Fuel 130 (2014) 135–141

Contents lists available at ScienceDirect

Fuel

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

Partial oxidative pyrolysis of acid infused red oak using a fluidized bed reactor to produce sugar rich bio-oil

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HIGHLIGHTS

- Partial oxidative pyrolysis of acid infused red oak was conducted.
- Char agglomeration was reduced by 88.9% compared to the control run.
- Sugar yield increased to 20.62 g/100 g biomass for 2.1 vol% oxygen.
- Up to 67% of SF1 bio-oil was hydrolysable sugar.

ARTICLE INFO

Article history:
Received 28 February 2014
Received in revised form 25 March 2014
Accepted 10 April 2014
Available online 26 April 2014

Keywords:
Acid infusion pretreatment
Oxidative pyrolysis
Bio-oil
Agglomeration
Levoglucosan and sugar

ABSTRACT

Acid infusion of lignocellulosic biomass as a pretreatment prior to fast pyrolysis has been shown to significantly increase the yield of sugar in the products. However, under these conditions char formation increases forming large agglomerates that clog the reactor and eventually interrupt operation of the system. In the present study, partial oxidative pyrolysis of acid infused red oak was performed in a fluidized bed reactor at 500 °C with the concentration of oxygen in the sweep gas ranged from 0 to 8.4 vol% in an effort to mitigate char agglomeration. The addition of oxygen reduced char agglomeration by up to 88.9% compared to the control run during pyrolysis ensuring continuous run of the reactor. Moreover, the addition of oxygen increased the total sugar content in the bio-oil to as high as 20.62 g/100 g biomass. Stage fraction 1 (heavy fraction) of bio-oil obtained from oxidative condition contained up to 67% of hydrolyzable sugar and it was less acidic compared to standard pyrolysis.

1. Introduction

Conversion of cellulosic biomass into sugars suitable for fermentation to alcohol fuels has been one of the leading challenges in developing advanced biofuels. Enzymatic hydrolysis of cellulose to sugars has been studied by the recalcitrance of biomass to biological degradation. Sugars can also be produced from fast pyrolysis of biomass. However, the detrimental catalytic effect of naturally occurring alkali and alkaline earth metals (AAEM) found in most biomass must be mitigated prior to pyrolysis in order to increase sugar content in bio-oil. It is known that AAEM strongly catalyzes pyranose ring scission by forming coordinate bonds with the oxygen atoms of vicinal hydroxyl groups of the glucose ring. This leads to homolytic scission of the ring during pyrolysis resulting in the formation of low molecular compounds [1].

Removing AAEM by hot water or diluted acid washing has been found to effectively increase the sugar yield in bio-oil [2–8]. It was also found that the pretreatment conditions, for example the concentration of the acid, temperature and pretreatment time, could influence the yield of levoglucosan in bio-oil when the dilute-acid washed biomass is pyrolyzed [9]. An infusion of small amount of acid into biomass prior to pyrolysis also has been proven to dramatically improve levoglucosan yield in bio-oil [9–11]. According to our previous study [9], this is because AAEM reacts with acid to form thermally stable salts that are less catalytically active during pyrolysis. The addition of optimum concentration of acid was also found to buffer the system to promote the depolymerization of cellulose. Compared to removing AAEM in biomass by acid washing, this method does not produce acidic waste water that has to be neutralized before disposal and also reduces the corrosion issue during the pretreatment process. Therefore, it appeared

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http://dx.doi.org/10.1016/j.fuel.2014.04.044
0016-2361/

to be a more economically-efficient way to produce sugars from biomass based on fast pyrolysis. However, pyrolysis of acid infused biomass in continuous reactors often causes char agglomeration inside the reactor [11]. If the pyrolysis is conducted in fluidized bed reactors, such char agglomerates reduce fluidization of the reactor bed and eventually result in clogging the reactors. Zhou et al. speculated that the agglomeration is possibly related to the formation of viscous liquid intermediates promoted under acidic condition [11].

On the other hand, although fast pyrolysis is conducted in the absence of oxygen due to high reactivity of oxygen for cracking, carefully controlled partial-oxidative pyrolysis could be beneficial to the selective depolymerization of biomass [12–14]. Recently, we found that introducing a small amount of oxygen during fast pyrolysis of biomass in a fluidized reactor improved sugar production when the oxygen concentration was carefully controlled [14]. The addition of the controlled amount of oxygen also promoted the depolymerization of lignin to smaller compounds and reduced the formation of phenolic oligomers. It was also found that the surface area of biochar greatly increased even when a very low concentration of oxygen was present, suggesting many micropores are created inside of biomass. It is possible that the increased diffusivity through the pores facilitates the volatiles escaping from biomass matrix. Therefore, we hypothesize that partial oxidative pyrolysis of acid infused biomass possibly mitigates the issue with char agglomeration occurring during non-oxidative pyrolysis. The hypothesis is tested in the present study by conducting partial oxidative pyrolysis of acid infused red oak in a fluidized bed reactor with varied oxygen concentrations in the sweep gas. To our best knowledge, this is the first time acid-infused biomass has been pyrolyzed under partial-oxidative conditions for increasing sugar in bio-oil.

2. Methods and materials

2.1. Feedstock

Red oak *(Quercus rubra)* wood chips obtained from Wood Residuals Solutions (Montello, WI) were ground and sieved to a constant size (250–400 μm). Sulfuric acid (H_2SO_4, Fisher Scientific, ACS Plus, purity: 96.6%) was then infused to the red oak with concentration of 0.004 g H_2SO_4/g dry red oak. Our previous study showed that this level of acid infusion produced the maximum yield of levoglucosan during pyrolysis [9]. Briefly, 4 g of H_2SO_4 was dissolved in 3 L of deionized water and mixed with 1 kg of red oak. After stirring for 2 h, the damp biomass was dried in an oven at 40 °C until the biomass appeared uniformly dry at 6–10% moisture. Actual moisture content of the infused red oak was measured before the pyrolysis experiments. Ultimate and proximate analyses of the feedstock are presented in Table 1.

Table 1
Ultimate and proximate analysis of red oak.

Ultimate analysis (wt.%)	
Carbon	46.39
Hydrogen	5.35
Oxygen[a]	48.15
Nitrogen	0.05
Sulfur	0.06
Proximate analysis (wt.%)	
Moisture content	5.08
Volatiles	86.22
Fixed carbon	8.54
Ash	0.21

[a] Determined by difference.

2.2. Partial oxidative pyrolysis of acid infused red oak

Partial oxidative pyrolysis of acid infused red oak was performed using a laboratory-scale, continuous fluidized bed reactor. The specification and design of the fluidized bed reactor have been described elsewhere [14]. Briefly, this system consisted of a biomass feeder, an injection auger, a stainless steel reactor, two cyclones, an electrostatic precipitator (ESP), and a condenser. All pyrolysis experiments were performed at 500 °C. Pyrolysis experiments performed with acid infused red oak but in the absence of oxygen are referred to as "control" cases throughout the study. For the control case, nitrogen sweep gas was added to the reactor at 8 standard liters per minute (SLPM) and purged through the feed system at 2 SLPM leading to a total flow rate of 10 SLPM. For the oxidative pyrolysis experiments, oxygen was added to the reactor in amounts between 1 and 4 SLPM while maintaining the total flow rate of sweep gas at 10 SLPM. Thus, the inlet concentrations of oxygen in the sweep gas ranged from 0 to 8.4 vol%, which corresponded to 0–54% of stoichiometric oxygen for combustion of the biomass feed. The bio-oil recovery system consisted of two stages with the heavy ends collected in an ESP and the light ends collected in a condenser [14]. The resulting bio-oil fractions are referred to as SF1 (stage fraction 1) and SF2 (stage fraction 2), respectively.

2.3. Characterization of reaction products

The yields of SF1 and SF2 bio-oils were determined by weighting the condensers and the bio-oil collection bottles. The yield of char agglomerates was measured gravimetrically by measuring the difference of the weights of the sand and the agglomerates collected from the reactor after each test. The composition of non-condensable gases (NCG) in the exhaust stream was measured with a micro-GC (Varian CP-4900). Before analysis, it was calibrated for nitrogen (N_2), hydrogen (H_2), carbon monoxide (CO), methane (CH_4), carbon dioxide (CO_2), ethylene (C_2H_4), ethane (C_2H_6) and propane (C_3H_8). The yield of NCG was calculated using a drum-type gas meter (Ritter, Germany) and the ideal gas law.

Carbon mass balance of the reaction products was determined using the methods described in following: carbon mass balance of bio-oil and char was calculated by the results of elemental carbon analysis and the yields of bio-oil and char; elemental composition (carbon, hydrogen, nitrogen and oxygen) of bio-oil and char was measured using an elemental analyzer (Elementar, vario MICRO cube); the char agglomerates were grounded to powder prior to the elemental analysis to exclude the fluidizing sand that agglomerated with char; carbon mass balance of NCG was calculated by the yields of NCG and their molecular formulas.

Water content of bio-oil was measured using a Karl-Fischer Titrator (KEM, MKS-500) with a Hydranal-composite 5 K solution. The acidity of bio-oil was determined through modified acid number (MAN) with titrator (Metrohm, 798 MPT Titrino) using N,N-dimethylformamide and methanol as reagents. MAN value was expressed as mg KOH/g of bio-oil.

The volatile content of bio-oil was determined with a Varian CP-3800 gas chromatograph (GC) equipped with flame ionization detector (FID). The column coupled with GC was a Phenomenez ZB-1701 (60 m × 0.25 mm × 0.25 μm). Methanol solution containing approximately 10 wt.% of bio-oil was prepared to quantify the compounds of interest. A 1 μL-aliquot of the bio-oil/methanol solution was injected into the GC system. Injection temperature was set at 275 °C with a split ratio of 20:1. The GC oven temperature was programmed from 35 °C (3 min hold) to 280 °C at a ramp of 3 °C/min, with a final hold time of 4 min. In this work, nine carbohydrates derivatives and fifteen lignin derivatives were quantified