Fuel 162 (2015) 74–83

Contents lists available at ScienceDirect

Fuel

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

Hydrothermal liquefaction of woody biomass in hot-compressed water: Catalyst screening and comprehensive characterization of bio-crude oils

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HIGHLIGHTS

- Catalyst screening was done for HTL of biomass in hot-compressed water.
- Bio-crude oil products were comprehensively characterized.
- Composition of the oils highly depends on catalyst type.
- The maximum oil yield of ~40 wt% was obtained with KOH catalyst.
- HT & KOH catalysts promoted formation of phenol derivatives and aliphatic compounds.

ARTICLE INFO

Article history:
Received 7 April 2015
Received in revised form 20 August 2015
Accepted 21 August 2015
Available online 4 September 2015

Keywords:
Biomass
Hydrothermal liquefaction
Catalyst screening
Bio-crude oil
Characterization

ABSTRACT

Hydrothermal liquefaction of woody biomass (birchwood sawdust) with and without catalyst was investigated at 300 °C for 30 min. The activities of KOH, $FeSO_4{\cdot}7H_2O$, K_2CO_3, MgO, synthetic hydrotalcite (HT), and ground colemanite (calcium borate mineral) as catalysts were compared. The alkaline catalysts (KOH, K_2CO_3 and colemanite) showed the best performance considering the oil yield and solid residue yield. The bio-crude oil yield with KOH was increased to around 40 wt%, more than double the yield of the uncatalyzed operation (~18 wt%). It also reduced the solid residue yield from approx. 33 to 12 wt%. Among all catalysts tested, the least active catalysts for bio-crude oil production are $FeSO_4$ and MgO. The bio-crude oil products were comprehensively characterized using an elemental analyzer, GC–MS, FT-IR, GPC and TGA. Occurrence of phenol derivatives (mainly 2-methoxy-phenol) and aliphatic compounds increased significantly in presence of catalysts, especially the alkaline ones such as HT and KOH. The GPC results indicate that the oils produced in the presence of catalysts have very similar molecular weights and distribution, which are slightly greater than the oil produced in absence of any catalyst, suggesting that the presence of a catalyst promoted certain condensation/polymerization of the reaction intermediates during the HTL process. The TGA results show that all bio-crude oils are similar with respect to thermal stability, irrespective of the presence or type of catalyst.

1. Introduction

The declining fossil fuel reserves and increasing concerns over greenhouse gas emissions and climate change have led to a worldwide interest in seeking alternatives to fossil resources for energy and chemical production. Biomass is a sustainable alternative to fossil fuels for fuels and chemicals due to its abundance and renewability [1–3]. However, biomass has a low energy density based on either volume or mass, e.g., its high heating value (HHV) (dry basis) is only 15–20 MJ/kg. Thus, a proper conversion method is required to densify biomass into gaseous or liquid biofuels. Hydrothermal liquefaction (HTL) is one of the promising techniques for conversion of biomass into bio-fuels. This process operates at high pressure (5–20 MPa) and high temperature (<400 °C) and uses water as solvent, mostly in subcritical or near critical conditions ($T < 374$ °C and $P < 22.1$ MPa) [4–6]. Water at elevated temperature and pressure (i.e., hot-compressed water) has remarkable properties. The dielectric constant of water affecting its polarity decreases significantly compared to ambient water. This increases the solubility of hydrophobic organic materials such as free fatty acids, which are normally more soluble in non-polar solvents [7,8]. Furthermore, the ionic product of water at hot-compressed conditions increases, which releases more H^+ and

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http://dx.doi.org/10.1016/j.fuel.2015.08.055
0016-2361/

OH^- in water promoting the acid or base-catalyzed reactions such as hydrolysis of cellulose, hemi-cellulose and lignin [7]. These characteristics of subcritical water play important roles in hydrothermal liquefaction of biomass.

Biomass in HTL is mostly converted to bio-crude oil, water-soluble product (WSP), bio char, and non-condensable gases. The characteristics and yields of the products highly depend on HTL operating conditions such as type of biomass, biomass to water ratio, temperature, pressure, residence time, process gas, and presence or absence of catalyst.

It has been widely demonstrated in many studies that use of a catalyst in HTL of biomass could effectively promote liquefaction efficiency leading to higher biomass conversion and bio-crude oil yields as well as improved oil quality (heating values) [9–12]. Different kinds of homogeneous and heterogeneous catalysts have been employed in hydrothermal liquefaction process, but the most common catalysts used are alkaline solutions, e.g. Na_2CO_3, NaOH, K_2CO_3, KOH, LiOH, RbOH, and CsOH [1,2,13]. Karagoz et al. studied the effect of using K_2CO_3 as an alkaline homogeneous catalyst in hydrothermal liquefaction of pinewood sawdust in a 200 mL autoclave reactor at 280 °C and 15 min residence time [9]. The bio-crude oil yield without catalyst was reported to be as low as 8.6 wt%, while by using 0.94 M of K_2CO_3 solution the bio-crude oil yield increased to 33.7 wt%. Zou et al. studied the effect of Na_2CO_3 on HTL of microalgae, where the biomass conversion and bio-crude oil yield were found to increase with increasing the catalyst dosage [14]. A few acid catalysts have also been tested for direct liquefaction of biomass. Ross et al. studied the effect of different organic acid and alkali catalysts on HTL of microalgae in a 75 mL batch reactor, and concluded that the catalytic activities for bio-crude yields follow the order of $HCOOH < KOH < CH_3COOH < Na_2CO_3$. The highest bio-crude oil yield was 27.3 wt% at 350 °C and 1 h residence time [10]. Although homogenous catalysts are commonly believed to be more active than heterogeneous ones, some researchers obtained good liquefaction yields with heterogeneous catalysts as well [15]. In a previous work from our research group, the effects of both homogeneous and heterogeneous catalysts (i.e., formic acid (HCO_2H), KOH, and FeS) on HTL of mixtures of secondary pulp/paper mill sludge and waste newspaper were studied. In terms of oil yield, the catalytic activity followed the order of $FeS > KOH > HCO_2H$, while in terms of biomass conversion, the order was $KOH > FeS > HCO_2H$. The highest oil yield obtained was 29.9 wt% with FeS catalyst at 300 °C and 2 MPa initial pressure of nitrogen, and 20 min reaction time [16]. In another study by the authors' group, a novel iron ore catalyst (heterogeneous catalyst) was demonstrated to be very effective for liquefactions of peat in supercritical water [1].

Most of the research in the field of biomass HTL is focused on finding the optimum operating conditions such as temperature, residence time, and substrate concentration for maximizing bio-crude oil yield and suppressing char formation. Although different catalysts have been tested in different studies, the results are not comparable due to differences in operating conditions and feedstocks. Earlier, some catalyst screening researches were conducted on different kinds of biomass. Wang et al. studied the effect of various supercritical solvents and different alkali salts and acidic zeolites as catalysts on liquefaction of pinewood sawdust at 300 °C for 2 h and concluded that the highest bio-crude oil yield (30.8 wt%) and lowest solid residue yield (28.9 wt%) were obtained using supercritical ethanol and K_2CO_3 catalyst [13]. However, more comprehensive catalyst screening studies are needed for HTL of woody biomass.

The objective of present study is thus to screen the activities of different homogeneous and heterogeneous catalysts for hydrothermal liquefaction of birch wood sawdust at 300 °C for 30 min. These conditions are chosen based on many literature studies on hydrothermal liquefaction of woody biomass [17–21]. Effects of 5 wt% KOH, $FeSO_4·7H_2O$, K_2CO_3, MgO, synthetic hydrotalcite (HT), and ground colemanite (calcium borate mineral) as well as a combination of a heterogeneous and homogeneous catalyst (HT/KOH) were studied. To the best of our knowledge, no work has been reported on HTL of woody biomass with hydrotalcite, or a combination of hydrotalcite and KOH. The aim of this work is to understand the role of catalysts and compare their effects on products distribution and yields, oil compositions and molecular weights, functional groups, boiling points, and thermal stability. Effects of different catalysts on thermal stability characteristics of the oils have not been reported earlier in literature.

2. Materials and methods

2.1. Materials

Birch wood sawdust was supplied from a local lumber mill in London, ON, Canada. The proximate and ultimate analysis results of sawdust sample are given in Table 1. The catalysts used in the experiments were reagent-grade iron (II) sulfate heptahydrate ($FeSO_4·7H_2O$), anhydrous potassium carbonate (K_2CO_3), magnesium oxide (MgO), synthetic hydrotalcite (HT) ($CH_{12}Al_2Mg_6O_{19}·4H_2O$), and potassium hydroxide (KOH), all purchased from Sigma–Aldrich and ground colemanite (calcium borate mineral) ($2CaO·3B_2O_3·5H_2O$) obtained from Etimine USA Inc. A combination of KOH and HT (HT/KOH) was also used as a mixture of homogeneous and heterogeneous catalyst.

Potassium carbonate, potassium hydroxide, colemanite and iron sulfate were used as received. Magnesium oxide was grounded and sieved to particle diameters less than 300 μm. Hydrotalcite was calcined for 4 h at 450 °C with the heating rate of 10 °C/min and was then rehydrated with distilled water to form a soft paste. The paste was dried overnight in an oven at 60 °C and then crushed and sieved to particle diameters less than 300 μm. HT/KOH was prepared by calcination of HT at 450 °C with the heating rate of 10 °C/min for 16 h. It was then mixed with KOH solution in distilled water with the weight ratio HT/K of 9/1 through incipient wetness impregnation method.

ACS reagent-grade acetone, purchased from Caledon Laboratory Chemicals (ON, Canada), was used as the reactor rinsing/washing solvent for product separation.

2.2. Experimental setup

Hydrothermal liquefaction experiments were performed in a 100 mL stirred reactor (Parr 4590 Micro Bench top reactor). The schematic diagram of the reactor is shown in Fig. 1. In a typical run, 4 g biomass and 33 g water as a solvent (equal to 10 wt% solid concentration-considering the moisture of biomass) together with 0.2 g catalyst (or approx. 5 wt% of biomass) were charged into the reactor. The reactor was then sealed and the residual air inside the reactor was removed by N_2 purging-vacuuming for at least five times. Then the reactor was pressurized to 2 MPa using nitrogen and then heated with stirring to the desired temperature (300 °C). Due to the water vapor pressure, the reactor pressure increased as the temperature was raised to the reaction temperature. The average pressure inside the reactor during reaction was 90 bar. Fig. 2 shows typical temperature and pressure profiles from a typical run. As soon as the reactor reached the reaction temperature, it was maintained at that temperature for 30 min. Then the reaction was stopped by quenching the reactor in a water/ice bath. 2–3 replicate runs were conducted for all the experiments and the reported results are the mean values. The relative errors in all runs were mainly within ±4%.