Biomass and Bioenergy 81 (2015) 256–264

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

# Manipulation of chemical species in bio-oil using *in situ* catalytic fast pyrolysis in both a bench-scale fluidized bed pyrolyzer and micropyrolyzer

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ARTICLE INFO

*Article history:*
Received 13 April 2015
Received in revised form
8 July 2015
Accepted 14 July 2015
Available online 20 July 2015

*Keywords:*
Catalytic fast pyrolysis
Chemical composition
Bio-oil
Micropyrolyzer

ABSTRACT

*In situ* catalytic fast pyrolysis (CFP) of biomass was conducted with base or acid catalysts in a bench-scale fluidized bed pyrolyzer. Complete mass balances were performed, allowing for quantitatively investigating the catalytic impacts on the final bio-oil composition. Acidic catalysts exhibited relatively higher activities for decomposition of sugar and pyrolytic lignin, dehydration, decarbonylation, and coke formation, as relative to base catalysts. Carbon balances revealed that a significant amount of carbon in bio-oil was transformed to coke during CFP. Due to the decrease in the bio-oil yield during CFP, significantly less energy was recovered in CFP products than in control fast pyrolysis products. CFP was also performed in micropyrolyzer and the results were compared with those in the bench-scale reactor to determine the consistency across the experimental systems. Different from the bench-scale pyrolyzer, the basic catalyst more strongly influenced the micropyrolyzer products and the discrepancies suggest a more rapid deactivation of the basic catalyst.

## 1. Introduction

Thermochemical conversion of lignocellulosic biomass via pyrolysis continues to attract attention as a potential pathway to renewable transportation fuels and chemicals. Biomass fast pyrolysis is defined as rapid thermal degradation of lignocelluloses in the absence of oxygen to primarily generate liquid bio-oil with a lesser amount of non-condensable gases and solid char [1]. Bio-oil is a complex mixture of over 300 oxygenated organic compounds [2], which can be broadly classified into anhydrosugars, phenolics, furan/pyran derivatives, and C2 to C4 low molecular weight compounds. Due to an abundance of oxygenated compounds, bio-oil has an oxygen content level, typically 35–40 wt%, which is similar to that of the biomass feedstock. This oxygen content generally precludes bio-oil from being directly utilized for fuels or other products and imparts a lower heating value for the bio-oil and higher reactivity during storage. Thus, for bio-oil to be used in fuel or chemical applications, oxygen elimination is necessary. Significant work has been performed on bio-oil deoxygenation after condensation of the pyrolysis vapors. Additionally, deoxygenation of pyrolysis vapors, either *in situ* or *ex situ* processing has been examined. During *in situ* upgrading processes, the pyrolysis vapors are immediately contacted with catalytic material in the pyrolysis reactor, whereas in *ex situ* processing the pyrolysis vapors undergo catalytic reactions in a downstream reactor.

Significant attention has been paid to zeolites and zeolite-like materials for biomass catalytic pyrolysis. Highly acidic zeolites have proven to be quite effective in reducing oxygen levels in bio-oil; however, the deoxygenation is accompanied by a large decrease in the amount of bio-oil produced and by increases in aromatic hydrocarbons and coke. Williams et al. performed catalytic fast pyrolysis of rice husks with a ZSM-5 in a fixed bed reactor, and reported that the oxygen removal down to 8.1 wt% relative to 37.7 wt% for the non-catalytic pyrolysis was achieved by dehydration, decarboxylation and decarbonylation, although it was accompanied with a large sacrifice of the organics from 37.0 wt% to 3.8 wt% [3]. They also found that not only mono-hydrocarbons but

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http://dx.doi.org/10.1016/j.biombioe.2015.07.017

also polycyclic aromatics hydrocarbon (PAH), known to be carcinogenic [4,5], were produced. Carlson et al. claimed that catalytic pyrolysis of carbohydrates with ZSM-5 generated more than 30 wt% (based on carbon yield) of aromatic hydrocarbons; however, a large amount of PAH (over 50% PAH selectivity) including naphthalene and indene, were also generated [6,7]. Severe coke formation on the catalyst was also observed when using zeolites for upgrading pyrolysis vapors. Over 35 wt% of the feedstock carbon ended up in the form of coke on ZSM-5, resulting in bio-oil carbon loss as well as rapid catalyst deactivation. To reduce coke deposition while maintaining a high deoxygenation level, researchers have tested mesoporous zeolite-like materials such as Al-MCM-41, MCM-41, SBA-15, and MSU-3 for catalytic pyrolysis [8–10]. However, the coke yields were at best only slightly lower than the base zeolite case.

Relatively fewer studies have been conducted on metal oxides for biomass catalytic pyrolysis, although the materials have been used in many catalytic processes due to their unique properties [11]. Lu et al. performed catalytic pyrolysis with 6 different metal oxides in a Pyroprobe-GC/MS, and reported that calcium oxide (CaO) significantly reduced anhydrosugars and removed organic acids with increases in phenol and cyclopentanones, while magnesium oxide (MgO) reduced levoglucosan slightly and increased linear aldehydes [12]. More recently, Lin et al. performed catalytic pyrolysis with CaO in a fluidized bed reactor, and reported a reduction in oxygen levels in bio-oil from 39 wt% to 31 wt%, resulting from a large decrease in compounds having high oxygen content such as levoglucosan, formic acid and acetic acid [13]. Instead, the amount of furanic compounds, which contain lower oxygen content, increased.

Although acid and base catalysts have been used for biomass catalytic pyrolysis by researchers, there has not been a systematic evaluation of the impact of acidity or basicity on the final bio-oil composition. More importantly, complete mass balances on all of products generated during pyrolysis were not been performed in previous studies, thereby limiting the insight that can be gained. Hence, in the current study complete product speciation analysis of bio-oil from catalytic experiments was performed by integrated use of GC, HPLC, IC, elemental analyzer and Karl Fischer, and the composition results were compared with that for non-catalytic fast pyrolysis, to quantitatively demonstrate the catalytic effects on the bio-oil chemical composition. Pyrolysis of a feedstock pretreated with $H_2SO_4$ was also conducted to explore the impact of this treatment on the resulting bio-oil quality. This study also investigates how much carbon is lost during catalytic pyrolysis by completing the carbon balance, which commonly has been neglected. By considering the bio-oil yield as well as its higher heating value (HHV), we were able to compare the total energy recovered from the feedstock in the bio-oil product for each pyrolysis experiment. In addition to the bench-scale fluidized bed pyrolyzer, catalytic pyrolysis was conducted in micropyrolyzer, to determine whether catalytic performance under micropyrolysis conditions can be used to project results to the bench-scale fluidized bed reactor.

## 2. Material and methods

### 2.1. Materials

Red oak was ground and sieved to 250–500 μm and was used as the feedstock for all of the pyrolysis experiments. For the catalytic experiments, four different catalysts were used: MgO (Sigma–Aldrich), MgO synthesized from $MgCO_3$ (Sigma–Aldrich), γ-$Al_2O_3$ (Fischer scientific), and silica-alumina (Sigma–Aldrich, $SiO_2$:$Al_2O_3$ ratio of 9.4:1).

#### 2.1.1. Catalyst preparation

Catalysts used in the study could be categorized as acidic or basic with fresh (and regenerated) γ-$Al_2O_3$, and silica-alumina representing acid catalysts, and low surface area MgO (Low MgO) and high surface area MgO (High MgO) representing base catalysts. The catalyst selections were made to investigate how acidity and basicity of the catalysts systematically influenced the composition of the resulting bio-oil. Since the surface area of commercially available MgO (Sigma–Aldrich), 1.2 $m^2/g$, is two orders of magnitude lower than that of the other catalysts, High MgO with a surface area of 161.5 $m^2/g$, was synthesized by calcination of $MgCO_3$ in static air using a ramp of 10 °C/min and hold at 550 °C for 2 h [14].

All catalysts were received in powder form and thus were pelletized, crushed, and sieved into a desired range of 0.4–0.6 mm, to ensure good fluidization for the catalytic pyrolysis experiments. By utilizing the density of each catalyst type, values of $U/U_{mf}$ and $d_{eq}/D$ for the 10 L/min of carrier gas rate were set between 2 and 3 and below 70% [15], respectively, by adjusting the particle size, where U is the superficial velocity at the given flowrate at 500 °C, $U_{mf}$ the minimum velocity for fluidization, $d_{eq}$ the volume-equivalent diameter of a bubble, and D the bed diameter. For the micropyrolyzer experiments, both the feedstock and catalysts (calcined at 520 °C for 1 h) were ground, sieved to 38–90 μm (to avoid transport limitations), and physically mixed prior to pyrolysis.

#### 2.1.2. Catalyst characterization

The acidity/basicity and surface area of the catalytic materials were measured by $NH_3$/$CO_2$-TPD and BET analysis, respectively. For measuring both the density and strength of the acid/base sites, $NH_3$/$CO_2$-TPD was performed using a Micromeritics AutoChem 2920. First, approximately 0.1 g of sample was calcined at 700 °C for 1 h to eliminate impurities, followed by an injection of either $NH_3$ or $CO_2$ into the sample until saturation was achieved. After saturation, the sample was heated at a rate of 10 °C/min to 700 °C, and simultaneously the desorbed $NH_3$ or $CO_2$ was recorded by a thermal conductivity detector (TCD). The desorbed amount of $NH_3$ or $CO_2$ was proportional to the levels of acid/base sites in the sample, respectively. The specific surface areas were measured by nitrogen physisorption (Micromeritics ASAP 2020) and calculated using the Brunauer–Emmett–Teller (BET) method. Approximately 0.1 g of sample was weighed and degassed at 350 °C for 5 h to remove physisorbed species on the surface of the sample. Nitrogen adsorption at relative pressure, $P/P_0$, between 0.05 and 0.25 was used to calculate the BET surface area.

#### 2.1.3. Preparation of acid-infused red oak

Approximately 500 g of red oak in a size range of 250–500 μm was weighed and mixed with sulfuric acid (0.4 wt% of red oak) and distilled water. The mixture was stirred for 20 min followed by drying at 50 °C for 5 days. The resulting moisture content of 5.7 wt %, which was 30% lower than untreated red oak, was determined by proximate analysis. It is likely that the decrease in moisture led to the slight reductions observed for the hydrogen and oxygen content with the treated feedstock.

### 2.2. Pyrolysis experiments

#### 2.2.1. Catalyst activation

Prior to reaction, 100 g of catalyst particles in the pyrolysis reactor were activated at 500 °C for at least 1 h in 10 L/min of nitrogen. After activation, cyclones downstream of the reactor were weighed to determine whether a significant amount of catalyst particles had elutriated at the specific nitrogen flow rate. For the micropyrolyzer, catalysts were activated prior to reaction in a muffle furnace in nitrogen environment at 520 °C for 1 h.