



The effect of low-concentration oxygen in sweep gas during pyrolysis of red oak using a fluidized bed reactor



Kwang Ho Kim^{a,c}, Xianglan Bai^{b,c,*}, Marjorie Rover^c, Robert C. Brown^{b,c}

^a Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA 50011, USA

^b Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, USA

^c Center for Sustainable Environmental Technologies, Iowa State University, Ames, IA 50011, USA

HIGHLIGHTS

- Red oak was fast pyrolyzed with the addition of low concentrations of oxygen.
- The bio-oil yield was not affected by the presence of oxygen in the applied concentration.
- A small amount of oxygen (0.525–1.05%) improved the yield of sugars.
- The yield of total monomeric phenols also increased over this oxygen range.
- The decrease in carbon balance of bio-oil was insignificant in the oxygen range.

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ABSTRACT

Partial oxidative pyrolysis of red oak was studied in a laboratory-scale, continuous fluidized bed reactor. The concentration of oxygen in sweep gas was between 0.525% and 8.40% (v/v), corresponding to equivalence ratios of 0.034–0.539. The influence of oxygen on the distribution and properties of pyrolysis products was investigated using various analytical methods, including GC–MS/FID, IC, HPLC and FT-IR. It was found that total bio-oil yield was not affected by varying oxygen concentration (61.2–64.8 g/100 g biomass) although the water content of the bio-oil increased. The elemental carbon content of bio-oil and biochar decreased with increasing oxygen concentration, being converted to non-condensable gases mainly CO and CO₂. As expected, the presence of high concentration of oxygen in the sweep gas stream had detrimental effects on the pyrolysis products, including increase in water and oxygen content. However, the results also revealed that a small amount of oxygen in the sweep gas (0.525–1.05%, v/v) improved the yield of hydrolyzable sugars and total yield of phenolic monomers. The bio-oil produced under oxidative pyrolysis also contained less acid and pyrolytic lignin. Oxygen increased the surface area of biochar. The results of this study suggest that carefully controlled partial oxidative pyrolysis can improve the quality of bio-oil from fast pyrolysis, increasing the content of sugars and phenolic monomers.

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1. Introduction

Biomass resources present opportunities to produce liquid fuels and chemicals as alternatives to petroleum-based products [1]. As a carbon-neutral renewable source, biomass presents a promising approach to sustainable energy production. Among several thermochemical biomass conversion technologies, fast pyrolysis is attractive because it can transform a variety of recalcitrant biomass

feedstocks into liquid fuels and other value-added products. Bio-oil produced from fast pyrolysis of biomass can be used directly as an energy source or it can be further upgraded into a higher quality fuel. For example, bio-oil can substitute for fuel oil in many applications, including boilers, furnaces, engines and turbines for electricity generation [2,3]. Bio-oil has also been studied for production of hydrogen [4] and platform chemicals, including BTX (benzene, toluene and xylene) by catalytic upgrading [5,6]. Fast pyrolysis produces gas, liquid and char as final products in different proportions. While it is well known that product distribution mainly depends on pyrolysis temperature and residence time [7], other experimental parameters also can influence the outcome of

* Corresponding author. Address: Iowa State University, 2070 Black Engineering Building, Ames, IA 50011, USA. Tel.: +1 515 294 6886; fax: +1 515 294 3261.

E-mail address: bxl9801@iastate.edu (X. Bai).

pyrolysis. Although fast pyrolysis of biomass is usually operated in an inert environment, several studies have investigated the effect of reactive gases on product distribution and properties of bio-oil and biochar. Marker et al. [8] studied hydrolysis of biomass using a fluidized bed reactor operated in 14–35 bar of hydrogen to produce gasoline and diesel fuels. Mante et al. [9] investigated the influence of recycling non-condensable gases including CO, CO₂ and H₂ as a part of sweep gas on pyrolysis of biomass and reported increased liquid yield and decreased char/coke yield compared to use of inert sweep gas.

It has been previously reported that oxygen can promote devolatilization reactions during pyrolysis [10–12]. Butt [11], investigating the influence of molecular oxygen during low-temperature (290–295 °C) fast pyrolysis of pine, reported a positive influence on increasing the yield of monomeric phenols. However, the total yield of phenolic monomers was very low (0.02–0.64%) due to the low pyrolysis temperatures where lignin only partly depolymerizes. Amutio et al. [13] used oxygen to achieve autothermal operation of a conical spouted bed pyrolyzer but found it decreased the yield of organic compounds in the bio-oil by 6%. Previous studies of oxidative pyrolysis used thermogravimetric analyzers to simulate fast pyrolysis and employed relatively high concentrations (approximately 5–21 vol%) of oxygen in the sweep gas [10,14–16]. Oxygen is usually excluded from pyrolyzers to the extent practical to prevent oxidation of biomass and pyrolysis products and formation of light gases and water. However, achieving a fully inert environment is difficult in continuous pyrolyzers because the void space in bulk biomass contains air. Thus, understanding the effect of oxygen on pyrolysis of biomass is important in predicting product yields. In order to better understand the effects of low concentrations of oxygen in the sweep gas of biomass pyrolyzers, we introduced a relatively small amount of oxygen to a laboratory-scale fluidized bed pyrolyzer. The influence of molecular oxygen on the distribution, compositions and properties of the resulting pyrolysis products was assessed in detail.

2. Materials and methods

2.1. Feedstock

Northern red oak (*Quercus Rubra*) used in this study was obtained from Wood Residuals Solutions (Montello, WI). Bark-free chips were ground and sieved to a constant size (250–400 μm) and then air dried to around 7–8 wt.% moisture content. Ultimate and proximate analyses of the red oak are presented in Table 1.

2.2. Pyrolysis

Fast pyrolysis of red oak was performed using a laboratory-scale, continuous fluidized bed reactor. A schematic diagram of the reactor is shown in Fig. 1. The reactor consisted of a feeder,

an injection auger, and a stainless steel reactor 0.34 m in height and 38.1 mm in diameter. The plenum, which was designed to pre-heat nitrogen sweep gas and provide a uniform supply of nitrogen through the porous distributor plate, was 0.17 m in height with an inner diameter of 38.1 mm. Silica sand with average diameter of 520 μm was used as a heat carrier. The feed rate of biomass was 100 g/h. For the control run, nitrogen sweep gas was introduced into the plenum 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. All pyrolysis experiments were performed at 500 °C. The calculated vapor residence time in the reactor was estimated to be 1.2 s. The concentration of oxygen molecules in void space of red oak feedstock carried in the reactor was approximately 0.1% of sweep gas in the control run.

For oxidative pyrolysis tests, oxygen was admitted to the plenum in the amount of 0.5–4 SLPM while maintaining total flow rate of sweep gas (nitrogen and oxygen) at 10 SLPM. Thus, the inlet concentration of oxygen ranged from 0 to 8.40 vol%, which corresponded to 3.4–53.9% of stoichiometric oxygen for combustion of the biomass feed. Since oxygen participates in the pyrolysis reactions, mass yields are reported on the basis of biomass processed (g/100 g biomass) instead of percentages to avoid any confusion when yields exceed 100%.

The effluent from the reactor passed through two cyclones in series to remove char and ash particles. The bio-oil recovery system consisted of two stages with heavy ends collected in an electrostatic precipitator (ESP) and the light ends collected in a condenser, the resulting bio-oil fractions referred to as SF1 (stage fraction 1) and SF2 (stage fraction 2), respectively. Liquid nitrogen was sprayed into the pyrolysis vapor stream just ahead of the ESP, which collected the aerosols formed from the heavy ends. The remaining pyrolysis vapor passed into a tubular heat exchanger where it was chilled to –10 °C causing water and light oxygenates to condense as an aqueous phase.

The yield of char was determined by weighing the particulate matter captured by the cyclones. The yield of bio-oil was determined by weighing the bio-oil recovery system before and after a run, which accounted for bio-oil that remained inside pipes and vessels. The composition of non-condensable gases (NCG) in the exhaust stream was measured with a micro-GC (Varian CP-4900) calibrated for nitrogen (N₂), hydrogen (H₂), carbon monoxide (CO), methane (CH₄), carbon dioxide (CO₂), ethylene (C₂H₄), ethane (C₂H₆), propane (C₃H₈). The yield of NCG was calculated using a drum-type gas meter (Ritter, Germany) and the ideal gas law.

2.3. Characterization of pyrolysis products

Several analytical methods were adopted to characterize the bio-oil. CHN elemental analysis of the bio-oil and biochar was performed using an elemental analyzer (Elementar, vario MICRO cube) with oxygen content determined by difference. The higher heating value (HHV) of bio-oil and biochar was determined theoretically using an equation developed by Demirbas based on elemental compositions [17]. Water content in bio-oil was measured using a Karl-Fischer Titrator (KEM, MKS-500) with Hydranal-composite 5 K solution. The acidity of bio-oil was determined as modified acid number (MAN) with titrator (Metrohm, 798 MPT Titrino) using N,N-dimethylformamide and methanol as solvents [18]. MAN value was expressed as mg KOH/g of bio-oil.

Identification and quantification of chemical compounds in bio-oil were performed using a Varian CP-3800 gas chromatography equipped with Saturn 2200 mass spectrometry and mass spectrometry (MS)/flame ionization detector (FID). Bio-oil sample was first analyzed using GC/MS to identify its composition. The chemicals identified by GC/MS were calibrated in GC/FID using authentic compounds. The bio-oil was then analyzed with GC/FID for

Table 1
Ultimate and proximate analysis of red oak.

<i>Ultimate analysis (wt.%)</i>	
Carbon	46.13
Hydrogen	6.38
Oxygen ^a	47.34
Nitrogen	0.15
<i>Proximate analysis (wt.%)</i>	
Moisture content	7.74
Volatiles	80.39
Fixed carbon	11.46
Ash	0.64

^a Determined by difference.

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