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Formate assisted pyrolysis of pine sawdust for in-situ oxygen removal and stabilization of bio-oil

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HIGHLIGHTS

- Pretreatment of pine with calcium compounds reduced oxygen content in the oil.
- Pretreatment of pine with calcium compounds improved stability of the pyrolysis oil.
- Calcium formate provides an in-situ hydrogen source.
- The process is simple, inexpensive and robust.

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ABSTRACT

Pine sawdust was pretreated with several calcium compounds and then pyrolyzed in a fluidized bed pyrolysis reactor at 500 °C. The catalytic action of the calcium compounds varies depending on the anion. Analysis of pyrolysis gas, liquid and char yields and compositions demonstrates that calcium sulfate is inert during pyrolysis while calcium formate, carbonate, hydroxide and oxide show significant deoxygenation activity. Of the salts which showed deoxygenation activity, calcium formate had the highest relative yield. This effect is likely attributable to the activity of calcium formate as a hydrogen donor at the pyrolysis temperature.

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1. Introduction

Commercial production of renewable transportation fuels and chemicals from lignocellulosic biomass is hindered by both high capital and operating costs. The capital cost stems from small processing scales (relative to petrochemical) which are limited by the high biomass transportation costs. The operating costs reflect the natural resistance of woody biomass to decomposition, and the cost of removing oxygen while maintaining an economical product yield. Biomass pyrolysis has been identified as a process which can overcome the capital cost barrier, but the upgrading of the resulting bio-oil is still difficult and costly because the complex chemical and oxygenated nature of the oil requires a number of reactors, catalysts and significant amounts of hydrogen, while the product yield is relatively low (Hicks, 2011; Kakzeski et al., 2010; Wildschut et al., 2009). To date, the development of catalysts for post-treating bio-oil have been challenged by high coke/char yields and deactivation, due to the highly reactive nature of bio-oil (Mortensen et al., 2011; Zacher et al., 2014).

To reduce the burden of hydrotreating bio-oil from pyrolysis, methods such as catalytic pyrolysis have been demonstrated (Agblevor et al., 2010; Mihalcik et al., 2011). In catalytic pyrolysis, a zeolite catalyst is used during fast pyrolysis to promote cracking reactions that increase the C/O ratio and aromatics concentration (Carlson et al., 2011). Oxygen is removed as CO_2 which reduces the carbon yield, yet does not require external hydrogen. While improvements in bio-oil quality have been reported, challenges such as process yields, catalyst regeneration and catalyst attrition remain. The composition of biomass limits mass yields because of the low H:C ratio of the starting material and the tendency of carbohydrates to undergo dehydration and condensation (coke forming) reactions. The use of hydrogen as a carrier gas during catalytic pyrolysis (catalytic hydropyrolysis) has been shown to improve both the quality and yield of bio-oil by removing oxygen from the biomass as water, increasing the carbon yield in the liquid

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(Marker et al., 2012; Meesuk et al., 2011; Venkatakrishnan et al., 2014).

As an alternative to zeolite-based catalytic pyrolysis, the effects of alkaline earth metal compounds on biomass pyrolysis have been explored by several groups. Wang et al. mixed calcium hydroxide physically with pine at weight loadings up to 22% (Wang et al., 2010). The authors found that the addition of the alkaline earth base slightly increased the overall yield while inhibiting the formation of acids, reducing the amount of sugars formed and increasing ketone and alcohol yields. Work by Lin et al. mixing calcium oxide with loadings of 100–500% on pine also showed an increase in bio-oil yield accompanied by a decrease in oxygen content from 39 to 31 wt% at the highest loading (Lin et al., 2010). Another recent study by Veses and coworkers demonstrated deoxygenation and decrease in acidity of bio-oil when calcium oxide and magnesium oxide were used as catalysts in an auger reactor (Veses et al., 2014). Pyrolysis of magnesium oxide loaded cotton seed was studied by Pütün. The addition of oxide decreased the oxygen content by 50%, but unlike the calcium studies, bio-oil yield decreased with the addition of the alkaline earth metal (Pütün, 2010). The differing results between these studies illustrate the effect of reactor design and feedstock choice, as well as the pre-treatment process.

Recently, a simple and robust modification to the pyrolysis process was reported, which has the potential to reduce the complexity of upgrading the oil and increases process yields compared to catalytic fast pyrolysis. The process, called formate-assisted fast pyrolysis or FAsP, has been demonstrated on lignin (Mukkamala et al., 2012). By pretreating the feedstock with calcium formate, a significantly deoxygenated bio-oil is produced in a single-step, atmospheric fast pyrolysis process.

In the current work, FAsP of pine (*Pinus strobus*) sawdust was compared to conventional pyrolysis and several other calcium pretreatments. For all of the calcium pretreatments (with the exception of calcium sulfate), the oil quality was superior to conventional pine pyrolysis oil, having a significantly lower oxygen content, lower degree of polymerization and increased stability. Because the oil was less oxygenated, less hydrogen would be required for upgrading, thereby reducing the cost and complexity of downstream processing.

2. Methods

2.1. Feedstock preparation

The calcium compounds were incorporated with the pine sawdust by forming a solution/suspension with the salt in deionized water, and then incorporating the dry sawdust. The mass loading of calcium was maintained constant for all experiments at 0.43 g calcium/g sawdust. This loading corresponds to the addition of 146 g calcium sulfate, 140 g calcium formate, 107 g calcium carbonate, 79 g calcium hydroxide and 60 g calcium oxide, respectively, each to 100 g pine sawdust. In all cases, the pretreated pine was oven dried to 5–10% moisture and sieved to achieve particles smaller than 1.5 mm.

2.2. Pyrolysis

The pretreated sawdust was pyrolyzed with 40–60 mesh sand as heat transfer medium in a 3.5 cm × 30 cm entrained flow reactor described in detail elsewhere (DeSisto et al., 2010). The reactor temperature was measured using two K-type thermocouples located on the vertical axis measured 3.0 and 9.5 in. from the top of the reactor. The pine/calcium formate mixture was metered through a screw feeder and pneumatically fed into the reactor, using a nitrogen flow rate of 6 L/min. The feed rate of the pretreated pine was approximately 1 g/min, and up to 1 kg of material could be processed in a run. The pyrolysis temperature was 500 °C. Immediately downstream of the reactor, char was separated using a hot gas filter (HGF) also maintained at 500 °C. The total vapor residence time in the fluidized bed reactor and the HGF was 12 s, with about 90% of that time in the HGF. After the vapor passed through the hot gas filter the liquid was collected in a condenser operated at 6 °C, followed by an electrostatic precipitator (ESP) to collect aerosols. The gas exhaust from the ESP was periodically sampled and analyzed by GC. The exhaust gas flow rate was measured using a dry gas meter. Liquid yield was determined by weighing the condenser and electrostatic precipitator before and after pyrolysis. The char yield was determined by weighing the material collected in the reactor and the char filter, and then subtracting the mass of calcium compounds). The gas yield was measured using a dry gas meter. Each of the experiments was performed in duplicate, at minimum.

2.3. Characterization

2.3.1. Bio-oil characterization

The bio-oil analyses were conducted on oils collected from the electrostatic precipitator to ensure a water-free sample, as water can affect the results obtained from elemental analysis and size exclusion chromatography.

2.3.1.1. Elemental analysis. Carbon, hydrogen and nitrogen analysis of the oil from the electrostatic precipitator was performed using a Thermo Scientific Flash 2000 elemental analyzer, and oxygen was calculated by subtracting the carbon, hydrogen and nitrogen from the total mass. This calculation has previously been compared to measured oxygen content using the same elemental analyzer and the difference method was found to be accurate for calculation of oxygen content for ash-free or low-ash samples.

2.3.1.2. Size exclusion chromatography. Size exclusion chromatography (SEC) was performed using an Shimadzu HPLC-GPC equipped with two columns measuring 0–1 k Daltons and 1–20 k Daltons, respectively, with N,N-dimethylformamide (DMF) as the mobile phase. Due to the relatively low molecular weight of the oils produced with hot gas filtration, a large fraction of the sample elutes at the end of the calibration range with low resolution, making it difficult to quantitatively determine the molecular weight distribution and average molecular weight. Therefore, results from this method were used for comparative purposes only.

2.3.1.3. Quantitative analysis by GC/MS. A Shimadzu Q2010 gas chromatograph-mass spectrometer (GC–MS) was used to characterize the composition of the oils. The samples were diluted with ethyl acetate solvent and prepared by adding butylated hydroxytoluene as a recovery standard and biphenyl as an internal standard. All of the samples were derivatized with N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) for one hour before analysis. Compounds reported were verified by both mass spectral fragmentation pattern and retention time matches to genuine standards.

2.3.2. Char characterization

The solid product (containing char and inorganic compounds from the various calcium pretreatments) was analyzed by thermogravimetric analysis using a TA instruments Q500 TGA with a heating rate of 10 °C/min in a nitrogen environment.

2.3.3. Gas characterization

The pyrolysis exhaust gas was measured using an SRI 8610C portable GC calibrated with a certified mixture of 1% methane,

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