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Impact of combined acid washing and acid impregnation on the pyrolysis of Douglas fir wood

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ABSTRACT

This study reports the impact of acid washing (to remove alkali and alkaline earth metals) followed by mild acid impregnation on the pyrolysis of Douglas fir wood. Dilute nitric acid was used in the washing and sulfuric acid, acetic acid, nitric acid, and phosphoric acid at acid loading levels of 0.05, 0.1, 0.3, and 0.5 wt.% were used for the acid impregnation to improve the yield of levoglucosan. A Py–GC/MS instrument was used to semi-quantitatively measure the impact of various acids and concentrations on the yield of low molecular weight compounds released during pyrolysis at 500 °C. The nitric acid wash removed 56% of the metal content. The results confirmed all the acids studied increased the production of levoglucosan, likely due to the mitigation of undesirable interactions between the cellulose and the other constituents of the lignocellulosic matrix. The highest yields of levoglucosan were achieved with the strong acids: sulfuric acid loading of 0.05 wt.%, nitric acid 0.05 wt.% and phosphoric acid 0.3 wt.%. Sulfuric and phosphoric acid also enhanced dehydration reactions in cellulose products and decreased the production of methoxylated phenolics from lignin. The very small range of concentration at which these acids increase levoglucosan yield makes it very difficult to control the process. In the case of acetic acid, it is not strong enough to catalyze dehydration reactions. Consequently a much wider range of concentrations can be used thus facilitating the control of the process. Acetic acid also does not affect the yield of lignin products. Therefore, acetic acid appears to be the most practical for acid impregnation (following mineral removal) in wood pyrolysis.

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1. Introduction

Pyrolysis is an ancient technology that can convert lignocellulosic materials like wood and straw into char, oil, and gas. Today, pyrolysis is considered one of the few carbon negative processes for producing chemicals and fuel from biological material. Originally used primarily to make low-smoking charcoal for indoor cooking, the processing parameters have been continually tweaked by scientists and engineers throughout the 20th and 21st century to maximize the oil production. Fast pyrolysis is a simple method primarily used for processing lignocellulosic material, such as wood, by which the material is heated to temperatures between 350 and 600 °C in the absence or near absence of oxygen.

Using high heating rates above 1000 °C/s at atmospheric pressure, fast pyrolysis of softwood typically yields a crude bio-oil (~75 wt.%), gases (10–20 wt.%), and char (10–15 wt.%) [1]. Bio-oil is made up of a mixture of water and oxygenated organic compounds which have a variety of industrial and food related uses. Natural lignin in the wood (around 25 wt.% of the material) can typically be converted into monomeric and oligomeric phenols at a 70% efficiency. These compounds have known uses for fuels and fuel additives [2]. However, pyrolysis systems typically only recover 10–20 wt.% of cellulose (which comprises 40–50% of wood) in the form of recoverable sugars, the desired products [3].

It is understood that the first reaction of cellulose during pyrolysis makes mono- and oligo-anhydrosugars (mainly levoglucosan and cellobiosan); however, secondary reactions in the liquid intermediate phase (still on the char) or in the gas phase (while leaving the reactor) convert the sugars into C1–C4 molecules and char through various forms of dehydration reactions followed by fragmentation, elimination, and transglycosylation reactions [4–8]. It is greatly desired to preserve the pyrolytic anhydrosugars, which

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have many known uses for polymer chemistry, pharmaceuticals, fermentation, and food applications [9–14]. Although the levoglucosan can be produced in large yields (60+ wt.%) from the pyrolysis of cellulose [7,15,16], yields of only around 20 wt.% (on cellulose basis) are obtained typically during the pyrolysis of lignocellulosic materials [3].

Secondary reactions are also well-known to affect lignin products, which break down the primary product oligomers (pyrolytic lignin) into monomers [17,18].

In fast pyrolysis, where vapor-phase reactions are minimized by a fast-flowing carrier gas, interactions in the liquid intermediate phase have a large impact on the chemical nature of collectible oils and char [7,19]. One well-understood cause is the catalytic properties of metals naturally present in the lignocellulose matrix. Douglas fir wood, for example, has measurable quantities of Na, K, Mg, Ca, Al, Mn, Co, Ni, Cu, Zn, and Ba. While the total mineral content in most woods is in the 1% range, it can be in the 10% range or higher for straws, grasses, and leaves.

Most interest lies in the alkaline and alkaline earth metals (AAEMs) due to their high abundance relative to other metals. Again and again, researchers find that sodium, potassium, and calcium increase the gas yield (particularly CO_2 and CO), decrease both the yield and molecular weight of the oil, and decrease the surface area of the char [20–25]. The influence of inorganics extends beyond the pyrolysis reactor. Their presence continues to degrade products during storage of pyrolysis oil [26,27]. These metals behave differently: with regards to their impact on pyrolysis by concentration, $K^+ > Na^+ > Li^+ > Ca^{2+} > Mg^{2+}$ [28–30]. Non-metals have a far less significant impact on pyrolysis, but experimentalists take care to compare metals using the same conjugate ions due to varying dissociation strengths, where $PO_4^{3-} \approx CO_3^{2-} > OH^- \approx NO_3^- > Cl^-$ [28].

The impact on the chemical makeup of the oil is best understood by the effects that AAEMs have on each biomass constituent: cellulose, hemicellulose, and lignin. The most significant impact of AAEMs on cellulose pyrolysis is the dramatic reduction of the product levoglucosan [28]. Instead of levoglucosan, enhanced production of polymer, furfural, 5-5-hydroxymethylfurfural, glycoaldehyde, hydroxyacetone, formic acid, CO_2, CO, and CH_4 is observed [25,28,30–33]. Except for cross-linked polymers, these products have lower molecular weights than sugars. Many hypotheses have been presented to explain the impact of AAEMs on cellulose pyrolysis. The current understanding, based on molecular modeling techniques, explains that AAEMs alter the electronic structure of the carbohydrate by interacting with oxygen, affecting the stereochemistry of the molecules during reactions; because of that, rearrangement and dehydration reactions are enhanced, followed by fragmentation reactions [34,35]. It is thought that AAEMs can directly attack the cellulose chain before and during depolymerization reactions as well as catalyze reactions in the liquid intermediate phase [34,36].

Hemicellulose, a carbohydrate polymer with a backbone made up of xylose, arabinose, glucose, galactose, and non-hydrolyzable sugars, is also influenced by metal content during pyrolysis. AAEMs increased production of char CO_2, water, 2-furaldehyde, and acetaldehyde. They did not affect acetic acid production, but they decreased production of dehydrated sugars, formic acid, and acetol [37].

Lignin products are also affected by minerals. It was found that the suppression of AAEMs with sulfuric acid actually reduced the production of methoxylated phenolic products as well as lignin oligomers [38]. Di Blasi et al. found that the addition sodium, potassium, and calcium in wood pyrolysis actually enhanced the production of phenols such as guaiacol, cresol, phenol, and isoeugenol [29,39] and greatly reduced the production of lignin oligomers (pyrolytic lignin) [22].

Fortunately, removal of AAEMs is relatively easy. Acid washing to remove a majority of the metals from lignocellulosic biomass has been shown to double the sugar yield [40,41]. This procedure can dramatically reduce the metal content but has trouble with calcium, which is more tightly bound to the chemical structure of lignocellulose [22,42].

Similarly, adding small amounts of acid to lignocellulosic materials without washing can increase the levoglucosan yield [23,40,43]. In 2012, Kuzhiyil et al. studied the potential effect of infusing switchgrass with various acids to passivate the catalytic effect of alkalines [23]. The authors found that sulfuric acid performed the best. Our group performed a similar study with a 0.05 wt.% sulfuric acid impregnation with Douglas fir in an oxygen-free auger reactor and achieved a 12 wt.% levoglucosan yield [43]. More recently, Kim et al., with red oak with a 0.4 wt.% sulfuric acid impregnation in a partial oxidation fluidized bed reactor, was able to reach a levoglucosan yield close to 20 wt.% [44].

The combination of acid washing and acid impregnation has also been explored. Levoglucosan yields of nearly 26 wt.% from wood (58% on a cellulose basis) were observed in the 1980s with Douglas fir pretreated with organic extraction, acid washing, and a mild acid addition followed by 400 °C pyrolysis at atmospheric pressure. In the same study, a water wash and a mild acid wash followed by 0.1 wt.% acid impregnation gave 14 and 19 wt.% levoglucosan yields, respectively [40,45].

This effect was not observed when these experiments were conducted with cellulose or with holocellulose (cellulose + hemicellulose). The authors explained these results with the hypothesis that this effect is caused by the effect of these acids on cellulose–lignin interactions. The nature of these interactions is still not well understood, but Matsuoka et al. recently proposed the hypothesis that they are associated with hydrogen bonding between the cellulose and lignin structures [46]. Similar experiments conducted by Zhou et al. reached the same conclusions [43,47]. These authors found that there is a concentration of sulfuric acid at which the production of levoglucosan is maximized. Other research comparing acid-washed material with combined pyrolysis of cellulose, hemicellose, and lignin indicate interactions between these constituents that are unique to the wood polymer properties, supporting the hypothesis discussed herein [48].

Table 1 highlights significant examples of acid pretreatment methods to increase levoglucosan yield. Based on our preliminary results and the literature, a combination of acid-wash and acid-impregnation seems to be the most viable approach to increasing levoglucosan yields, though it has not been fully explored.

In this paper, we hypothesize that this combination of acid washing and acid impregnation could also work for other acids. Nitric acid was chosen for the acid wash to remove metals before the water wash. Four different acids are considered for impregnation into the biomass: sulfuric acid, acetic acid, phosphoric acid, and nitric acid. Py–GC/MS will be used to parametrically study acid impregnations ranging from 0.05 to 0.5 wt.% relative to the feedstock to determine the impact of each acid on the production of volatiles in the pyrolysis of Douglas fir wood. The removal of minerals will be studied by measuring the ash content before and after the acid wash as well as quantitative measurement of metals via induced coupled mass spectrometry (ICP-MS).

2. Materials and methods

2.1. Wood grinding, acid washing, and acid addition

All tests were conducted as illustrated in Fig. 1. Bark-free Douglas fir wood chips (*Pseudotsuga menziesii*) were provided by Herman Brothers Logging and Construction (Port Angeles, WA), harvested