and it was purchased from Parr Co. (Moline, IL, USA, Parr 4848 High Pressure High Temperature Reactor). The maximum operation temperature and pressure of the reactor are 500 °C and 35 MPa, respectively.

Our experiments were conducted in a typical way previously used in the literature (Tekin and Karagoz, 2013b). In non-catalytic runs, 10 g (dry basis) of biomass and 100 mL of distilled water were put inside the reactor. In catalytic runs, the reactor was loaded with 10 g (dry basis) of woody biomass, 100 mL of water and 1 g of catalyst. The reactor was then purged with nitrogen three times to remove the air inside. The reactor was heated to the desired temperature (250, 300 and 350 °C). The heating was stopped when the desired temperature was achieved, corresponding to a reaction time of 0 min. As the focus of this study is upon the liquefaction of wood in hydrothermal media, relatively low temperatures were chosen and the gas yield was not determined. The hydrothermal liquefaction experiments were repeated three times with LBOs, HBOs and SRs, with average standard deviations of ±0.3, ±1.0, and ±1.3 wt%, respectively.

2.3. Separation and extraction procedures

The liquid and solid byproducts of the hydrothermal treatment were rinsed with 100 mL of distilled water and acidified with HCl (1.0 M) to obtain a pH of 1–2. Then, they were separated by filtration under a vacuum. The liquid portion was extracted with an equal amount of diethyl ether (300 mL). The etheral solution was dried over anhydrous sodium sulfate, filtered and evaporated in a rotary evaporator at room temperature. After removing the diethyl ether, the remaining fraction was quantified and labeled as LBO. The remaining solid products on the filter paper and the autoclave were washed several times with 250 mL of acetone. After removal of the acetone under reduced pressure, the remaining products were quantified and labeled as HBO. The TBO is therefore the sum of the LBO and HBO fractions. The remaining solid residues from the filter paper were dried at 105 °C in an oven for 2 h. After drying, the filter paper and the SR were removed from the oven, air equilibrated, and weighed.

2.4. Analysis

The bio-oils (LBOs and HBOs) were analyzed by a GC–MS. An Agilent 6890 Gas Chromatograph containing 30 m × 0.25 mm i.d. phenyl methyl siloxane capillary column (HP-5MS) with a film thickness of 0.25 mm was utilized for the determination of major compounds in the bio-oils. The GC oven temperature for the analysis of LBOs was as follows: started at 40 °C; held for 10 min, raised at a rate of 2 °C/min to 170 °C; held for 5 min; raised to 250 °C at a rate of 6 °C/min; held for 10 min, raised to 300 °C at a rate 15 °C/min; and held at this final temperature for 10 min. Similarly, the GC oven temperature program for the analysis of the HBOs was set to start at 40 °C; held for 10 min; raised at a rate of 3 °C/min to 170 °C; held for 5 min; raised to 270 °C at a rate of 4 °C/min; held for 10 min; raised to 300 °C at a rate 12 °C/min and held at this final temperature for 10 min. The injector temperature was 250 °C with a split mode. Helium was used as the carrier gas at a flow rate of 1 mL/min. The column was directly introduced into the ion source of an Agilent 5973 series mass selective detector operated with an