J. of Supercritical Fluids 72 (2012) 134–139

Contents lists available at SciVerse ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Hydrothermal liquefaction of beech wood using a natural calcium borate mineral

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ARTICLE INFO

Article history:
Received 15 July 2012
Received in revised form 28 August 2012
Accepted 30 August 2012

Keywords:
Biomass
Hydrothermal liquefaction
Light bio-oil
Heavy bio-oil
Colemanite

ABSTRACT

This study reports the effects of a natural calcium borate mineral, colemanite, on the hydrothermal liquefaction of beech wood biomass. Hydrothermal liquefaction experiments were performed at 250, 300 and 350 °C with and without colemanite. The highest light bio-oil yield (11.1 wt%) and the highest heavy bio-oil yield (29.8 wt%) were obtained at 300 °C with colemanite. The total bio-oil yields were 22 wt% and 41 wt% ca. at 300 °C without and with colemanite, respectively. The highest heating values were obtained from the hydrothermal liquefaction of biomass using colemanite at 350 °C: 23.81 MJ/kg for LBO and 27.53 MJ/kg for HBO. Most of the identified compounds in the light bio-oils were phenols. The light bio-oil obtained without the catalyst at 300 °C contained furfurals. However, these compounds were not observed in the run with colemanite at the same temperature. The heavy bio-oils from the runs both without and with colemanite are composed of phenols, aldehydes, ketones, acids, and benzene derivatives. 4-Methyl-3-penten-2-one was the major compound in the heavy bio-oils produced in the catalytic runs.

1. Introduction

Hydrothermal biomass processing is one of the most promising approaches to converting any type of biomass into bio-fuel and/or chemicals. The use of water as a solvent in chemical reactions is an application of green chemistry, as water is a unique and environmentally friendly solvent [1]. Its distinct advantages (i.e., applicability for wet biomass, ability to co-process the biomass with waste materials, use of lower temperatures than such processes as pyrolysis, and high energy efficiency) make hydrothermal liquefaction the most attractive thermochemical process [2,3].

Various types of biomass (e.g., cellulose, saccarides, pinewood, poplar, and rye straw lignin) have been tested to produce bio-oils and/or other desirable products in hydrothermal media [4–10]. Among these types, woody biomass is one of the most frequently used types of biomass for hydrothermal processing.

Sugi (*Cryptomeria japonica D. Don* wood) was liquefied under sub-critical water conditions at 260–360 °C and 15–25 MPa [8]. The highest reported yield of total saccharides was approximately 50 wt%.

Poplar wood flour was hydrolyzed under sub-critical (325 and 350 °C) and supercritical water (380, 400, 425 °C) for 60 s at 22.3 MPa ±1 using hydrochloric acid as a catalyst [9]. The yields of undegraded solids were temperature-dependent, and the solids were primarily composed of lignin fragments.

In another study, the direct liquefaction of Jack pine sawdust was performed with and without catalysts (alkaline earth and iron ions) under sub-/near-critical conditions [10]. The heavy oil and total oil product yields were highest between 280 and 340 °C for all runs regardless of the presence or type of catalyst.

Alkaline solutions are very effective for de-polymerizing lignocellulose in hydrothermal media [11–13]. The use of alkaline solutions for the liquefaction of lignocellulosic materials improves the bio-oil yields. A recent study explored the catalytic performance of B_2O_3 on the pyrolysis of EFB and OPF in a fixed-bed reactor at 400 °C [14]. The use of B_2O_3 in both types of biomass decreased the non-water-soluble fraction. The liquid products obtained using B_2O_3 had higher yields for EFB but lower yields for OPF compared to the yields from the thermal runs.

Turkey contains the largest boron reserves in the world. In this study, we attempted to use a natural calcium borate mineral, which has two main components (B_2O_3 and CaO), as a catalyst in the hydrothermal processing of biomass. The effect of colemanite on

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Abbreviations: EFB, empty palm oil fruit bunch; OPF, oil palm fronds; LBO, light bio-oil; HBO, heavy bio-oil; SR, solid residue; TBO, total bio-oil; SEM, scanning electron microscope; XRD, x-ray diffraction; BET, brunauer emmett and teller; HHV, higher heating value; GC–MS, gas chromatograph–mass spectrometer; HP-5MS, hewlett packard 5-mass.

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http://dx.doi.org/10.1016/j.supflu.2012.08.016

both the product distribution and bio-oil compositions were investigated at different temperatures (250, 300 and 350 °C).

2. Experimental

2.1. Feedstock and additive

Beech wood (the bole of the tree) was used in the hydrothermal liquefaction experiments. The proximate analysis of the beech wood biomass is 9.2 wt% moisture, 0.45 wt% ash, and 87.12 wt% volatile matter. The component analyses of the beech wood were performed using a previously reported method [15]. The composition of the beech wood is 22.25 wt% lignin, 45.05 wt% cellulose, 31.5 wt% hemicellulose, and 0.75 wt% extractives. Ground colemanite was obtained from Eti Mine Works, Turkey. The colemanite had a particle size of 75 μm for 90% of the material by weight. The BET surface area of colemanite is 4.32 m^2/g.

2.2. Hydrothermal liquefaction procedure

In brief, 10 g of biomass and 100 mL of water were placed in an autoclave (Parr 4848; 500 mL capacity and a maximum temperature and pressure of 500 °C and 35 MPa, respectively). The autoclave was heated to the desired temperature (250, 300 or 350 °C) for a residence time of 0 min. In the catalytic runs, the experiments were conducted with 10 g of biomass, 100 mL of water and 1 g of the colemanite catalyst. After the temperature reached the desired levels, the heating was halted (refer to 0 min residence time) and the reactor was cooled to room temperature. The corresponding pressures at 250, 300 and 350 °C are 4.0, 8.5, and 16.5 MPa, respectively, which are the maximum pressures during the hydrothermal processing. The hydrothermal liquefaction experiments were repeated three times, yielding average standard deviations of ±0.5, ±1.2 and ±1.5 wt% for LBO, HBO and SR, respectively. The experimental details for the hydrothermal liquefaction and the experimental set-up are available in the literature [16].

2.3. Separation and extraction procedures

Following hydrothermal liquefaction, the solid and liquid products were rinsed with 100 mL of water and the pH of the slurry was adjusted to 1–2 by adding HCl (1 M). Vacuum filtration was applied to separate the liquid and solid products. The liquid portion was extracted with an equal (300 mL) amount of diethyl ether. The resulting solution was dried over anhydrous sodium sulfate, filtered and evaporated in a rotary evaporator. The evaporation process for the ether removal was performed at the room temperature until the solution became viscous. During long evaporation processes, compounds with low boiling points might become volatile. Upon the removal of the diethyl ether, the remaining portion was quantified as LBO. The solid products remaining on the filter paper and the autoclave were washed several times with 250 mL of acetone. The acetone removal was performed in a rotary evaporator at 70 °C. After the acetone was removed, the remaining substance was quantified as HBO. The TBO is the sum of the LBO and HBO. The remaining SR products from filter paper was dried at 105 °C and quantified. A flow chart for the separation and extraction of the products can be found elsewhere in the literature [16].

2.4. Analysis

The LBOs and HBOs were analyzed using gas chromatography–mass spectrometry (30 m × 0.25 mm i.d., phenyl methyl siloxane capillary column (HP-5MS) with 0.25 mm film thickness, Agilent 6890 gas chromatograph). LBO temperature program: 40 °C (hold for 10 min) → 170 °C (3 °C/min, hold for 6 min) → 250 °C (5 °C/min, hold for 10 min) → 300 °C (15 °C/min, hold for 10 min). HBO temperature program: 40 °C (hold for 10 min) → 170 °C (3 °C/min, hold for 5 min) → 250 °C (4 °C/min, hold for 10 min) → 300 °C (12 °C/min, hold for 10 min).

Table 1
Colemanite components.

Components	wt%
B_2O_3	40.35
CaO	27.25
SiO_2	5.5
SO_4	0.20
Fe_2O_3	0.06
Al_2O_3	0.40
MgO	1.96
SrO	1.87
Na_2O	0.20
H_2O[a]	22.21

[a] Crystallization water.

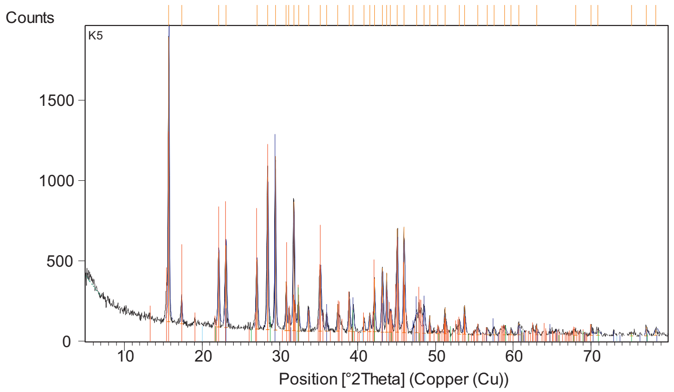
The carbon (C) and hydrogen (H) contents in the raw material, bio-oil, and solid residue were determined by elemental analysis using a LECO CHNS 932 elemental analyzer. Each analysis was repeated twice, and the means of these two measurements are reported. The higher heating values of the biomass and bio-chars were calculated according to the Dulong formula.

The SEM analysis for SRs was performed using a microscope (Philips Model XL-30). XRD diffractograms were recorded at ambient atmosphere on a Philips X'Pert Pro using Cu Kα radiation. The BET surface area was measured by nitrogen adsorption at 77 K using a Micromeritics Gemini V instrument.

3. Results and discussion

Table 1 shows the colemanite components, which are primarily B_2O_3 and CaO. The XRD pattern of the colemanite is shown in Fig. 1.

Fig. 2 shows the yields of the hydrothermal liquefaction products with and without colemanite at 250, 300 and 350 °C. The decomposition temperature for each biomass component is different: 220 °C for hemicellulose, 200 to 500 °C for lignin, and approximately 280 °C for cellulose [17]. To assess the



Visible	Ref. Code	Compound Name	Chemical Formula
*	01-072-1264	Colemanite	$CaB_3O_4(OH)_3H_2O$
*	01-086-0174	Calcite, syn	$CaCO_3$
*	01-071-0262	Calcium silicide	$CaSi_2$

Fig. 1. XRD pattern of colemanite.