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Increase in bio-oil quality from improvements on fast pyrolysis fluidized beds

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Increase in bio-oil quality from improvements on fast pyrolysis fluidized beds

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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

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DEDICATION

This thesis is dedicated to my parents who have always believed in me and pushed me to become a better version of myself. Thank you for all the love and support you have given me along the way.

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ABSTRACT

Through the pretreatment of lignocellulose, sugars can be major products of fast pyrolysis, most prominently the anhydrosugar levoglucosan. The analytical pyrolysis of pure cellulose can produce up to 60 wt.% yields of levoglucosan. However, in continuous pyrolysis trials, levoglucosan yields are significantly lower, suggesting that significant secondary reactions occur before the levoglucosan can be removed from the reactor and quenched. Previous research has revealed that biochar can catalyze the decomposition of levoglucosan at pyrolysis temperatures. Biochar has been shown to accumulate near the surface of a fluidized bed pyrolyzer, reaching a steady-state loading through which pyrolysis vapors must pass. However, it has not been determined whether gas-solid reactions of levoglucosan and biochar occur to an appreciable extent in a continuous fluidized bed pyrolyzer. We have performed experiments to test this hypothesis that limiting the gas-solid reactions would improve our overall bio-oil yield.

Micropyrolysis experiments were performed to better understand the mechanism of sugar degradation. A significant loss in sugar yield was observed for cellulose overlain with biochar powder compared to the pure cellulose control sample. Further tests were performed in a micropyrolyzer to investigate the effect of iron sulfate pretreated biomass which is meant to passivate the biochar's catalytic activity. In the worst case of both biochar mixed into the sample and overlain, there was a reduction of levoglucosan from 60% to 25% with untreated biochar. On the other hand, iron sulfate biochar only saw a drop down to 53% levoglucosan yield.

Due to this drop to 25% levoglucosan in micropyrolyzer testing, the interaction between cellulose and biochar was tested using a mixture of 85 wt.% cellulose and 15 wt.% untreated corn stover biochar by continuously feeding in a fluidized bed reactor under both conventional and autothermal operation. Bio-oil produced in the reaction was recovered, and the yield of

levoglucosan was determined through acid hydrolysis and HPLC analysis. Sugars decreased from 61.3 wt.% to 21.3 wt.% and 41.5 wt.% to 11.6 wt.% for conventional and autothermal operation, respectively.

The significant drop in sugar yield due to biochar interaction encouraged changes in the design or operation of continuous pyrolysis reactors to reduce vapor-product interactions with the goal of diminishing secondary reactions responsible for loss of levoglucosan yield. The injection of biomass was changed to be above the bed rather than feeding directly into the bed. This change reduced the exposure of pyrolysis vapors to the biochar layer at the fluidized bed's surface, increasing bio-oil and sugar yields by 9.3% and 9.1%, respectively.

CHAPTER 1. INTRODUCTION

1.1 Motivation

Biomass has the potential to help end the reliance on fossil fuels and reduce our dependence on foreign oil. More than one billion tons of biomass resources from agricultural land and forestland are available and have the potential to displace more than 30% of the 2005 U.S. petroleum consumption [1]. An obstacle currently limiting this potential solution is the sugar production in oils produced within fast pyrolysis reactors. Sugars are needed to upgrade bio-oil into useable products more effectively. More specifically, the anhydrosugar levoglucosan production is observed due to the greater opportunity to convert into a usable fuel product.

Although renewable energy sources are the prime focus for reducing greenhouse gases, there is still a need for liquid fuels. Primarily with transportation vehicles where batteries cannot be easily implemented due to the weight and size needed to transport vehicles over large distances without recharging. Therefore, it is essential to continue improving our knowledge of biofuels until some of the drawbacks of battery power can be improved. This can be done by improving research on ethanol and other liquid fuels that come from bio-oil.

As oil becomes scarcer around the world and expensive to extract, the demand continues to increase. Less oil creates an imbalance and forces oil companies to start drilling in harder-to-reach areas. Not only would this cause an increase in oil prices, but it increases the chance of mistakes happening. Disasters worldwide due to oil spills have caused years' worth of damage to the environment around them. The continued release of greenhouse gases due to transportation and refining plants continues to provide climate change challenges. The transportation sector accounts for nearly 15% of the global greenhouse gas emissions and over 20% of the energy-

related CO_2 emissions [2]. Finding a more sustainable alternative that has less impact on the world and climate change is vital to the planet's future.

Biomass can be processed into bio-oil with a few different methods. The thermochemical conversion of biomass can generally be categorized into gasification, liquefaction and pyrolysis. Although all three methods allow for biomass processing, they all operate differently and provide slightly different products. This allows for different processes to occur depending on which end product is desired. However, fluidized bed pyrolysis reactors are more common when trying to get the highest yield of bio-oil.

In general, having a drop-in fuel from bio-oil would allow transportation to continue to operate as usual without altering the already existing systems. Every year, forests provide trimmings that could be used as a feedstock to produce bio-oils [1]. Likewise, waste products such as corn stover (*Zea mays ssp. Mays L)* and short-rotation woody biomass such as poplar are ideal due to their excellent availability. Although harvesting and growing some of these products can be an energy-intensive process, it is still believed to reduce greenhouse gas emissions by up to 80% if the biomass is used to create fuels that replace fossil fuels in heat and power applications [3]. In turn, the world would see a reduction in overall emissions while generally unwanted residues would be put to greater use. If a bio-oil product could be made using the available resources, millions of dollars could be saved trying to clean up spills.

1.2 Objective

This study aims to evaluate the interaction of biochar with pyrolytic vapors within fluidized bed reactors and make modifications to improve overall quality. Fluidized bed reactors are very well known in the oil industry (FCC), but as pyrolysis is still maturing, optimization is

still ongoing. It is still unclear why some small-scale testing yields do not match when testing is upscaled to larger reactors. This thesis aims to cover some of these issues and explain why the overall product may decrease quality. Microscale testing is also performed to understand how biochar interacts with biomass while being pyrolyzed. More detailed descriptions of the results are discussed further in Chapter 4.

1.3 Organization

The organization of this thesis is as follows:

- Chapter 2 goes into depth on the background of this research and what helped guide this research towards these findings.
- Chapter 3 describes the methods used in this research and details experimental trials.
- Chapter 4 introduces the results found using the micropyrolyzer/tandem system and the fluidized bed reactor with modifications to optimize the overall product yield further.
- Chapter 5 summarizes the overall findings in the thesis and includes the possible future opportunities of the work.

CHAPTER 2. LITERATURE REVIEW

2.1 Thermochemical Conversion

Thermochemical processing uses heat and catalysts to promote chemical transformations of biomass into energy and chemical products. Each conversion method operates at different conditions and favors different products. Gasification reactors operate in the temperature range of 250-700 °C and produce biochar, tars and pyrolysis gas, mainly containing hydrogen, carbon monoxide, carbon dioxide and light hydrocarbons [4]. These gases can be used in similar ways as gas fuels for combustion processes. The percentage of each fraction depends on the operating temperature and what type of gasifier is being used, such as a fluidized bed or fixed bed gasifier. Hydrothermal liquefaction of biomass is more commonly performed when wet material is processed and uses the water as the processing medium. The liquefaction process generally occurs between 250-375°C, with lower temperatures producing a hydrochar similar to low-rank coal and more ideal intermediate temperatures producing a liquid fuel known as biocrude, similar to petroleum crude [5]. Fast pyrolysis is generally defined as a high-temperature process in which biomass is rapidly heated in the absence of oxygen [6]. Fast pyrolysis operates in temperature ranges of 400-600°C with high biomass particle heating rates of >100°C/min and ideally short residence times of 0.5-2 seconds [7]. From this, it is clear that it is essential to know the desired end product before starting to process biomass.

Each thermochemical processing method has a common reason why they are used but also generally comes with some drawbacks as to why it is not perfect. This has led to continued research to get a better understanding of the products and methods. Gasification is one of the older technologies that has widely been researched. It is most commonly used to produce either

hydrogen or syngas due to its economic viability [8]. The main problem seen with gasification is the relatively low calorific value of products and the impurities present, such as tar and dust in the fuel gas [9]. This can be an issue when trying to run the fuel through engines or machinery with rigid specifications. Liquefaction has many promising advantages. Some of these include the mild operating conditions which save energy, the feedstock does not need to undergo an energy-intensive drying process and there are limited emissions produced during the process [8]. On the other hand, liquefaction has some issues that need to be addressed before it has the chance to operate in a full-scale industry. The optimal operating conditions are still not fully known, and the high viscosity of the bio-oil product causes difficulties in the long run [8]. Lastly, fast pyrolysis is known in the industry due to its ability to produce a large quantity of bio-oil. However, due to the high heating rate needed to allow the fast pyrolysis method to operate, small particle sizes are required and moisture content typically needs to be under 10% to ensure a rapid reaction [10]. Even with these bottlenecks, fast pyrolysis is still an up-and-coming technology continuously being improved for future use.

Depending on the exact operating condition, different products can be obtained. Slower heating rates and lower temperatures will favor more biochar production, slow heating rates with high temperatures favor fuel gas production, and high heating rates favor tar production [11]. Depending on what type of biomass is being processed and the end product in mind, it is crucial to look through all the possible conversion processes to find an ideal combination in that situation.

2.2 Fluidized Bed Reactor

A fluidized bed is a bed of particles, generally sand or similar material, which are freely suspended due to an upward fluidizing medium of air or liquid which passes through a distributor plate. The particles are fluidized when the upward drag and buoyancy forces are equal to the downward force of gravity [12]. With the particles suspended, the bed behaves like a liquid. This allows for a constant and even high heating rate of around 1000°C/s [13] to the particles being processed since the bed material fully encompasses the particle.

Depending on the velocity of the fluidizing medium, the fluidized bed will behave in different manners. The different regimes can be classified as fixed, bubbling, slugging/turbulent, and entrainment. In the fixed bed regime seen in Figure 2.1(a), the superficial velocity is lower than the minimum fluidizing velocity of the bed material; therefore, the bed acts as a solid-state. This only allows for the gasses to pass through the bed. As the superficial velocity begins to increase, the fluidized bed will rise in height, as seen in Figure 2.1(b), until bubbles start to form and rise in the bed [14] and form a bubbling bed such as Figure 2.1(c). Bubble growth and velocity depend heavily on the bed particle properties. The smaller the particle size, the longer it takes for bubbles to form, which causes the bed to expand more before bubbling [15]. The ratio of minimum bubbling velocity to minimum fluidizing velocity determines how the bed will react as the superficial velocity increases [15]. Eventually, as the superficial velocity continues to increase, the bubbles will coalesce, and a slugging occurs (Figure 2.1(d)). This is a result of the bubbles passing through the bed being too large and carrying the bed particles up as well. Depending on the particle type, the bed begins to slug when the bubble diameter reaches 0.3-0.6 the diameter of the bed [14]. As the bubble breaks down further up in the fluidized bed, the bed

material is able to fall back down. Lastly, at very high superficial velocities, entrainment occurs (Figure 2.1(e)), pneumatically transporting the bed particles.

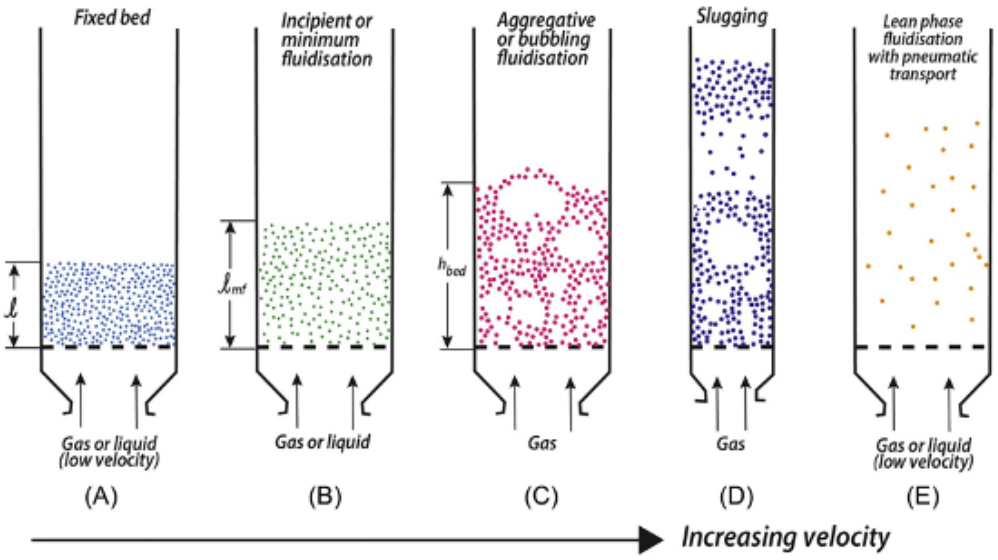

Figure 2.1 Representation of a fluidized bed as superficial velocity increases. (a) the starting bed height; (b) minimum fluidization with a bed height of (l_{mf}) as fluidization begins; (c) corresponds to a fluidized bed with properly sized bubbles; (d) slugging regime occurs with large bubble formation; (e) is an entrainment bed in which particles are mostly all removed [16].

For biomass fast pyrolysis, fluidized beds typically operate in the bubbling regime. As previously discussed, this regime allows for a high level of mixing, providing a high heat transfer to the biomass particles. When slugging occurs, biomass particles attempting to devolatilize can get caught in the bubbles, therefore negatively impacting the heating rate and possibly not allowing the biomass to fully devolatilize before being entrained out of the bed.

2.3 Feedstock

In general, lignocellulosic biomass is used as a feedstock for biofuel production. The main components of lignocellulosic biomass are cellulose, hemicellulose and lignin, which decompose into different products [8]. Feedstocks can be separated into several categories:

edible crops, nonfood and aquatic feedstocks. Edible feedstocks are products that are more commonly used in daily life, such as starch crops (wheat, barley and corn), sugars (sugar cane and sugar beet) and oil crops (rapeseed, soybeans, sunflower and palm) [8]. Nonfood-based crops can be categorized as biomass, such as forest residue, agricultural biomass (straw/grass), energy crops (cassava and miscanthus) and municipal solid waste [8] Lastly, the aquatic biomass is primarily microalgae or seaweed. Aquatic biomass may have the greatest possibility for a wide range of fuels; however, the required fertilization and water to grow the feedstock makes it less attractive as an overall option [8]. Continued research will allow for the best feedstock for fuels to become more available.

Different types of feedstocks provide advantages and disadvantages when it comes to producing bio-oil. In general, before choosing a feedstock, a proximate analysis, ultimate analysis and energy content will be determined. The proximate analysis measures the moisture, volatile matter, fixed carbon and ash content. Ultimate analysis measures the carbon, oxygen, hydrogen, nitrogen and sulfur contained in the biomass. Lastly, the energy content is found using a bomb calorimeter to see the higher heating value (HHV) from the biomass. These analyses determine whether or not the feedstock can be used efficiently and what might need to be done to the feedstock to process the biomass more smoothly.

Different biomass parts can have negative or positive implications when trying to feed it through a fluidized bed successfully. Biomass moisture plays a sizable role during the combustion process. Moisture slows down the heating rate of the biomass particle, which reduces the overall efficiency of the process and negatively affects the flame stability [17]. Similarly, ash in biomass can create a shift in desired products. Generally, the greater the amount

of ash content, the less bio-oil is seen [18]. Therefore, it is clear that correct feedstocks need to be chosen in order to get the desired products.

Availability plays an important role when trying to select an appropriate feedstock to use for processing. One of these largely available feedstocks is agricultural residue. Some of the most widely grown crops in the United States include corn and soybean, but due to the minimal residue left behind by soybeans and the rapid degradation in the field, corn residue is a better option [19]. Corn residue, better known as corn stover, is mainly comprised of the leftover portion of the above-ground corn plant. This includes the stalk, leaves, cob and husk, which can be produced at the rate of 1 kg of stover per 1 kg of grain [20]. The proximate analysis and energy content of the corn stover are shown below in Table 2.1 [21] on a dry basis.

Table 2.1 Proximate analysis and energy content of feedstocks (wt.%, dry basis).

Properties	Corn Stover	Beaupré Poplar		
		Top	Middle	Base
Moisture Content	6.1	4.5	5.0	4.1
Volatile Content	68.8	81.9	83.8	83.7
Fixed Carbon	15.4	17.1	15.6	15.6
Ash Content	9.7	1.1	0.6	0.7
Higher Heating Value (kJ/kg)	20.9	19.8	19.6	19.5

On the other hand, some crops are grown specifically to be used as energy crops, such as short-rotation woody crops (SRWC). These crops are meant to produce high biomass yields in 3-10 years, depending on the crop and land quality [22]. However, this biomass varies depending upon what part of the crop is used. As shown in the Beaupré Poplar section of Table 2.1 [22], the

top section has a higher ash content due to leaves and more bark being present. This slight variation in feedstock ash content can significantly change reactor operation [23].

2.4 Bio-Oil Upgrading

Bio-oil is the liquid product that comes from the thermochemical conversion of biomass. In general, fast pyrolysis provides the highest high-grade bio-oil yield due to the short vapor residence time and high heating rate [24]. The exact composition of the bio-oil varies significantly with the biomass being used. One of the greatest differences between bio-oil and conventional petroleum fuels is the amount of oxygen present in the bio-oil. In general, bio-oil contains 35-40 wt.% oxygen, while fuel oil only has around 1 wt.%, as can be seen in Table 2.2 below [25], [26]. This leads to more problems due to organic acids increasing the bio-oil's acidity and instability [26].

Table 2.2 Typical bio-oil properties compared to heavy fuel oil [25]

Physical Property	Bio-oil	Fuel Oil
Moisture content, wt.%	15-30	0.1
pH	2.5	-
Specific gravity	1.2	0.94
Elemental composition, wt.%		
C	54-58	85
H	5.5-7.0	11
O	35-40	1
N	0-0.2	0.3
Ash	0-0.2	0.1
HHV, MJ/kg	16-19	40
Viscosity (at 50 °C), cP	40-100	180
Solids, wt.%	0.2-1	1
Distillation residue, wt.%	up to 50	1

The other main difference between bio-oil and fuel oil is the moisture content present in the oil. Bio-oil has a high moisture content due to the original moisture present in the feedstock and through dehydration reactions during fast pyrolysis. This moisture has negative implications, such as reducing the bio-oil's energy value and flame temperature [25]. However, moisture helps reduce the viscosity of the oil and leads to a more uniform temperature profile inside [25]. Lastly, moisture can influence the composition of organic liquid products as well. Higher moisture is shown to increase the intensity of the phenol groups, and other oxygenates due to increased compound cracking, which leads to lighter factions [27]. The different bio-oil properties lead to difficulties when trying to use them in current real-world applications. Still, additional options are available to allow bio-oil to be used in the real-world market.

Bio-oil upgrading is necessary to use the product in a manner similar to petroleum fuel. Upgrading is essential to reduce the acidity and lower the oxygen content, yielding a more hydrocarbon product [25], [28].

There are different possibilities when it comes to upgrading bio-oil into a useable product, including catalytic cracking, esterification, supercritical extraction, steam reforming and hydrotreatment [29]. Out of these, hydrotreatment, or hydrodeoxygenation, is promising due to the already well-established technology for upgrading crude-oils [30]. The upgraded bio-oil from hydrotreatment has the potential for many different uses. These include a possible substitute for fossil fuels as a transportation fuel [31], production of resins and chemicals [32], combustion fuel [33] and power generation [34]. All of the possible substitutions would allow for more carbon-neutral options, which would help reduce fossil fuel dependence. It is essential to keep taking a step forward in more environmentally friendly alternatives to minimize the negative global

impact which fossil fuels have caused. The processing of biomass into bio-oil and upgrading the bio-oil into a useable product is a promising step in the right direction.

2.5 Influence of Catalytic Activity on Sugar Yields

Sugars are not usually thought to be a major product of biomass pyrolysis. However, removing or passivating the alkali and alkaline metal (AAEM) content of biomass can dramatically increase sugar yields [35], [36]. Thermal depolymerization of cellulose produces anhydrosugars instead of the more familiar monosaccharides from acid or enzymatic hydrolysis [37]. This suggests an alternative approach for producing cellulosic sugars that is much faster and potentially more economical than hydrolysis [38]. More closely approaching the maximum sugar yields observed during analytical pyrolysis would advance the prospects for this approach for cellulosic sugar production.

Cellulose comprises the largest portion of lignocellulosic material. For example, red oak is comprised of approximately 50% cellulose with smaller amounts of hemicellulose, lignin and extractables [39]. Fast pyrolysis of pure cellulose can produce levoglucosan yields as high as 53-60% at 500°C [40]–[42]. However, pyrolysis of native biomass yields significantly less levoglucosan than might be expected from the cellulose content.

AAEM found naturally in biomass are known to drastically reduce anhydrosugar yields during pyrolysis by catalyzing furanose and pyranose ring fragmentation [23]. Different methods have been used to mitigate the impact of AAEM on pyrolysis [23]. Water washing can be used to remove select AAEM content. However, water washing is unlikely to be viable at scale due to the large amount of water required to thoroughly remove AAEM and the energy required to dry the biomass prior to pyrolysis [43]. Instead of removing the AAEM, sulfuric and phosphoric acid

can be used to treat the biomass, passivating the metals to thermally stable salts and improving levoglucosan yield [36]. Passivation of the AAEM through acid infusion has been shown to enhance levoglucosan yields from woody biomass by up to 80% [36]. A closely related technique employs ferrous sulfate instead of mineral acids to passivate AAEM with the advantage of eliminating the biochar agglomeration observed with acid infusion or washing of biomass [44]. However, it is important to note that although AAEM are all detrimental to the yield of levoglucosan, some have more impact than others. Less than 0.05 mmoles/g of sodium chloride and potassium chloride showed to reduce the levoglucosan yield of cellulose pyrolysis from 60 to 20 wt.% [45]. On the other hand, calcium and magnesium chloride only saw a reduction down to approximately 38 wt.% [45]. While they are all impactful to the yield of sugars present in the pyrolysis product, knowing which parts cause more impact is important to know.

CHAPTER 3. APPROACH/METHODOLOGY

3.1 Materials

Red oak (*Quercus rubra*) wood chips were obtained from Wood Residuals Solutions (Montello, WI) with a moisture content under 10%. Wood chips were hammer milled through a 1/8-in. screen and then knife milled through a 1/16-in. screen to provide appropriately sized particles for the continuous pyrolysis reactor system. A full proximate and ultimate analysis of this red oak has been previously reported [46]. Preliminary experiments were performed using Sigmacell Type 50 (Sigma-Aldrich) cellulose. Corn stover biochar was sourced from previous experiments' products in a continuous fluidized bed pyrolyzer in our laboratory under autothermal pyrolysis conditions (equivalence ratio of 0.11) [44]. Both biochar produced from untreated corn stover and corn stover pretreated with ferrous sulfate were evaluated.

3.1.1 Micropyrolyzer Sample Preparation

Mixtures and layers of cellulose and biochar were prepared consisting of 85 wt.% cellulose and 15 wt.% biochar, as seen in Figure 3.1. Mixtures were prepared by loading the appropriate proportions of cellulose and biochar into centrifuge tubes. The tubes were vortexed for two minutes to produce a homogenous mixture of cellulose and biochar. Layers of cellulose and biochar were prepared by first loading cellulose into the bottom of a sample cup followed by a thin round of quartz wool upon which the biochar was loaded. This configuration forced volatiles released from the pyrolyzing cellulose to flow through the biochar before escaping the sample cup. The use of layers is intended to simulate the passage of pyrolysis vapors through the layer of biochar known to accumulate at the surface of a fluidized bed pyrolyzer [21].

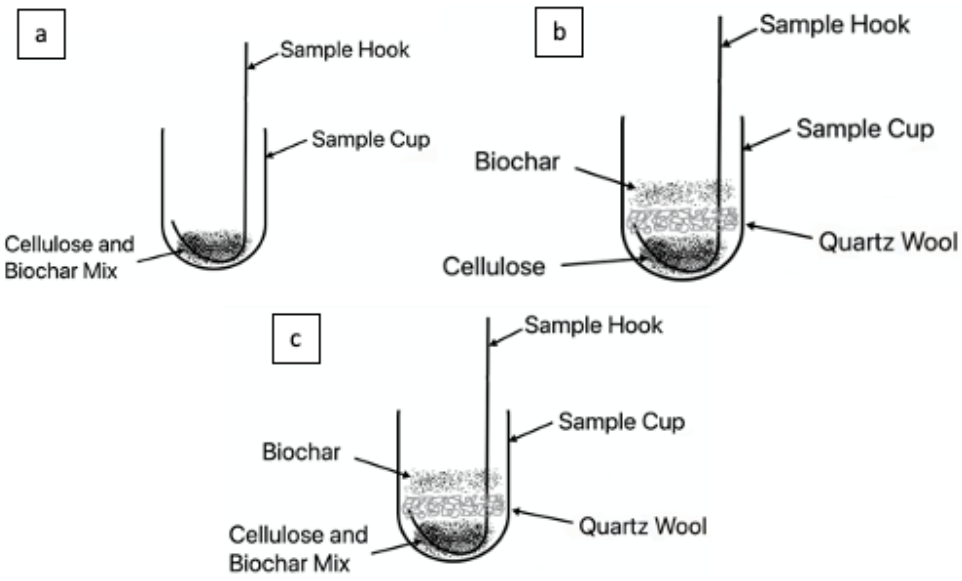

Figure 3.1 Biochar loading into the sample cup during micropyrolysis experimentation. Figure (a) showcases only the cellulose and biochar mixture; (b) demonstrates pure cellulose with a biochar layer; (c) has both a cellulose/biochar mixture and a layer of biochar

3.2 Pyrolysis Product Analysis

3.2.1 Sugar Quantification

Sugar quantification was determined by acid hydrolysis of the heavy ends of bio-oil. Virtually all of the sugars and anhydrosugar produced during pyrolysis were converted to simple sugars following the method established by Johnston et al. [47]. Sixty milligrams of bio-oil were mixed with 6 mL of 400 mM sulfuric acid, sealed in a glass vial, and heated to 125°C for 44 minutes [48]. The sample was then cooled to room temperature and filtered through a 0.45 μm Whatman filter into a 2 mL glass vial using a syringe. The samples are analyzed using a Dionex Ultimate 3000 series High Performance Liquid Chromatography (HPLC) with a water mobile phase and Shodex refractive index detector to measure the levels of glucose and xylose present [47].

3.2.2 Thermogravimetric Analysis

Proximate analysis of the biochar was performed using a Thermo-gravimetric analysis (TGA) on a Metler Toledo TGA/DSC1 STAR system. Samples were weighed out to approximately 20 mg in ceramic crucibles and then loaded into the instrument. The sample was then heated from 25 to 105°C at 10°C/min with 100 mL/min of N_2 and held at 105°C for 40 minutes to remove any moisture within the sample. Temperature was then increased to 900°C at 10°C/min and held for 20 minutes to quantify volatiles. Lastly, 100 mL/min of air was introduced at 900°C for 30 minutes to burn off the remainder of the sample. The resultant weight loss was deemed to be fixed carbon. Any remaining weight within the crucible is regarded as the ash content. Similar methodology is more heavily described by Choi et al [49].

3.2.3 Ion Chromatography

Acid content within the bio-oil was analyzed using a Dionex Ion Chromatography (IC) Model 3000 equipped with a conductivity detector and Anion Micromembrane Suppressor AMMS-ICE 300. The suppressor regenerant was 5 mM tetrabutylammonium hydroxide at a flow rate of 3 mL/min. The mobile phase contained 1.0 mM heptafluorobutyric acid used in an IonPac® ICE-AS1 analytical column with a flow rate of 0.120 mL/min at 19°C. Acids quantified included: glycolate, formate and acetate. One hundred milligrams of bio-oil was measured into a centrifuge tube. Then, 1.5 mg of methanol and 6, 25, 80 or 100 mL of deionized water were added to dilute the acids enough to fall within the calibration curve. The calibration curve was made using a standard solution (Inorganic Ventures) containing the acids, which was diluted into five concentrations between 10-200 mg/L. The centrifuge tube was vortexed for 30 minutes to mix the contents. After it was sufficiently mixed, a sample was taken from the centrifuge tube

and filtered with a syringe filter (0.45 μm) into a sample vial. These samples were analyzed twice with the IC. This was repeated for each stage fraction and reported on a bio-oil basis. More information on the analytical method can be found in Choi et al. [49].

3.2.4 Liquid Extraction

The bio-oil was analyzed for water-soluble sugars and phenolic content. Approximately 5g of bio-oil were measured into a centrifuge tube with 5 mL of deionized water. The centrifuge tube was heated to 65° C for 25 minutes and vortexed to mix the contents. The centrifuge tube was then placed in a centrifuge for 25 minutes at 3000 rpm to separate the sugars from the phenolic content. The remaining liquid was separated into another vial and quantified as the water-soluble sugars. Remaining content in the centrifuge tubes is considered to be the phenolic content. This was repeated for the heavy ends of bio-oil and reported on a biomass basis.

3.3 Micropyrolysis System

Fast pyrolysis of cellulose and cellulose-biochar mixtures were performed in a Frontier single-shot micropyrolyzer system (Rx-3030 TR, Frontier Laboratories, Japan) illustrated in Figure 3.2. For these tests, the furnace and interface were heated to 500°C and 450°C, respectively. A sample of reactants weighing approximately 150 μg was loaded into a stainless-steel sample cup fixed with a sample hook and inserted into the sample holder. These relatively low loadings assured that the gas chromatography (GC) (7890A, Agilent Technologies, USA) system connected to the micropyrolyzer was not overwhelmed by the relatively high yields of levoglucosan anticipated.

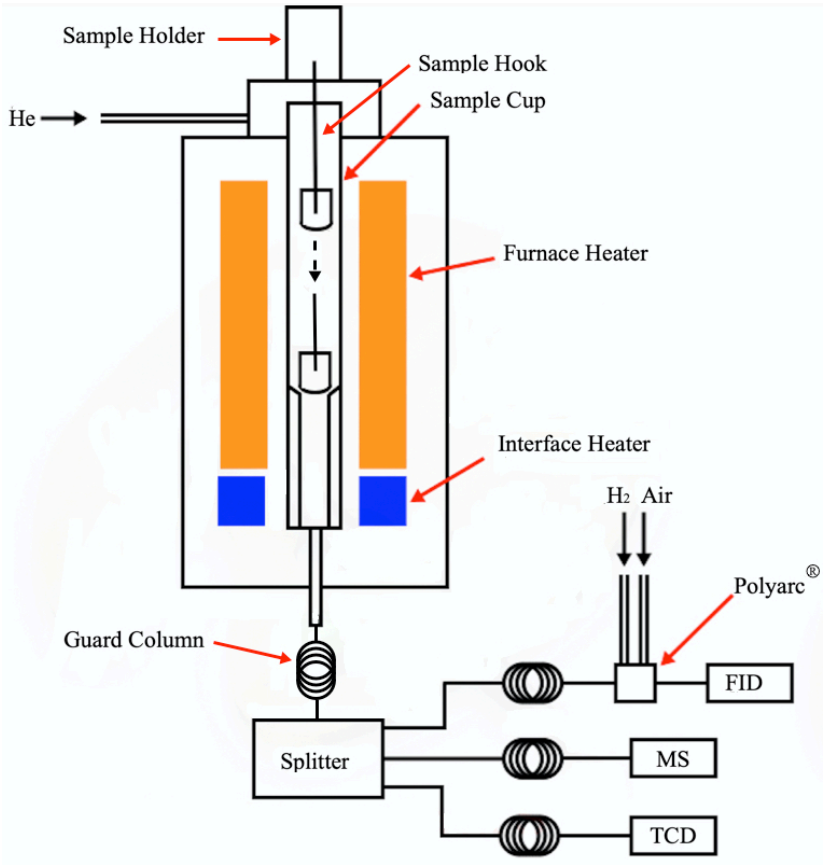

Figure 3.2 Schematic of micropyrolyzer with GC analysis of products. Pyrolysis vapors released from the sample in the furnace are swept into one of three GC columns for identification via MS or quantification via Polyarc/FID or TCD.

Prior to dropping the sample into the preheated surface, a blank run of 16 minutes was performed with helium sweep gas to remove any air and other impurities from the system. After the blank had concluded, the GC was allowed to cool back down to 35°C before the sample was dropped into the reactor tube. Once the sample was dropped, the vapors released from the pyrolyzing sample were swept into the attached GC system and through a deactivated guard column (1 m x 0.25 mm) before entering a three-way splitter which sent the vapors into three separate GC columns. The GC injector operated at 280°C with a split ratio of 30:1 to help not overwhelm the GC columns5. The GC program was set to start at 35°C and hold for 3 minutes. The temperature then ramped from 35°C to 280°C at 5°C min^{-1}, with a six minute hold. Two matching Agilent DB-1701 (60 m x 0.25 mm ID, 0.25 µm film thickness) were used to separate

compounds into a mass spectrometer (MS) (5975C, Agilent Technologies, USA) and flame ionization detector (FID) system. Compounds were identified with the MS and quantified with the FID system and a Polyarc® reactor (Activated Research Company). A Porous Layer Open Tubular (PLOT) column (60 m x 0.320 mm) (GS-GasPro, Agilent, USA) is set up to a thermal conductivity detector (TCD) to analyze NCG but was not used in this experimentation. A four-point levoglucosan calibration curve was made to determine the yields. Replicate cellulose trials were periodically performed, ensuring repeatable results. The GC and micropyrolyzer system has been described in more detail in our previous studies [50]–[52].

3.4 Fluidized Bed Pyrolysis System

Continuous pyrolysis trials were performed with a fluidized bed reactor previously described by Rollag et al. [44] capable of running either in conventional or autothermal mode. Conventional pyrolysis was performed with nitrogen as the fluidizing gas. In contrast, autothermal pyrolysis was performed with a mixture of nitrogen and air to fluidize the bed and allow partial oxidation of pyrolysis products, providing the enthalpy for pyrolysis without an external source of energy [21]. The 3.8 cm dia. fluidized bed reactor is generally fluidized with 20 SLPM of nitrogen or air and nitrogen for conventional and autothermal operation, respectively. However, different size bed materials can be used to allow different fluidization rates. Gas flow rates were controlled with Alicat Scientific mass flow controllers. The tests performed here were at a biomass feed rate of 500 g $hour^{-1}$ for 20 minutes and 1000 g $hour^{-1}$ for 50 minutes in order to get 1 kg of biomass through the system for a mass balance.

The optimal reactor temperature to maximize liquid yield is between 400-600°C. Accordingly, experiments were performed at 500°C. For conventional pyrolysis trials, two Watlow clam-shell ceramic heaters were used to provide the enthalpy for pyrolysis. For

autothermal pyrolysis, the role of the heaters was limited to overcoming parasitic heat losses, while partial oxidation of pyrolysis products provided the enthalpy for pyrolysis, as described by Polin et al. [46]. Pyrolysis products exited the fluidized bed reactor through a 2.3 cm diameter tube at the top of the reactor to enter the collection system.

The product collection system is comprised of several unit operations in series collecting multiple stage fractions (SF): two char cyclones, a heavy ends condenser (SF 1) followed by a hot electrostatic precipitator (ESP) to collect aerosols referred to as SF 2, a light ends condenser precipitated (SF 3) and a cold electrostatic precipitator recovered (SF 4). The heavy end condenser consisted of a single shell condenser maintained at 90°C, cooling the vapors in a single pass tube to an exit temperature of 120°C. The ESP of SF2 operated at 15 kV at 120°C to capture heavy aerosols. SF1 and SF2 collect most of the anhydrosugars and phenolic compounds produced in the pyrolyzer. The light ends condenser operated at 0°C while the ESP of SF4 operated at 15 kV and -15°C to collect light ends of bio-oil, which includes water, furans, organic acids, and other low molecular-weight oxygenated compounds [53]. NCG passed through a wet test meter to determine total gas flow while a sample was extracted to a gas chromatograph (GC) (Agilent Varian CP-4900 Micro-GC model) to determine NCG composition. The MicroGC measured the yield of CO2, CO, and several light alkanes and alkenes.

The pyrolysis reactor was modified to allow injection of red oak at the base or the top of the fluidized bed, as shown in Figure 3.3. When biomass was injected at the top of the bed, temperature gradients and pressure drop across the bed need to be closely monitored to assure adequate fluidization and isothermal operation of the bed.

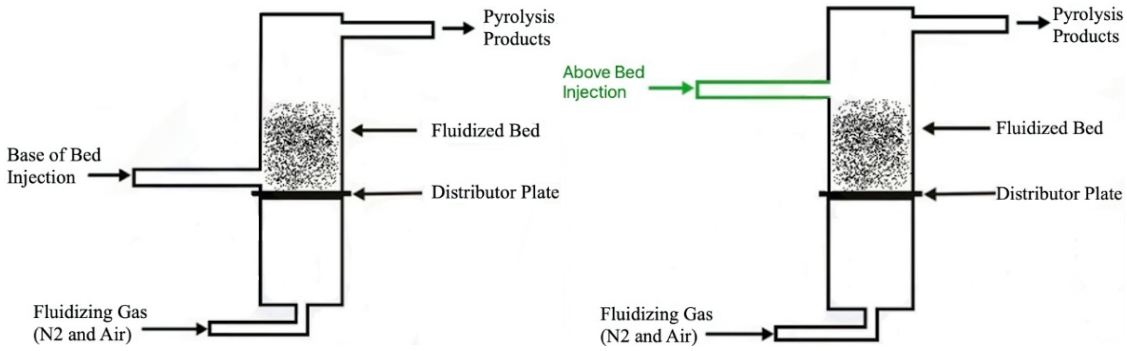

Figure 3.3 Diagram showing a cross section view of change being made which shows the base of bed injection (left) versus the new above bed injection (right).

Gas flow rate was a variable in these continuous pyrolysis tests. To avoid excessive elutriation of bed material, the average particle size of sand was increased as fluidization velocity in the bed was raised, as detailed in Table 3.1. The ratio of fluidization velocity (U) to the minimum fluidization velocity (U_{mf}) was calculated based on the volumetric flow rate within the reactor and average sand sizes. This velocity ratio (U/U_{mf}), ranging from 2.68 to 8.02, served as a measure of the extent of fluidization in the reactor. A plug flow reactor (PFR) model was used to calculate gas residence time as a function of gas flow velocity.

Table 3.1 Testing particle size and U/U_{mf} for the continuous pyrolysis system. Control test at 20 SLPM performed with in-bed injection

SLPM	**Sand Mesh Size**	**Avg. Particle Size (µm)**	**U_{mf} (cm/s)**	**U (cm/s)**	**U/U_{mf}**	**Residence time (s)**
Control (20)	16/30	741	22.67	78.23	3.45	0.438
6	30/50	417	5.85	23.47	4.01	0.595
12	30/50	417	5.85	46.94	8.02	0.298
14	20/40	565	20.47	54.76	2.68	0.255
15	20/40	565	20.47	58.68	2.87	0.238
16	20/40	565	20.47	62.59	3.06	0.223
18	16/30	741	22.67	70.41	3.11	0.198
20	16/30	741	22.67	78.23	3.45	0.179

CHAPTER 4. RESULTS

4.1 Effect of Biochar on Micropyrolysis of Cellulose

Micropyrolysis testing showed how detrimental biochar could be to sugar yields. The effect of biochar mixed and layered with cellulose in sample cups on levoglucosan yield is shown in Figure 4.1.

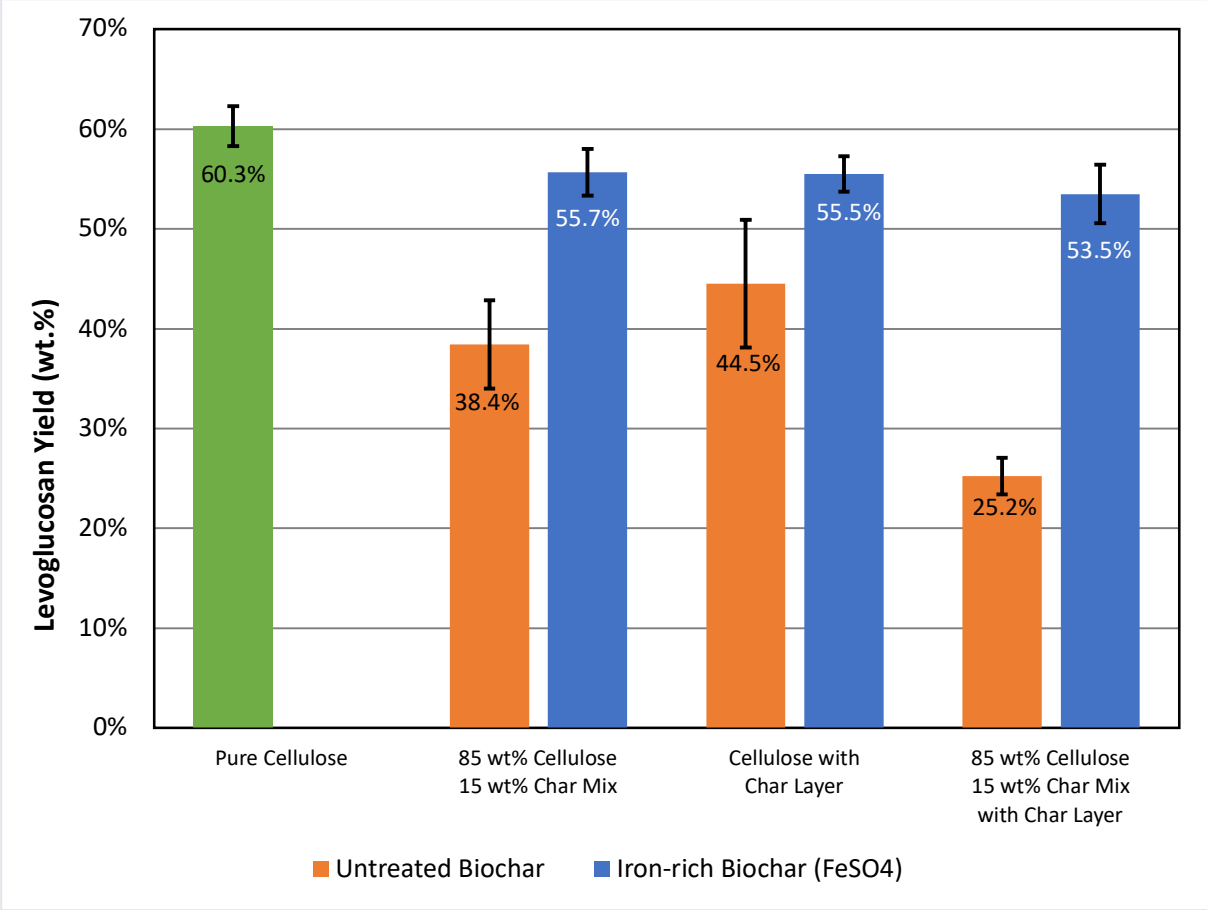

Figure 4.1 Untreated biochar reduced yields of levoglucosan while pretreated biochar did not substantially degrade levoglucosan yields.

Comparing levoglucosan yield from mixed and layered testing showed a minimal change for the iron-rich biochar with a 0.3% difference. On the other hand, untreated biochar resulted in a difference of 15.9% levoglucosan, with mixing having a more significant impact on the yield. The importance of the iron-rich pretreatment becomes more prevalent when comparing results

from the individual tests. Mixed testing showed a decrease in levoglucosan by 31% from the iron-rich biochar to the untreated biochar. The layered test showed a slightly smaller decrease in yield at 19.8%. Most notably, when mixing and layering was tested, there was a difference of 52.8%. This shows how the catalytic activity present in the non-passivated (untreated) biochar significantly impacts the levoglucosan yield produced in testing. Thermal activity in the biochar has a lesser (but still meaningful) impact on the sugar yield from fast pyrolysis.

Performing a statistical analysis allowed significance between the control cellulose test and untreated biochar to be found. An ANOVA test resulted in a P-value greater than 0.05 for both the cellulose/biochar mixture (0.07) and the cellulose with a biochar layer (0.17). However, the combination of both the mixture and biochar layer resulted in a P-value of 0.02. Therefore, although the first two results may not be considered statistically significant, we can confidently say that the combination results in a statistically significant result.

These results are similar to those reported by Ronsse et al. [54] using a Pyroprobe microreactor for pyrolysis of cellulose with unwashed and acid washed biochar in which cellulose was pyrolyzed, and the vapors were forced to pass through a biochar bed. For temperatures above 300°C, the presence of acid washed biochar increased levoglucosan yield by 64% compared to unwashed biochar [21]. The difference was attributed to the removal of AAEM, which catalyzed secondary decomposition reactions.

4.2 Effect of Biochar on Sugar Yields in a Continuous Pyrolysis Fluidized Bed System

In order to understand the impact of biochar on levoglucosan yields during continuous pyrolysis, cellulose was pyrolyzed in a fluidized bed reactor with and without biochar. The tests were performed under both conventional and autothermal (oxidative) pyrolysis conditions with

cellulose directly injected into the bottom of the bed with an auger feeder (normal configuration). The addition of biochar to the reactor, representing 15 wt.% of the cellulose-biochar mixture injected into the reactor, resulted in varying bio-oil yields. The various stage fractions for these tests are shown in Figure 4.2.

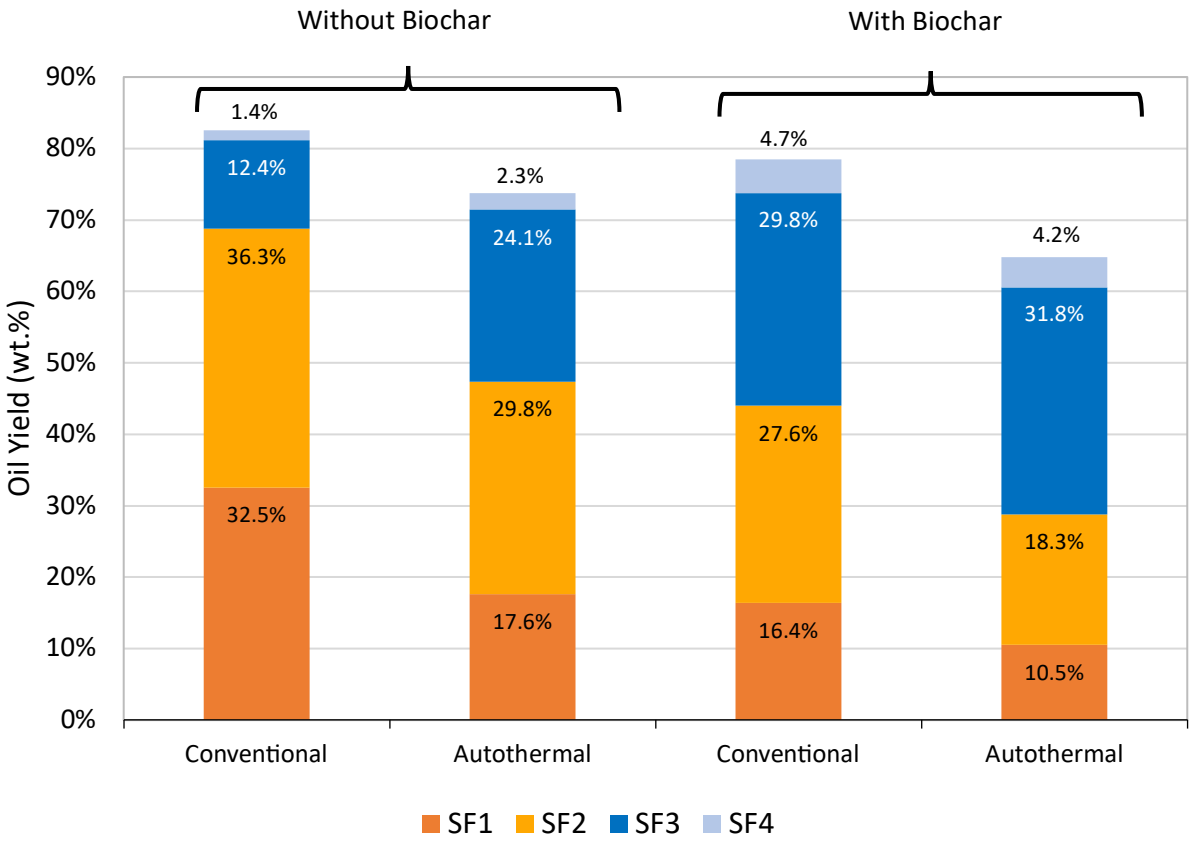

Figure 4.2 Yield of heavy ends (SF1 and 2) and light ends (SF3 and 4) from pyrolysis of cellulose in a continuous fluidized bed reactor under conventional (N_2) and autothermal (AT) conditions. The tests with biochar consist of 85 wt.% cellulose 15 wt.% untreated corn stover biochar, while the other tests are pure cellulose.

Some notable changes in bio-oil yield were seen. There was a 5% decrease in bio-oil yield with the added biochar under nitrogen conditions. The autothermal conditions saw a reduction of 12% bio-oil when biochar was mixed in with the cellulose. In pyrolysis without biochar, the heavy ends (SF1 and SF2) encompassed 83.3% and 64.2% of the oil yield for conventional and autothermal conditions, respectively. On the other hand, when biochar was

added, the heavy ends were only comprised of 56.1% and 44.4% of the overall oil yield for the respective tests. The shift from the heavy ends to the light ends (SF3 and SF4) results from secondary cracking of products that yields more low molecular weight compounds. It is crucial to find the right balance of biochar within the reactor to get the fully optimized yields of the desired products.

Due to the majority of the bio-oil sugars being present in the heavy ends, it is clear that the reduction in overall sugar yield for the mixture is a direct result of increased cracking of sugars due to biochar. As shown in Figure 4.3, sugar yield decreased by 65% during conventional pyrolysis.

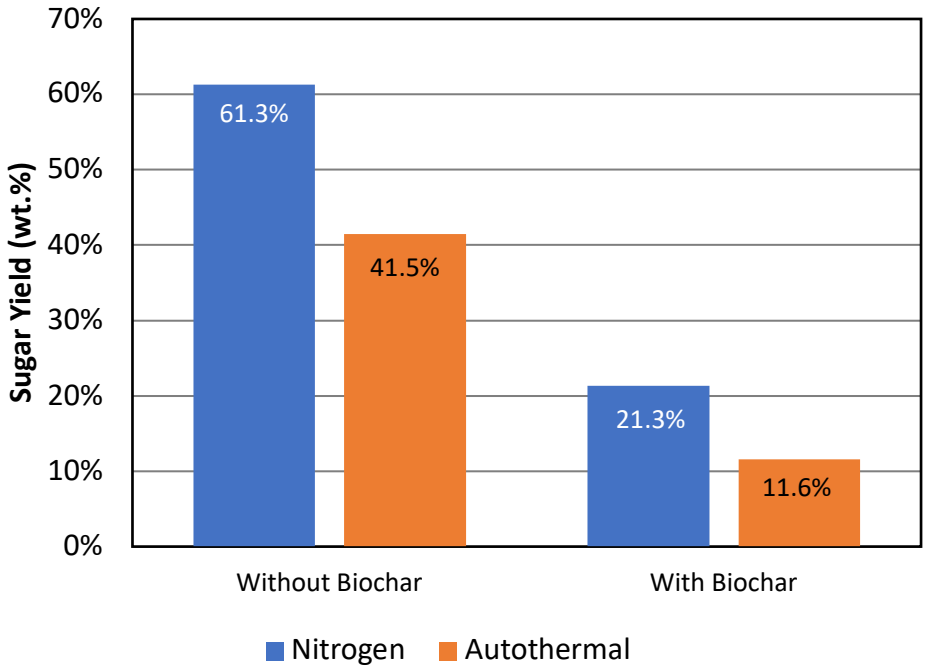

Figure 4.3 Result of adding untreated corn stover biochar to cellulose while running a fluidized bed reactor in both autothermal and conventional pyrolysis conditions. Autothermal runs maintained an equivalence ratio of 12% throughout testing, but temperatures were unable to stay steady without the added biochar

The lower yield of levoglucosan from autothermal pyrolysis of cellulose in the absence of added char (41.5 wt.%) reflects the loss of levoglucosan through its oxidation. Usually, other

pyrolysis products, especially biochar, are oxidized to provide the energy to support autothermal pyrolysis [21]. Significantly, when biochar is added during autothermal pyrolysis, levoglucosan yield further drops even though oxidation is expected to shift from levoglucosan to the added biochar. Clearly, biochar is a powerful catalyst for decomposing levoglucosan.

The amount of biochar that accumulates in the reactor is controlled by the superficial gas velocity with a lower velocity resulting in a greater biochar buildup [55]. For the tests with biochar, it was seen that the nitrogen conditions had a biochar loss of 1.3%, while the autothermal had a loss of 3.7%. This loss represents a negative biochar yield from the starting 15 wt.% that was added for testing. Due to the minimal amount of biochar produced from pyrolyzing cellulose (approximately 2 wt.%)[56], this shows that some of the biochar oxidized in the autothermal case and some volatiles from biochar burned in the nitrogen case, which steadied the operating conditions. The lack of biochar in the pure cellulose tests created difficulties in maintaining stable temperature running conditions. Therefore, although the presence of biochar in the bed can be detrimental to the sugar yields, it is still helpful to have some biochar to overcome the heat transfer bottleneck which is present during fast pyrolysis.

4.3 Biomass Feed Location Implications

Having established the deleterious impacts of biochar accumulation in the fluidized bed, we explored ways to segregate volatiles from biochar. The current arrangement of injecting biomass below the bed results in volatiles passing through the biochar layer that accumulates at the surface of the bed. Based on results described in the previous experiments, significant cracking of vapors is expected. Considering that devolatilization is substantially completed in a matter of seconds [57], we explored the possibility of moving the biomass injection location

from the interior of the bed to above the bed. In this way, at least some of the volatiles would escape without passing through the biochar layer on the bed surface. However, pyrolysis takes minutes to completely devolatilize, suggesting that volatiles slow to release will have to pass through the biochar layer [51]. Fluidization velocities in the range of 6-20 SLPM were tested for pyrolysis of red oak biomass to find the optimal fluidization conditions. Operation at 6 SLPM was unsuitable as the bed was insufficiently fluidized to prevent the accumulation of biomass at the surface of the bed while biochar accumulated at the bottom of the bed, creating respective cold and hot zones at the top and bottom of the bed. At the other extreme, 20 SLPM entrained both biomass and biochar from the bed, causing the bed temperature to quickly drop since not enough biochar was available to burn and heat the bed. While testing 18 SLPM, it was found that temperature stabilized at 460°C well below the set-point temperature of 500°C.

Ideally, the optimal operating condition would achieve in the reactor a combination of short vapor residence time and long solids residence time, thus promoting complete devolatilization of biomass and significant oxidation of biochar. Stable temperatures were achieved for gas flows of 12-16 SLPM. These tests were performed in duplicate to check for repeatability. Figure 4.4 illustrates the effect of volumetric gas flow on yields of heavy and light ends of bio-oil.

All the stable fluidization points resulted in a shift from light ends to heavy ends. Most drastic is at 12 SLPM which showed an increase in 36% over the control in-bed test. A higher heavy ends yield would then hopefully result in more valuable product yield. The decrease in light ends is acceptable as more heavy ends get produced. The control test gave only a 63 wt.% bio-oil yield, while the best overall bio-oil yields for over bed injection were found at 12, 15 and

16 SLPM with 69 wt.%. Therefore, feeding over the bed allowed for a better bio-oil product yield by reducing vapor residence time with biochar.

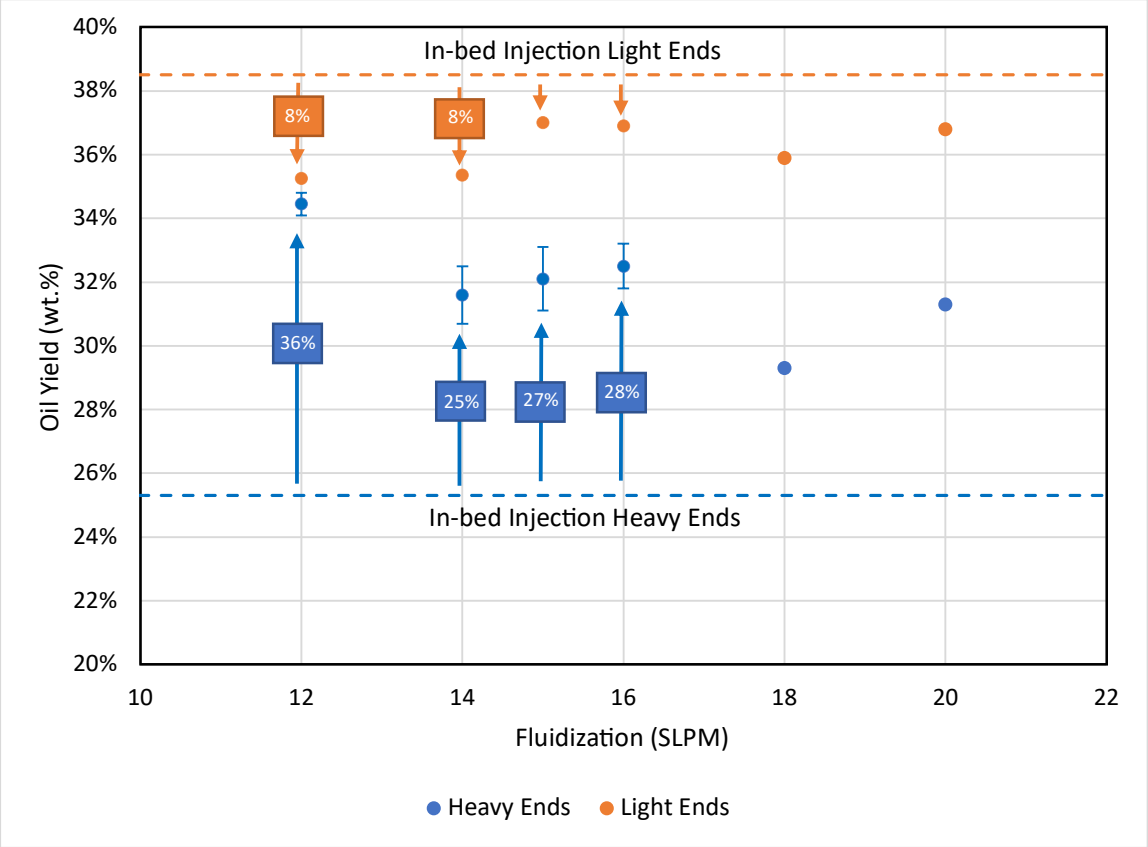

Figure 4.4 Heavy and light end yields for red oak above-bed injection at different fluidization velocities (error for light ends was less than 0.5 wt.%). The dashed lines represent the in-bed control test with red oak at 20 SLPM.

On the other hand, Fig. 8 shows that the highest sugar yield was obtained at 12 SLPM. Due to the majority of the sugars being present in the heavy ends, it makes sense how 12 SLPM had a higher sugar yield since it had the highest yield of heavy ends. Having a higher yield of light ends generally represents cracking of heavy end products, such as levoglucosan, into the light oxygenates present in light ends. Considering the difference in heavy end oil yield going from 15/16 SLPM to 12 SLPM, it appears that 12 SLPM is the most optimal operating fluidization in this configuration. This optimal condition for the new configuration represents a 9.3% and 9.1% improvement in oil and sugar yield respectively when compared to the in-bed

control run. Although there is a vast improvement on the heavy ends yield, the sugar yield does not fully reflect the change. This could be due to increase in other products in the heavy ends such as the phenolic content. Lignin may be interacting less with biochar and therefore producing a larger overall fraction of phenolic compounds in the heavy ends and accounting for some increased yield.

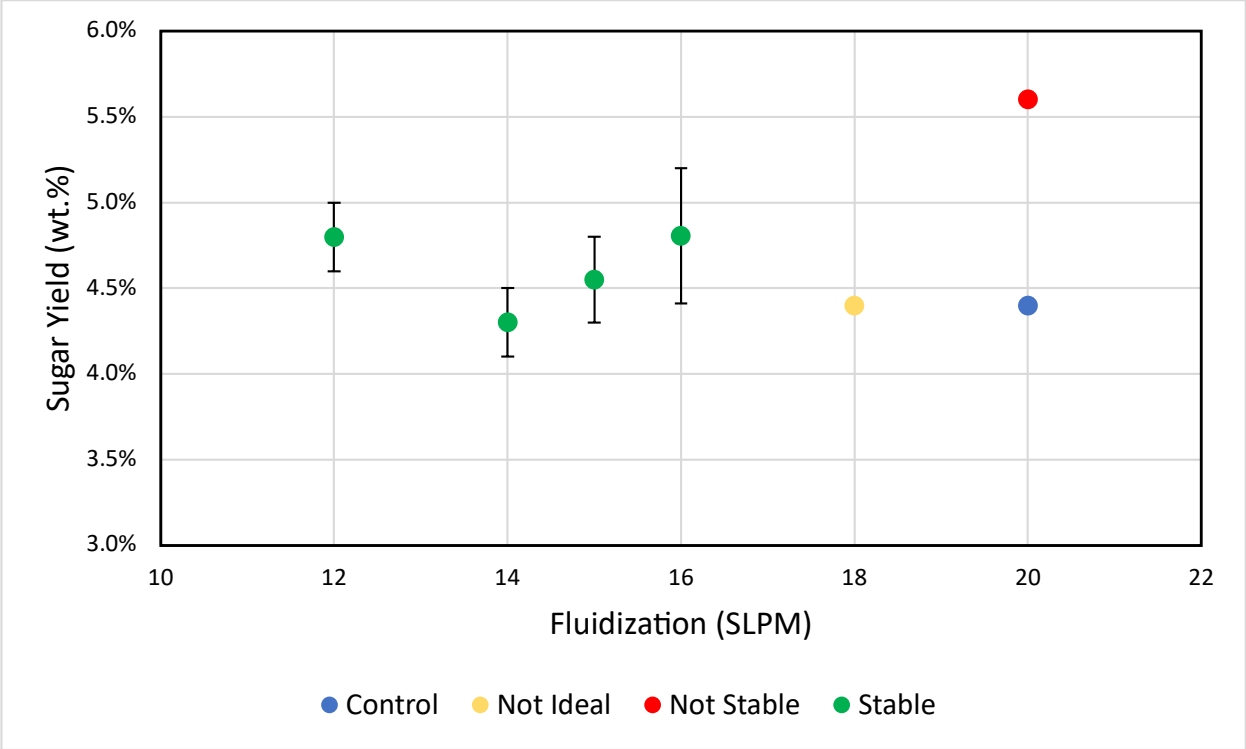

Figure 4.5 Sugar yield comparison to the different fluidization velocities used during the above bed feeding tests. Red points (●) (6 and 20 SLPM) represent tests that failed due to temperatures falling below or above the acceptable safety range. The yellow point (●) (18 SLPM) shows a test that had temperatures drop below ideal running conditions but still able to continue. Green points (●) (12-16 SLPM) show tests that are stable and do not have issues with temperature or fluidization. The blue control point (●) (20 SLPM) is a test that was performed under the original in-bed configuration.

Feeding biomass from the top of the reactor creates a residence time change that can account for some increased yields. As previously shown in Table 3.1, the above bed feeding configuration had greatly reduced residence times compared to the control in-bed 20 SLPM configuration. The difference in residence time is expected to impact the extent of sugar

degradation due to secondary reactions. Knowing the difference in height from the original configuration to the top feeding reactor position, we calculated a residence time decrease by approximately 0.43 seconds in the above bed configuration at the optimal 12 SLPM of fluidization compared to a 12 SLPM in the in-bed feeding configuration. Given the fluidization rate and levoglucosan decomposition rate of 0.21 s^{-1} at 500°C [57], 0.4% of the levoglucosan increase in the above bed feeding reactor could be due to the reduced residence time. Accounting for the sugar from the change of residence time would change the control test sugar yield to be nearly the same as the 12 SLPM sugar yield. This helps explains why some of the overall sugar and oil yields are improved. However, this change in residence time doesn't account for the measured difference. Thus, our hypothesis of changing to the injection point to minimize biochar interaction is confirmed. However, although there is evidence of increased sugars, more testing may need to be performed to determine more conclusive results.

4.3.1 High Injection Product Analysis

The products of each test were thoroughly analyzed to get a better understanding of which tests performed best. Bio-oil was analyzed for acid content to see if some of the increased bio-oil could be further explained, as seen in Figure 4.6. In general, the yield of acetic acid is generated from the decomposition of hemicellulose. Glycolate and formate acids, on the other hand, are formed from the pyrolysis of mostly cellulose and some hemicellulose. Although there are no significant differences between the fluidizations, it could be said that there was a slightly better decomposition in the 12 and 16 SLPM tests as these resulted in the greatest overall acid yield. However, due to the majority of the acids resulting in similar yields, it would appear as though the majority of the hemicellulose and cellulose is being fully decomposed during testing.

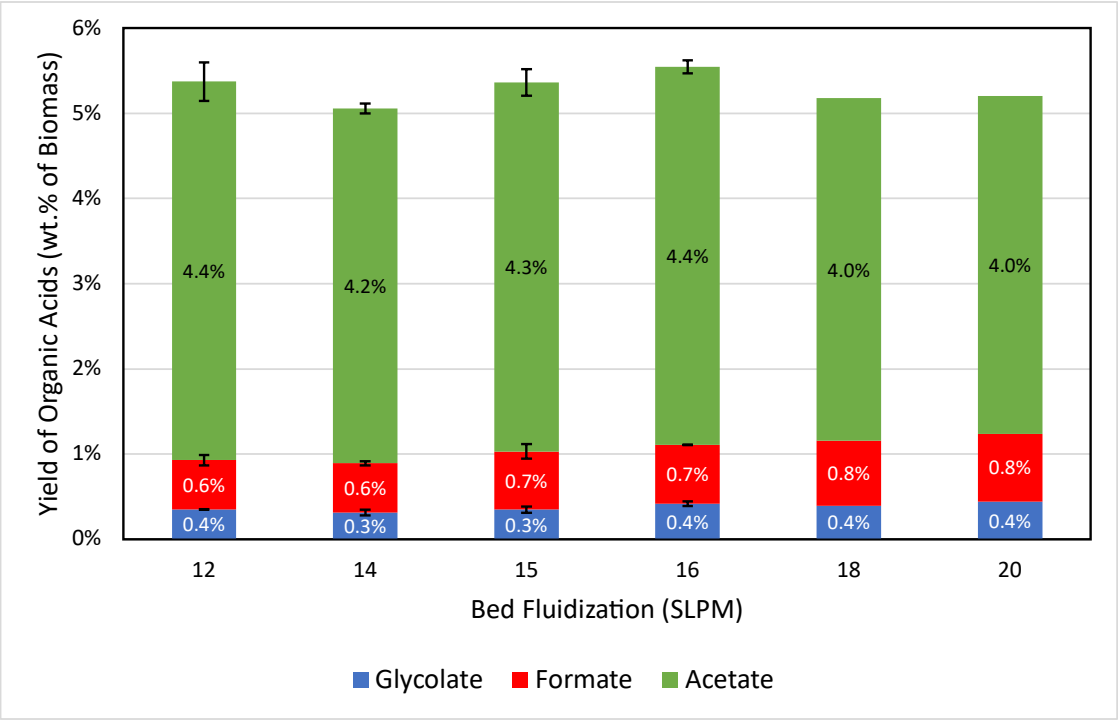

Figure 4.6 Effect of different fluidization rates on the decomposition of products to acids.

Analysis of the water-soluble fraction of bio-oil gave a good understanding as to why some tests resulted in a better sugar yield. As seen in Figure 4.7, the 12 SLPM condition resulted in a higher water-soluble sugar fraction. This coincides with what was seen previously with this test having a high overall sugar composition. Although the 16 SLPM run previously resulted in the same average sugar yield as the 12 SLPM test, there was an 11% difference between the water-soluble sugars here. Also, it is important to note the 19% and 43% increase in phenolic oil and water-soluble sugars, respectively, over the control in-bed test. This increase helps explain the overall increased yield found over the control case. Therefore, it could be said that 12 SLPM is the best overall condition for the high injection configuration to give a higher sugar-yielding bio-oil.

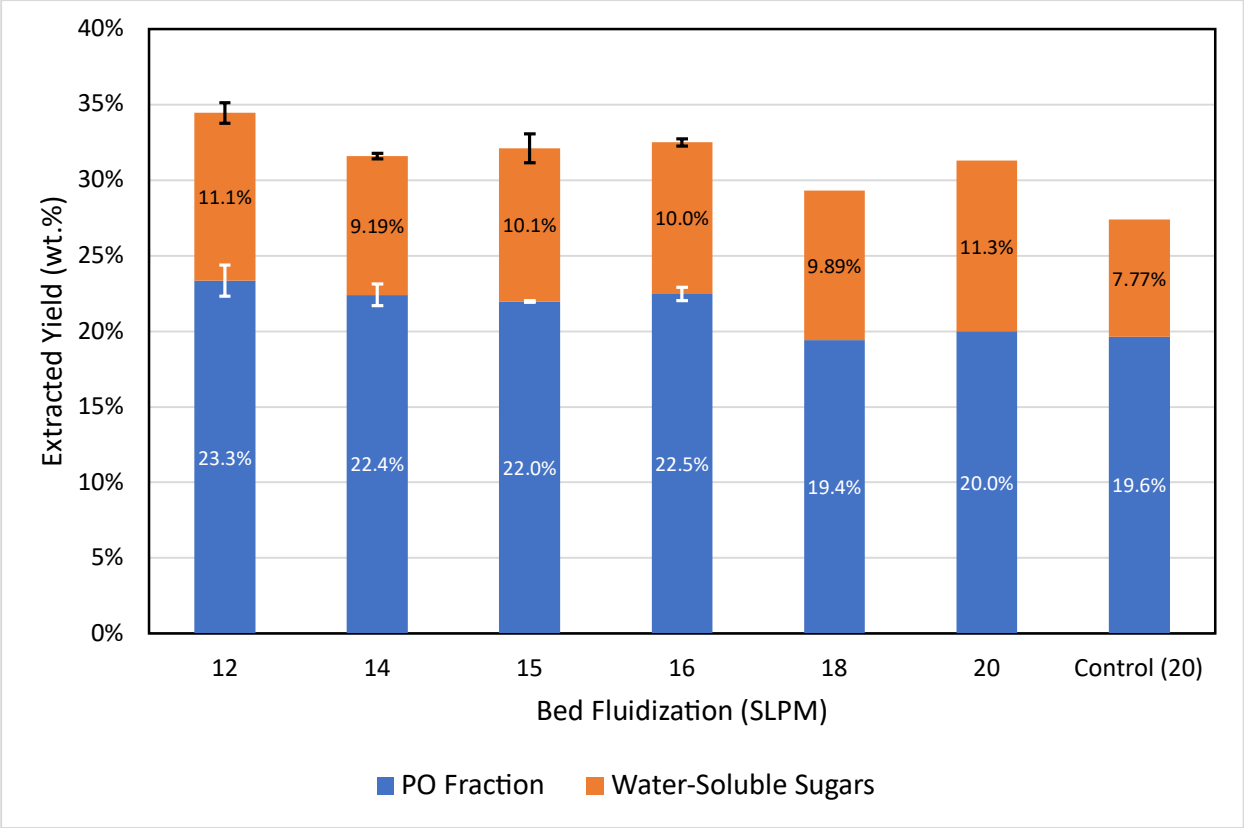

Figure 4.7 Effect of bed fluidization on the extractable yield of phenolic oil and water-soluble sugars

Proximate analysis of the biochar gave a complete view of how biomass was decomposing inside the reactor and whether or not the biochar was devolatilizing completely. As seen in Figure 4.8, fixed carbon decreases slightly as volatiles increase from 12 to 15 SLPM. This suggests that the biochar spends enough time in the fluidized bed to devolatilize more completely. The overall yield from 16 to 20 SLPM increases drastically, which could be due to the overall higher biochar mass yield seen in Figure 4.9. Increased biochar yield in these tests could be due to higher fluidization rates which result in biochar being entrained out of the reactor more quickly and not fully devolatilizing. For the 12 SLPM case, volatiles represented approximately 30% of the biochar collected, while the control had a 37% biochar volatile content. Therefore, it can be reasoned that the top of bed injection allows biochar to more

completely devolatilize while still allowing vapors to escape more easily with fewer secondary reactions.

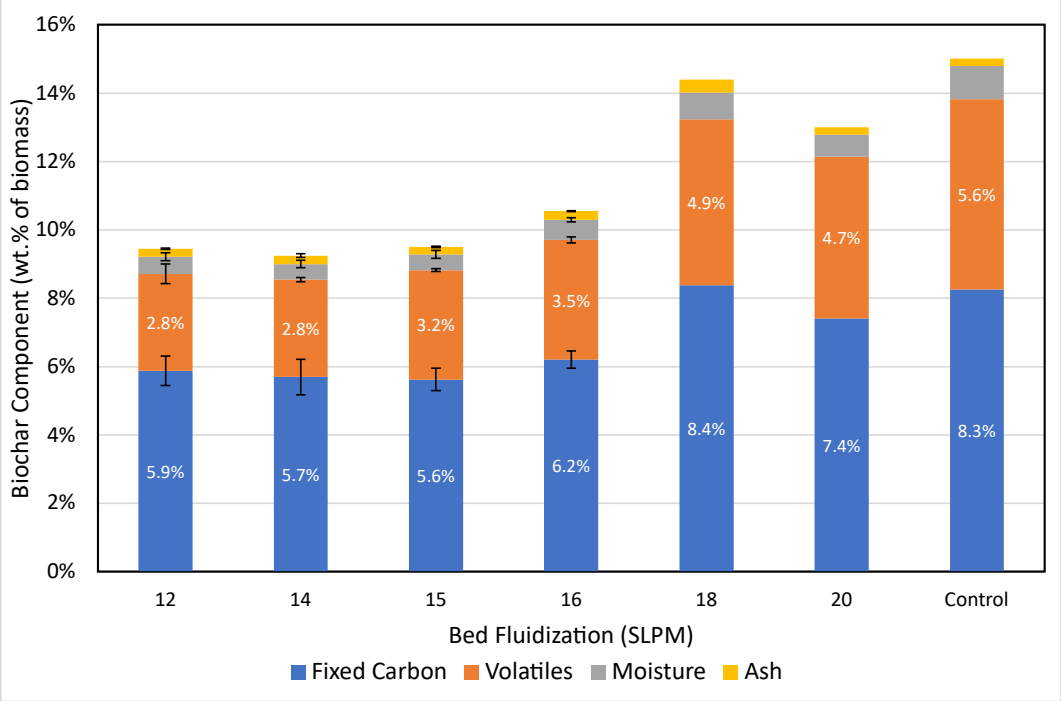

Figure 4.8 Impact of bed fluidization on the amount of biochar components present. Control test is at 20 SLPM in-bed injection.

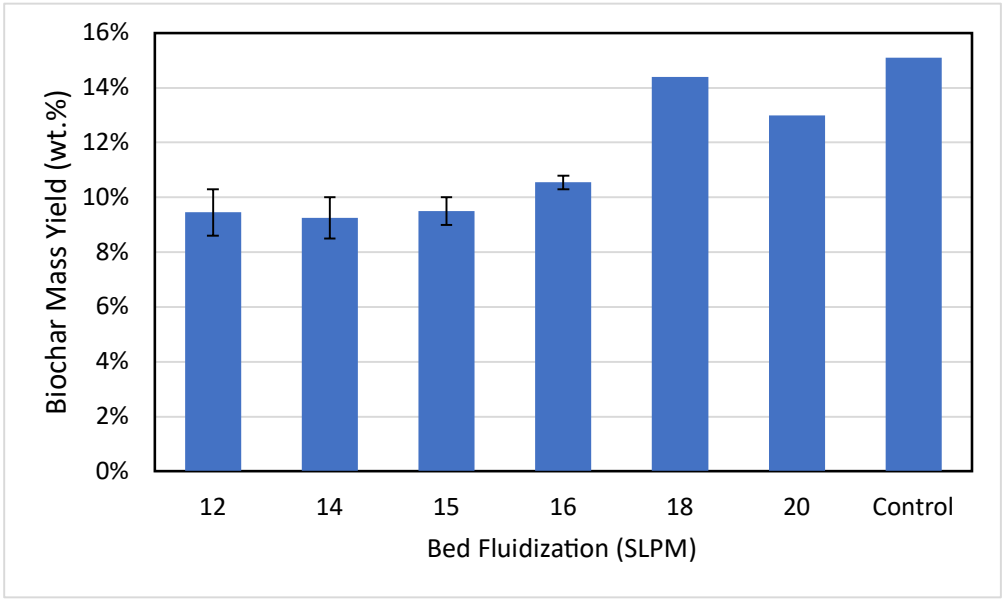

Figure 4.9 Mass yield of biochar throughout different in-bed injection tests. Control was performed at 20 SLPM with in-bed injection.

CHAPTER 5. CONCLUSIONS

The thermal and catalytic activity present in the biochar plays a significant role in degrading the pyrolytic vapors being released during fast pyrolysis. Micropyrolysis experiments showed that biochar negatively impacted the levoglucosan yield. It also allowed the importance of biomass pretreatment to be more noticeable as there was a 52.8% decrease in levoglucosan levels during the mixed and layered testing from iron-rich biochar to untreated biochar. This led to a hypothesis that biomass feed location could help reduce the negative biochar implications with pyrolysis vapors. Full scale reactor testing indicated testing in the conventional (in-bed) configuration caused biochar to interact with vapors too long and reduce sugar and oil yield. By feeding red oak biomass over the fluidized bed, some of the negative implications of biochar were reduced. Biochar was still retained in the reactor long enough for the autothermal process to run successfully but not causing secondary reactions to the pyrolytic vapors as extensively. This allowed for the sugar yield in the bio-oil to increase while maintaining optimal temperature running conditions in the modified reactor.

A complete product analysis gave a complete understanding of how some tests gave more promising results. Higher water-soluble sugars in the bio-oil with lower overall volatile content in the biochar show that the 12 SLPM condition is an ideal fluidization for over bed injection. Not only do the running temperatures stay within the ideal bio-oil levels, but biochar seems to be interacting less with pyrolytic vapors. This allows for the sugar and bio-oil yield to increase compared to the conventional fluidized bed running conditions.

The full extent of secondary reactions due to biochar has yet to be fully explored; therefore, further work will be required to entirely understand how crucial it is to limit the biochar and vapor interaction. This could be explored with more biochar and vapor residence time kinetics to see how much contact between the two degrades the products. Furthermore, if a biochar and pyrolytic vapor residence time was able to be determined within a fluidized bed reactor, we could then give an accurate depiction as to why it is so important to remove vapors quickly from the reactor and limit the biochar interaction.

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