

## **The role of catalytic iron in enhancing volumetric sugar productivity during autothermal pyrolysis of woody biomass**

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### **Abstract**

Passivation of naturally occurring AAEM in biomass enhances sugar yields from the fast pyrolysis of biomass by preventing these metals from catalyzing the fragmentation of pyranose rings in cellulose and hemicellulose. However, because AAEM also catalyzes lignin depolymerization, its passivation can be accompanied by undesirable char agglomeration. Pretreatment of biomass with ferrous sulfate both passivates AAEM and substitutes ferrous ions as lignin depolymerization catalysts. This pretreatment has been particularly successful for high ash biomass like corn stover, but of limited value for low ash biomass like wood. This study explores the reasons for this discrepancy and offers a combined pretreatment of ferrous sulfate and ferrous acetate pretreatment to overcome char agglomeration in wood. This new pretreatment increased sugar yields from 4.4 wt.% to 15.5 wt.% and 5.4 wt.% to 19.0 wt.% for hardwood and softwood biomasses, respectively. This pretreatment produces an iron-rich biochar that catalyzes oxidation of the biochar under the oxygen-rich conditions of autothermal pyrolysis, which is preferentially consumed to provide the enthalpy for pyrolysis, preserving bio-oil as a more desirable energy product. Instead of producing carbon monoxide, which dominates oxidation of biochar from untreated biomass, the iron catalyzes oxidation to carbon dioxide, producing more energy per mole of oxygen consumed. In fact, oxygen demand to support

autothermal pyrolysis of red oak and southern yellow pine was reduced 15% by the presence of iron in the biochar.

## **1. Introduction**

Wood is an important feedstock for second generation bio-refineries. Currently, the majority of wood harvested is used in the pulp and lumber industries (225 MT).[1] However, pulp processing waste and enhanced harvesting techniques could readily provide an additional ~100 MT of waste feedstock for use in these bio-refineries.[2] Another ~100 MT of dedicated woody biomass could be available each year by 2030 if demand is sufficient.[3] Due to years of fire prevention in the nation's forests, the U.S. Forest Service estimates there are 8.4 billion tons of excess material that places U.S. forests at high risk for massive wildfires.[4] This biomass could be employed in the production of biofuels and biobased chemicals.

The main components of woody biomass are the polysaccharides cellulose and hemicellulose. Whole biomass is resistant to deconstruction for a number of reasons. Among the most prominent is the protective sheath of branched phenolic compounds called lignin. The goal of most biomass conversion technologies is to liberate carbohydrates as fermentable sugars. Various technologies have been developed to achieve this. Current commercial systems employ thermal and/or chemical pretreatments followed by enzymatic hydrolysis to produce glucose and xylose, with yields approaching 100% in the laboratory.[5,6] This process requires several days to complete, leading to massive production facilities at commercial scale.[7]

Through the use of high temperatures, around 500 °C, biomass can be quickly deconstructed in a process called fast pyrolysis, potentially leading to significant process intensification.[8] Due to the lack of product selectivity and low yields of sugars, fast pyrolysis has received little attention as a method to produce fermentable sugars, but the recent

developments of pretreatments that enhance pyrolytic sugar production give encouragement to the idea.[9,10]

As a result of its lower ash content, higher lignin content, and relatively high bulk density, woody biomass is often thought to be a more suitable feedstock for pyrolysis than herbaceous feedstocks (e.g., corn stover and switchgrass). The low ash content of woody feedstocks reduces equipment wear while producing more bio-oil containing less water and more organic liquid compared to herbaceous feedstocks.[11,12] Likewise, the yield of valuable anhydrosugars is much higher from woody biomass than herbaceous biomass.[13] This enhanced sugar yield arises not only from the higher cellulose content of wood but its lower ash content compared to most herbaceous biomass. During fast pyrolysis, naturally occurring alkali and alkaline earth metals (AAEM) in biomass catalyze fragmentation of pyranose rings,[14,15] dramatically reducing the yield of sugars that otherwise would be produced during pyrolysis. Potassium, the most catalytically active of these metals, is more abundant in herbaceous biomass,[16] further enhancing differences in sugar yields for woody and herbaceous biomass. Water extraction or acid infusion of biomass can be effective in removing or passivating AAEM, resulting in enhanced sugar yields upon pyrolysis.[17,18] Acid passivation of herbaceous and woody biomass has achieved sugar yields from pyrolysis comparable to pure cellulose.[10] With appropriate filtering to remove phenolic contaminants and hydrolysis of the anhydrosugars to monosaccharides, the sugars are readily fermented.[19]

Acid pretreatment has the drawback of causing char agglomeration during pyrolysis, compromising reactor operability.[13,20–22] Recent work in our laboratory[23] has shown that pretreating corn stover with ferrous sulfate can greatly increase yields and volumetric productivity of pyrolytic sugar without promoting char agglomeration. We found that the sulfate

anions of this salt passivate AAEM while the ferrous cations restore catalytic depolymerization of lignin lost upon passivation of AAEM, which is important in preventing melting and agglomeration of lignin. In the absence of AAEM or ferrous cations, lignin deconstructs more slowly than it melts, producing a liquid that dehydrates into char agglomerates instead of fine particles.[23] Ferrous ions appear to have little or no detrimental effect on polysaccharide depolymerization; thus sugar yields comparable to those achieved through sulfuric acid pretreatment are possible.[23,24] The combination of ferrous sulfate pretreatment and autothermal pyrolysis resulted in orders of magnitude increases in volumetric sugar productivity from the pyrolysis of corn stover (defined as sugar yield multiplied by biomass throughput divided by fluidized bed volume).[23]

Ferrous sulfate pretreatment yields iron-rich biochar. Because iron is a well-known oxidation catalyst,[25] its presence has important implications for autothermal operation of pyrolyzers, an emerging approach for process intensification in thermochemical processing.[26,27] Autothermal pyrolysis introduces a small amount of oxygen into the reactor for the purpose of internally providing the enthalpy of pyrolysis through partial oxidation of pyrolysis products. Our previous work on autothermal pyrolysis of untreated woody biomass found a small loss of carbon from the heavy ends of bio-oil, which contains high value phenolic compounds and sugars.[26] Fast pyrolysis of untreated corn stover under similar autothermal reaction conditions experienced no loss in carbon from the heavy ends.[27] Peterson et al.[28] found this effect was due to the higher AAEM content of corn stover, which enhanced oxidation of char compared to the bio-oil vapors. Passivation of AAEM with sulfate is likely to reduce its effectiveness as an oxidation catalyst. Thus, ferrous iron is expected to not only catalyze lignin depolymerization but enhance oxidation of char during autothermal pyrolysis.

In his study of char oxidation, Peterson et al.[28] observed that AAEM catalyzed a shift in gas production from carbon monoxide to carbon dioxide. Because the oxidation of char to carbon dioxide releases several times more energy than does oxidation to carbon monoxide, the amount of oxygen required to support autothermal pyrolysis is expected to be significantly reduced as the ash content of the biomass increases. Accordingly, if ferrous iron proves to be an effective oxidation catalyst for autothermal pyrolysis, operation at lower equivalence ratios should be possible through pretreatment of woody biomass.

A previous study by Richards et al.[24] investigating the effect of copper and iron salts on thermochemical processing of woody biomass identified ferrous sulfate as an effective catalyst for increasing sugar yields, which they mistakenly attributed to the interaction of ferrous cations and lignin rather than the passivation of AAEMs by the sulfate anions. They noted that “the sample erupted from the pyrolysis boat” at high pyrolysis temperatures, which suggests the sample was melting and bubbling. Although only revealed in a footnote and not fully investigated,[24] we surmise from this observation that their ferrous sulfate pretreatment did not provide enough ferrous cations to prevent agglomeration during pyrolysis of the wood samples. Our preliminary work on pyrolysis of ferrous sulfate pretreated wood suggested the same thing.

We hypothesize that the inadequacy of ferrous sulfate pretreatment of wood to prevent char agglomeration is the result of its incomplete ionic dissociation and ion exchange with AAEM bound to lignin. The pretreatment involves spraying an aqueous solution of ferrous sulfate on the biomass where it diffuses into the interior of the biomass. Effective pretreatment requires ferrous cations to ion exchange with AAEM cations bound to the lignin, a thermodynamically favorable reaction. The AAEM cations combine with the sulfate anions to form thermally stable salts while the ferrous cations bound to the lignin are catalytically active

toward lignin depolymerization during pyrolysis. Ferrous cations not exchanged with AAEM cations remain bound to sulfate anions as thermally stable salt, passivating their catalytic activity. Accordingly, biomass with intrinsically low AAEM content will be unable to exchange enough ferrous ion into the lignin to be effective in catalyzing lignin depolymerization. An alternative method is needed to introduce a ferrous salt into the wood that decomposes at pyrolysis temperatures, making the ferrous cation available as a lignin depolymerization catalyst.[10] We have identified ferrous acetate, with a decomposition temperature of around 200°C compared to 680°C for ferrous sulfate, as a suitable salt.

This study investigates why ferrous sulfate pretreatment, which is so effective in preventing char agglomeration during pyrolysis of herbaceous biomass, fails to prevent agglomeration during pyrolysis of woody biomass. We explore the hypothesis that ferrous sulfate pretreatment does not supply enough catalytically active metal cations into woody biomass to effectively depolymerize lignin, resulting in char agglomeration. We propose the supplemental addition of ferrous ions into low ash biomass (wood) in the form of ferrous acetate to prevent char agglomeration. We also explore the possibility that addition of ferrous iron enhances biochar oxidation, reducing the amount of oxygen required to support autothermal pyrolysis of the biomass.

## **2. Material and Methods**

### **2.1 Pretreatment methods**

Biomass used in this research included red oak (*Quercus rubra*), hybrid poplar (*Populus deltoides x Populus nigra*), willow (*Salix caprea*), southern yellow pine (*Pinus echinata*), douglas fir (*Pseudotsuga menziesii*), switchgrass (*Panicum virgatum*), wheat straw (*Triticum aestivum*), miscanthus (*Miscanthus giganteus*), and corn stover (*Zea mays L.*).

For micropyrolysis experiments, biomass was milled to a powder (< 50  $\mu\text{m}$ ) in a Retsch planetary ball mill. Powdered biomass (250 mg) was weighed and transferred to a 50 mL glass beaker to which the desired amounts of ferrous sulfate (Alfa Aesar) and ferrous acetate (Fischer Scientific) were added. Deionized (DI) water in the amount of 25 mL was then added, and the samples mixed for 4 hours before drying overnight at 105  $^{\circ}\text{C}$ .

For experiments in a continuous, bubbling fluidized bed, biomass was knife milled to 1.5 mm. The pretreatment solution was prepared by mixing ferrous sulfate and water or via the ferrous acetate production method described in section 2.4. This solution was slowly sprayed on the biomass as it was agitated in an ERWEK paddle mixer. After mixing, the biomass was dried at 105  $^{\circ}\text{C}$  until the moisture content was below 10%. Further details on pretreatment of biomass can be found in Rollag et al.[23]

Inductively Coupled Plasma with Optical Emission Spectroscopy (ICP-OES), described in Section 2.5, was used to quantify the AAEM content of each kind of biomass. This information was used to calculate the amount of ferrous iron required for stoichiometric replacement of AAEM during pretreatment. Table 1 shows the pretreatment levels used for each feedstock. For high ash feedstocks, the treatment level was rounded up to the nearest 0.5 wt.% to

Table 1. Ferrous sulfate pretreatment levels for various kinds of biomass tested. A minimum treatment of 1 wt.% was applied to low ash biomass.

<i>Biomass</i>	AAEM ash content (mmol/g)	Ferrous sulfate (wt.% biomass basis)
<i>Red Oak</i>	0.088	1.0
<i>Hybrid Poplar</i>	0.079	1.0
<i>Willow*</i>	0.321	8.0
<i>Southern Yellow Pine</i>	0.066	1.0
<i>Pine Forest Thinnings*</i>	0.155	4.0
<i>Douglas Fir</i>	0.028	1.0
<i>Switchgrass</i>	0.263	5.0
<i>Wheat Straw</i>	0.475	10.0
<i>Miscanthus</i>	0.227	4.0
<i>Corn Stover</i>	0.431	7.5

*\*Material contained bark*

ensure complete passivation of AAEM. For low ash biomass, ferrous sulfate treatment levels were set at 1 wt.%, which is significantly above the stoichiometric requirement to passivate AAEM in the feedstock but simplifies pretreatment and causes no detrimental effects on sugar production.[23]

## **2.2 Bubbling fluidized bed pyrolyzer**

The 3.8 cm dia. bubbling fluidized bed pyrolyzer employed in this study was previously described by Rollag et al.[23] Bed material consisted of 250 grams of 16/30 mesh silica sand. The reactor utilized a biomass feed system capable of continuous feed rates from 50 g/h to 2500 g/h through the use of two different diameter metering augers, one providing 50 – 1000 g/h feed rates with the other providing 250 - 2500 g/h feed rates. This metering auger was followed by a constant speed injection auger to quickly and smoothly convey biomass into the electrically heated fluidized bed reactor. Fluidizing gas flow was maintained at 20 standard liters per minute (SLPM) for all experiments. However, equivalence ratios could be varied through various combinations of pure nitrogen and air. For all experiments the electric heaters were used solely to overcome parasitic heat losses and did not provide the enthalpy for pyrolysis, which was provided through admission of sufficient air to achieve autothermal operation as described by Polin et al. [26]

Product separation was performed in stages, with two gas cyclones removing solid particles, mainly biochar and a small amount of fine sand elutriated from the fluidized bed. Vapor collection was accomplished in multiple stages, beginning with a heat exchanger that lowered the temperature from 500°C to 120°C to condense phenolic compounds and anhydrosugars, which were collected as stage fraction 1 (SF1). Aerosols generated during condensation were recovered at 120°C as stage fraction 2 (SF2) using an electrostatic

precipitator (ESP). The vapors entered another heat exchanger where they were cooled in a second condenser to around 10°C followed by an ESP to produce stage fractions SF3 and SF4, respectively. The SF1 and SF2 products, referred to as heavy ends, are composed of phenolic compounds and sugars. Products collected in SF 3 and SF 4, referred to as light ends, consist of water and low molecular weight oxygenated compounds (mostly acetic acid). Non-condensable gases (NCG) flowed through a desiccant trap to remove any remaining moisture before passage through a wet test meter. This gas stream was periodically sampled by a Varian (CP-4900) micro gas chromatograph (GC) to determine gas composition using two separate columns a Molsieve (CP740148) and a PoraPLOT U (CP740152).

Sustainable operation, regardless of the feedstock used, was determined as the maximum biomass feed rate that could be maintained for 30 minutes without fouling the fluidized bed. This determination involved starting the biomass feed rate at 250 g/h and increasing it by 250 g/h every 30 minutes until symptoms of unstable system operation were evident. These symptoms included large temperature fluctuations within the bed (due to agglomerate formation); rapidly increasing system pressure (due to char agglomerates constricting gas flow in the fluidized bed) or exceeding the maximum condensation rate of the bio-oil collection system (typically occurring for biomass feed rates above 2500 g/h). During the feed rate ramp the equivalence ratio (ER) was held at 10% until a feed rate of 1000 g/h was reached. Feedstock specific ERs for autothermal operation were then determined by adjusting the amount of oxygen in the fluidizing gas until heater power matched the level required to just overcome parasitic heat losses, as described by Polin et al. [26] The feed rate ramp continued above 1000 g/h at the new ER. Once operational parameters were established for each feedstock, a second pyrolysis trial was conducted for each feedstock at feed rates of 500 g/h for 20 minutes, ramping to 1000 g/h for 50

minutes, followed by system shutdown. Yields of bio-oil, biochar, and NCG and bio-oil composition were determined for these standard runs.

### **2.3 Micropyrolysis experiments**

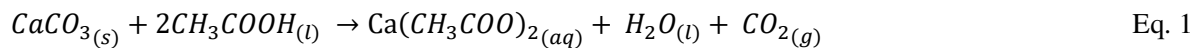
A conventionally operated 3030D Frontier micropyrolyzer coupled to a gas chromatograph (GC) (Agilent 7890 GC) was used to investigate the composition of vapor products from pyrolysis of pretreated biomass. The Agilent GC system utilized two separate 60 m x 0.25 mm ID capillary columns (Phenomenex DB-1701 fused silica 0.25  $\mu\text{m}$  film thickness) connected to two kinds of detectors. Identification of products was done via mass spectroscopy (Agilent 5975C GC/MSD). Quantification of yields was accomplished through the combination of a PolyARC® system (Activated Research Company) and flame ionization detector that used an internal phenanthrene standard.

For studying changes in the solid phase of biomass during pyrolysis, a Controlled Pyrolysis Duration-Quench (CPD)-Quench system described by Lindstrom et al.[29] was used. The system is capable of rapidly heating a biomass sample following a well characterized temperature profile [30] and quenching reactions in the condensed-phase sample after a prescribed time. A computer-controlled mechanical arm lowered samples into the furnace of a 3030D Frontier micropyrolyzer modified to allow ejection of sample cups from the bottom of the furnace after a prescribed period of time. By changing dwell time of a sample in the furnace, the final sample temperature could be controlled, allowing different thermal stages of pyrolysis to be investigated. After holding the sample for the defined time (2 – 3 s) the sample cup was automatically released from the mechanical arm and fell by gravity into a chilled glass vessel where further condense-phase reaction was rapidly quenched. Sample cups contained an

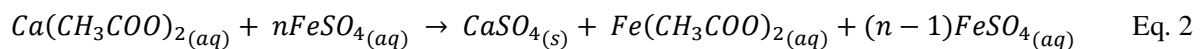
aluminum liner that eased removal of melted samples and served as sample holders for subsequent SEM analysis.

## 2.4 Production of iron acetate

Ferrous acetate was synthesized in the laboratory to provide the relatively large quantities needed to pretreat biomass used in continuous pyrolysis experiments subsequently described. Limestone acquired from ILC Resources was reacted with glacial acetic acid (Fischer Scientific) in a solution of DI water to produce calcium acetate:



Once the limestone had completely reacted and off gassing from the solution ceased, ferrous sulfate (BeanTown Chemical) was added to the solution to produce ferrous acetate:



Ferrous sulfate was added in excess ( $n$  greater than 1 in Equation 2) to achieve a product solution containing ferrous sulfate in sufficient quantity to fully passivate AAEM in the biomass and ferrous acetate as a supplementary source of ferrous cations for the purpose of catalytically depolymerizing lignin in the biomass. As an example, for a pretreatment containing 1 wt.% ferrous acetate and 1 wt.% ferrous sulfate the value of  $n$  is 2.145. Ferrous sulfate and ferrous acetate are highly soluble in water while the calcium sulfate by-product is insoluble, which was removed by filtration. Magnesium acetate can also be used to produce ferrous acetate and has the advantage of the magnesium sulfate byproduct being water soluble, eliminating the filtration step. However, all experiments reported in this paper used calcium acetate as reactant in the production of ferrous acetate.

## **2.5 Inorganic ash analysis**

The AAEM content of the biomass samples was measured via ICP-OES (PerkinElmer Optima 8000) using a method described by Chi et al.[31] Biomass was mixed with 20 wt.% nitric acid and placed in Teflon-lined reactor vessels. The mixtures were heated in a microwave oven for 15 minutes. The digested samples were diluted 10,000x with DI water to achieve concentrations within the ICP calibration curve. All biomass types were tested in duplicate.

## **2.6 Pyrolytic sugar analysis**

Sugar analysis was accomplished through acid hydrolysis of SF1 and SF2, which contain more than 90% of the sugars and anhydrosugars produced during pyrolysis,[32] using the method developed by Bennet et al.[33] The process involves mixing a small amount (60 mg) of bio-oil into a solution of 400 mM sulfuric acid (6 mL) and heating in a sealed vessel to 125 °C for 44 minutes, followed by rapid cooling. After hydrolysis, the solution was syringe filtered through 0.45 µm Whatman filters into glass vials. The concentration of glucose and xylose was then determined by high performance liquid chromatography (HPLC) using a Dionex Ultimate 3000 series HPLC with DI water mobile phase and refractive index detector. The combined SF1 and SF2 yield of sugar represented the total yield of sugar for the experiment.

## **2.7 Scanning electron microscopy**

Scanning electron microscopy (SEM) was used to image char particles. Char samples were prepared by mounting them on conductive carbon tape followed by sputter coating with 5 nm of iridium (Quorum Q150TS). Samples were then loaded into a FEI Quanta 250 field emission SEM and the chamber was pumped down to high vacuum. A 10 keV electron beam was used to provide a signal to the secondary electron and backscattered electron detectors.

### 3. Results and discussion

#### 3.1 Continuous pyrolysis of acid pretreated woody biomass and herbaceous biomass

Initial testing was performed with 0.5 wt.% sulfuric acid pretreated red oak pyrolyzed in the bubbling fluidized bed reactor to establish baseline operability. The maximum sustainable feed rate for sulfuric acid pretreated red oak was only 100 g/h, which is even lower than achieved with sulfuric acid pretreated corn stover. [23]

The pyrolysis of acid pretreated red oak yielded char particles with smooth surfaces, clear evidence that the lignin melted during pyrolysis, while the acid pretreated corn stover produced char that retained the porous surface of the original biomass (see Fig. 1 and supplement materials

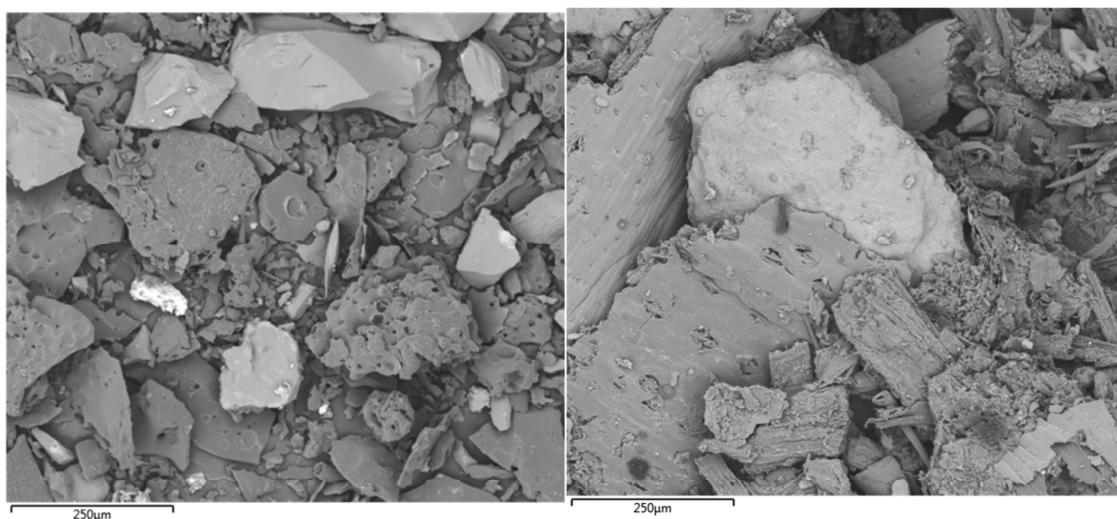


Figure 1. SEM micrographs of 0.5 wt.% sulfuric acid pretreated red oak biochar (left) and 3.5 wt.% sulfuric acid pretreated corn stover biochar (right). The lighter fragments are composed of silica and result from the bed sand fracturing. The darker fragments are carbon-rich biochar. Corn stover fragments retain identifiable cell wall structure while red oak appears as smooth surfaces pocketed with voids.

Fig. A). This difference is somewhat surprising considering that both produced agglomerated char. These differences likely arise from differences in the homogeneity of the two kinds of biomass. Red oak particles are primarily heartwood, which yields particles that closely resemble

one another and likely have similar composition. Corn stover, on the other hand, includes every plant part from tassel to brace roots, excepting the kernels. Each of these parts has distinct structure and chemical composition. The lignin in some of these plant parts melt and participate in agglomeration while other plant parts do not melt.

We attempted to overcome agglomeration of red oak by substituting ferrous sulfate for sulfuric acid in the same manner that successfully prevented char agglomeration during pyrolysis of pretreated corn stover.[23] However, very quickly ferrous sulfate pretreated red oak produced char agglomerates that plugged the reactor when feed rate exceeded 250 g/h (at lower feed rates, char attrition and elutriation were able to keep pace with char agglomeration). While an improvement over the baseline test with sulfuric acid, ferrous sulfate pretreatment of red oak did not eliminate char agglomeration of this woody feedstock. We increased ferrous sulfate pretreatment of red oak from 1 wt.% to 7.5 wt.%, which is the level that successfully passivated AAEM and prevented char agglomeration in high ash corn stover.[23] Despite this several fold increase in the amount of ferrous sulfate added to the wood, sustainable operation was still limited to only 250 g/h. We realized that ferrous sulfate was ineffective in delivering ferrous cations to lignin in wood when further increasing pretreatment levels to 20 wt.% ferrous sulfate did not overcome char agglomeration.

The ineffectiveness of ferrous sulfate pretreatment demonstrates its dependence upon dissociation of the salt into catalytically active ferrous cations and sulfate anions, a process that is thermodynamically favorable in the presence of naturally occurring AAEM cations in biomass. The ferrous cations ion exchange with the AAEM cations in the biomass where they serve as an alternative lignin depolymerization catalyst while the sulfate anions react with AAEM cations to form thermally stable and catalytically inactive salts (see Fig. 2A). In high ash

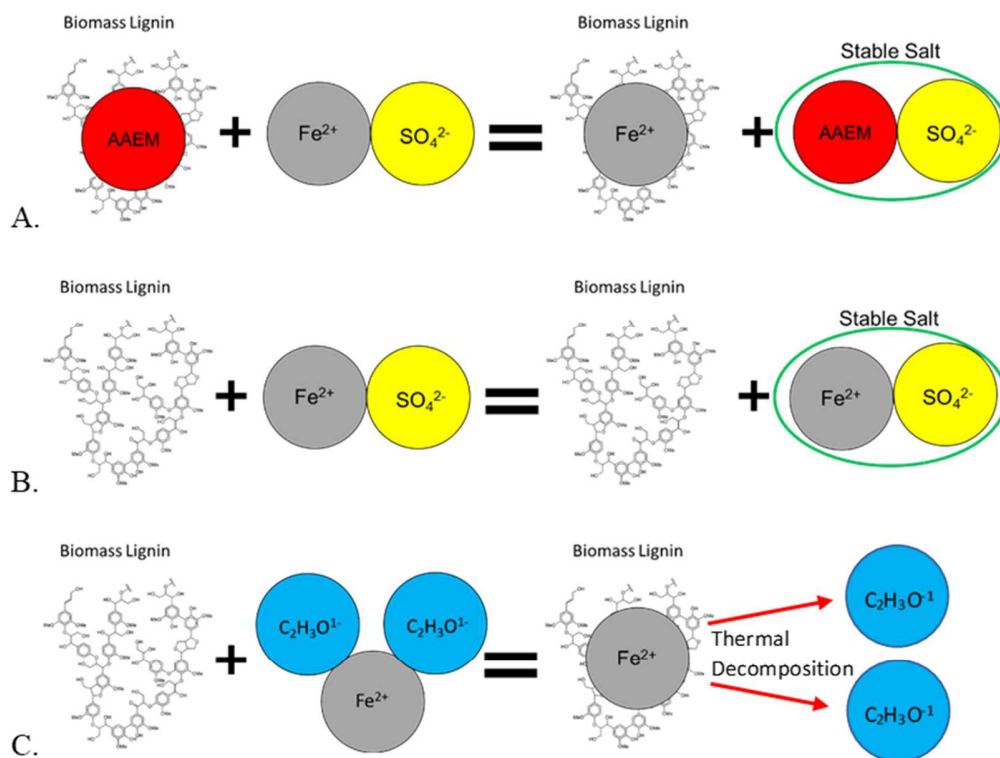


Figure 2. Proposed reaction mechanisms of pretreatment of low ash biomass with ferrous sulfate. (A) Ion exchange of ferrous with AAEM forming thermally stable sulfate salt and active catalytic iron. (B) Lack of biomass AAEM prevents ferrous sulfate from separating and it remains and catalytically inactive ferrous sulfate. (C) Proposed method of introducing active iron catalyst when no AAEM is present by thermal decomposition of ferrous acetate to free up ferrous catalyst.

biomass like corn stover there are sufficient AAEM cations to exchange enough ferrous cations into the biomass to effectively depolymerize lignin during pyrolysis. However, once all the AAEM cations have been ion exchanged and passivated as sulfate, no further infusion of ferrous cations into the biomass is possible, but instead exists as thermally stable and catalytically inactive ferrous sulfate (See Fig. 2B). This is what occurred in the red oak when it was pretreated at 7.5 wt.% and 20 wt.% ferrous sulfate.

We hypothesize that increasing the loading of catalytically active ferrous cations into low ash wood biomass beyond what can be achieved via ion exchange with AAEM requires pretreatment with a ferrous salt that is not stable at pyrolysis temperatures. Its thermal

decomposition releases ferrous cations that are catalytically active toward depolymerizing lignin. A good candidate for this role is ferrous acetate, which decomposes at temperatures as low as 150° C, releasing ferrous cations to the biomass (see Figure 2C). For the purpose of this study, we have termed the combined total of iron exchanged with AAEM and iron introduced as ferrous acetate as ferrous catalyst measured in mmole/g.

### **3.2 Impact of ferrous acetate on depolymerization of lignin in wood biomass**

Understanding the effects of ferrous pretreatment on lignin depolymerization in different biomass feedstocks is important to commercial applications of the process. Red oak, southern yellow pine, and corn stover were selected as representative of hardwood, softwood, and herbaceous biomass, respectively. Although hardwood and softwoods are both low ash feedstocks compared to corn stover, the composition of the lignin is distinct for these two kinds of woody biomass. Specifically, hardwood lignin consists up to 16% syringyl while softwoods contain virtually no syringyl.[34]

The CPD-quench system was used to determine the amount of ferrous catalysts that prevented melting of lignin during pyrolysis of red oak and southern yellow pine. Baseline ferrous catalyst loading was 0.07 mmole/g red oak and 0.06 mmole/g southern yellow pine, the theoretical amount ferrous catalyst introduced to the lignin after a 1 wt% ferrous sulfate passivation of AAEM. Behavioral differences between the woody biomasses were obvious from visual inspection of the pyrolyzed samples. The red oak produced an amorphous carbonaceous residue in the sample cup, indicating it had melted during pyrolysis. In contrast, southern yellow pine produced a structured char similar to that produced from pyrolysis of untreated biomass. Since these two woody feedstocks contained similar amounts of AAEM, an additional factor

appears to influence propensity for char to melt and agglomerate, which is subsequently explored.

To test the hypothesis that the thermal instability of ferrous acetate allows ferrous cations to react with lignin in the low ash woody biomass, pretreatments were devised that added both ferrous sulfate at levels appropriate to passivating AAEM and ferrous acetate to provide supplemental ferrous cations to the lignin upon its decomposition at pyrolysis temperatures. Ferrous catalyst loading was incrementally increased in increments of approximately 0.06 mmole/g biomass until char residue showed no evidence of melting. When total ferrous catalyst loading reached 0.31 mmole/g of red oak, the char recovered upon pyrolysis was a fine powder. Pyrolysis in nitrogen using a Frontier micropyrolyzer/GC-FID demonstrated enhanced sugar production for this “supplemental iron” pretreatment with ferrous acetate, the results of which can be seen in Figure 3. This indicates that the addition of ferrous acetate did not interfere with

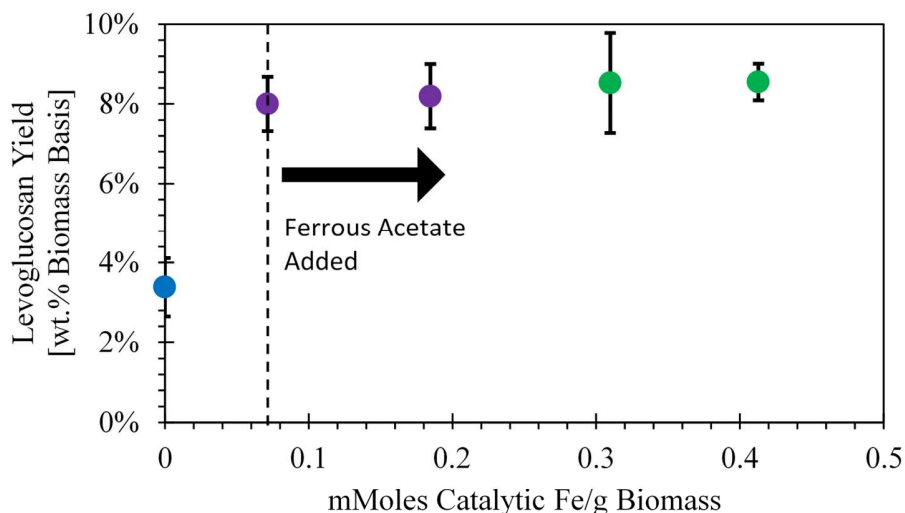


Figure 3. Ferrous sulfate was effective in enhancing sugar production with the introduction of additional ferrous catalyst melting of lignin was prevented in batch micropyrolysis experiments. No statistical difference was found between the yields of ferrous treated red oak. (●) Control, (●) pretreated with melting observed (●) pretreated with no melting observed. Error bars represent 95 % confidence intervals. Biomass basis indicates mass of sample before pretreatment.

AAEM passivation. As apparent in Figure 3, and validated by a Student t-test, there was no statistically significant difference between levoglucosan yields of red oak treated with ferrous sulfate and those with the supplemental iron addition. The previous literature includes no description of the mechanism by which ferrous cations catalyzed depolymerization of lignin. We hypothesize that the binding of ferrous iron into the lignin structure causes  $\beta$ -O-4 ether bonds to elongate, increasing their susceptibility to fragmentation during pyrolysis. This hypothesis is the subject of a future study.

Batch pyrolysis experiments demonstrates that supplemental iron pretreatment in the form of ferrous acetate in combination with ferrous sulfate pretreatment enhances levoglucosan yields while preventing char agglomeration during pyrolysis of low ash red oak.

### **3.3 The effect of lignin composition on char agglomeration**

Trials in a fluidized bed pyrolyzer were performed to demonstrate improved operability under continuous operation during pyrolysis of a variety of pretreated biomass feedstocks. Improved operability was observed using a 1 wt% ferrous sulfate base pretreatment and a ferrous acetate pretreatment level of 4 wt.% (0.31mmoles Fe/g of biomass), the same level that prevented char agglomeration in the micropyrolysis experiments. However, agglomeration still occurred for feed rates above 750 g/h. Southern yellow pine with a 1 wt% ferrous sulfate (0.06 mmoles Fe/g of biomass) pretreatment had similar behavior during continuous pyrolysis. Reactor operation was sustainable at 250 g/h; however, five minutes after ramping up to 500 g/h the char began to agglomerate in the fluidized bed. Clearly, the simple visual observations during micropyrolysis biomass melting test did not capture all the nuances of fluidized bed operability, where a continuum of operating conditions exists.

We theorize that increasing catalyst loading, by increasing the ratio of ferrous cations to lignin bonds, increases the rate of lignin depolymerization compared to the rate at which the lignin melts. Further increases in catalyst loading will reduce the melting occurring during the continuous pyrolysis tests and enable unrestricted reactor operation.

Increasing ferrous iron loading from 4 wt.% ferrous acetate to 6 wt.% for red oak and introducing 2 wt.% ferrous acetate to the southern yellow pine pretreatment was enough to allow for operation up to 2.5 kg/h. The optimal pretreatment for sustained pyrolysis of red oak and southern yellow pine is 1 wt.% ferrous sulfate with 6 wt.% and 2 wt.% ferrous acetate for red oak and southern yellow pine, respectively. At this loading the ferrous iron in the red oak was at a higher level than employed to overcome agglomeration during pyrolysis of corn stover;[23] however, southern yellow pine only required approximately half as much ferrous iron.

As previously observed, differences in agglomeration behavior of hardwood and softwoods, both of which have comparable levels of AAEM, suggest that compositional difference in lignin for these two types of feedstock play a role in the effectiveness of the ferrous iron pretreatment. To explore this possibility, several biomass feedstocks, listed in Table 1, were selected for diversity in lignin composition and AAEM. As shown in Figure 4, there was a strong correlation between the concentration of syringyl units in the lignin and the required ferrous iron loading to prevent melting and enable reactor operability. We note that syringyl (S) lignin has more methoxy groups per phenyl propane unit, lower redox potential, and generally fewer aryl-aryl linkages than guaiacyl (G) lignin or 4-hydroxyphenyl (H) lignin.[35] Interestingly, S lignin is more susceptible to microbial degradation than other kinds of lignin.

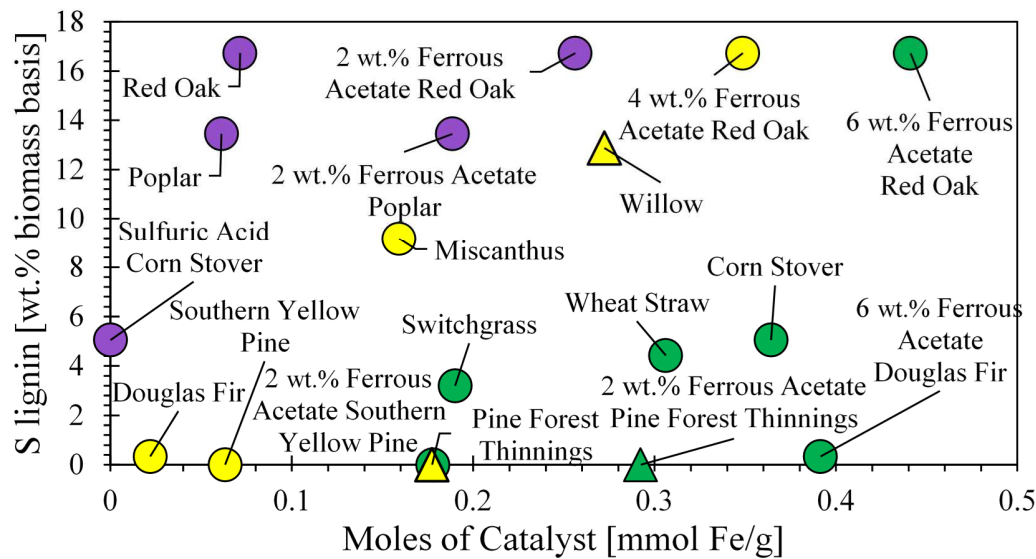


Figure 4. Reactor operability of various feedstocks showing dependence upon both S lignin content of the biomass and ferrous catalyst loading. ( $\blacktriangle$ ) shape indicates wood sample contained bark. S lignin composition was based upon published data from the following sources: [36–40] ( $\bullet$ ) Melt observed during micropyrolysis testing. ( $\circ$ ) Agglomeration experienced during continuous pyrolysis testing. ( $\bullet$ ) Full operability of reactor achieved. All feedstocks fully passivated with ferrous sulfate according to table 1. in section 2.2, except sulfuric acid corn stover.

The impact of feedstock heterogeneity on the effectiveness of ferrous iron pretreatments was explored using thinnings from harvesting of willow and pine wood. Unlike the other woody biomass feedstocks, these samples were not debarked resulting in high AAEM loadings compared to heartwood.[41] Not surprisingly, these samples agglomerated during continuous pyrolysis when pretreated with high levels of ferrous sulfate. Figure 4 suggests that ferrous sulfate pretreatment of pine forest thinnings introduces the same amount of ferrous catalyst as required for full operability of debarked southern yellow pine, which required 2 wt% ferrous acetate. Agglomeration of the pine thinnings occurred at 500 g/h, and full reactor operability was not reached until the supplementary iron pretreatment reached 2 wt.% ferrous acetate. Using this treatment, the heart wood fraction received the same ferrous catalyst loading that prevented agglomeration for clean, debarked pine. Although the ferrous sulfate pretreatment was high enough to prevent agglomeration in the high ash bark fraction, it was not enough to prevent

melting of lignin in the low ash heartwood fraction. This result illustrates that feedstocks of heterogeneous composition, such as corn stover or wood containing significant bark, pretreatment levels higher than expected from the average AAEM content of the material may be required.

### **3.4 Continuous pyrolysis of ferrous iron treated woody biomass**

The ferrous sulfate, ferrous acetate pretreatment produced significant changes to the distribution of products from autothermal pyrolysis. As demonstrated in (Figure 5), light ends decreased while heavy ends increased after pretreatment, which is highly desirable. For red oak, heavy ends increased 56%, which is attributed to reduced cracking of sugars by AAEM. Sugars increased approximately 350% from 4.4 wt.% to 15.5 wt.% as a result of AAEM passivation by the ferrous sulfate. This was accompanied by a 21% reduction in light ends. This increase in sugars is similar to that observed by Dalluge et al.[13] for sulfuric acid pretreated red oak pyrolyzed in an auger reactor who reported sugar yields of 15.9 wt.%. This suggests that full passivation of the AAEM was achieved by the ferrous sulfate pretreatment of red oak.

Southern yellow pine experienced a 78% increase of heavy ends after pretreatment. Most of this increase is attributed to improved sugar production, which increased by 350%, which is comparable to the increase for pretreated red oak. Total hydrolyzed sugars yields increased from 5.4 wt.% on a biomass basis for untreated pine to 19.0 wt.% for pretreated pine. Light ends increased by 26% as less sugar cracked to light oxygenated compounds.

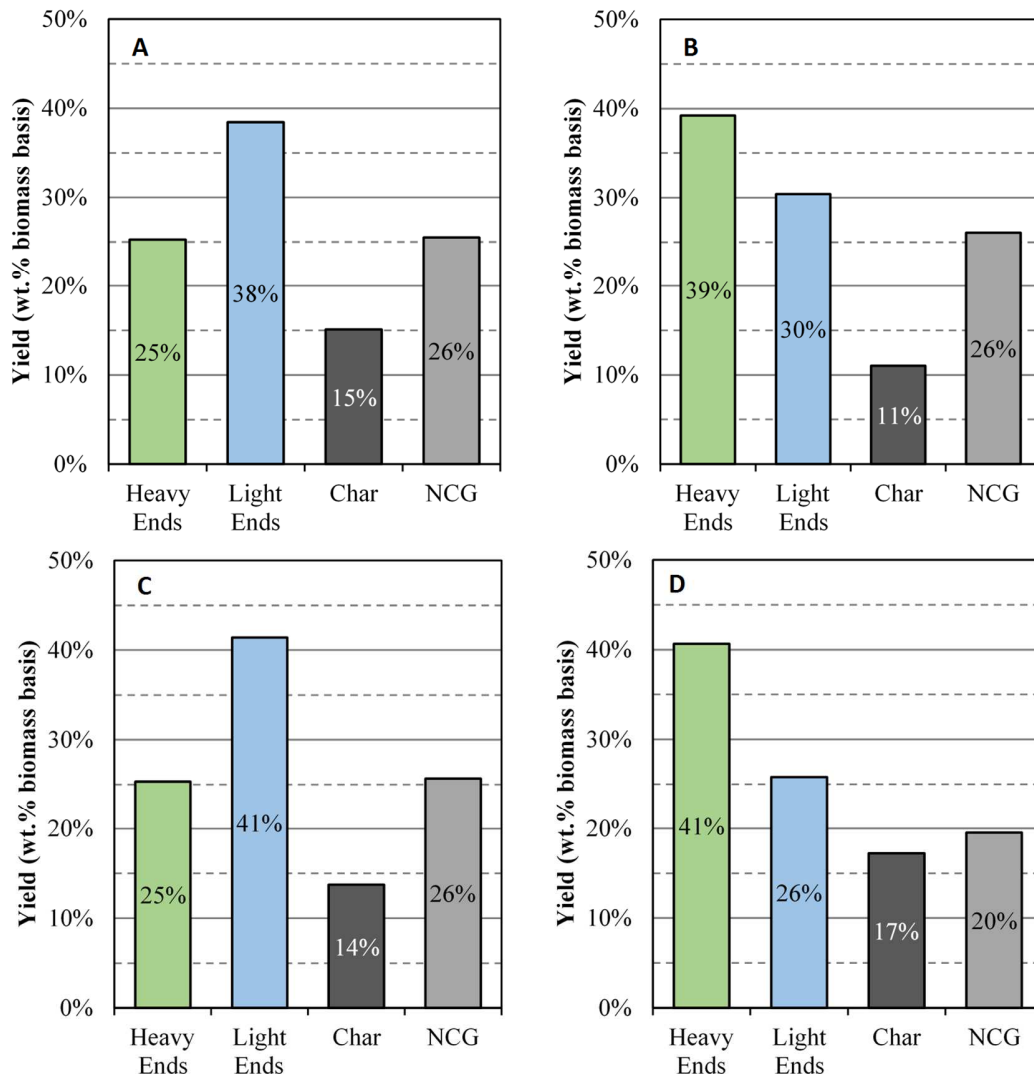


Figure 5. Total mass balance and product distribution from autothermal pyrolysis of (A) untreated red oak ER=10.1%; (B) 1 wt.% ferrous sulfate 6 wt.% ferrous acetate pretreated red oak ER=8.7%; (C) untreated southern yellow pine ER=9.6%; and (D) 1 wt.% ferrous sulfate 2 wt.% ferrous acetate pretreated southern yellow pine ER=8.3%. Yields sum to more than 100% due to not accounting for oxygen introduced into the reactor since its distribution into the products is unknown. The feed rate for all runs was fixed at 1 kg/h and the reactor was maintained at 500 °C by controlling the air content of the fluidizing gas. Biomass basis indicates the pretreatment mass has been removed from the fed mass. Mass closure for all runs was above 90%.

By increasing sugars yields and preventing char agglomeration the combined ferrous sulfate and ferrous acetate pretreatment dramatically increased volumetric sugar productivity from the autothermal fast pyrolysis of woody biomass. Based on previous established reactor parameters the volumetric sugar productivity was 2,680 g/L/h for ferrous iron pretreated red oak and an even more impressive 3,290 g/L/h for southern yellow pine. Earlier work with ferrous

sulfate treated corn stover achieved 2,041 g/L/h using the same reactor system.[23] In contrast, volumetric sugar productivity via enzymatic hydrolysis is only about 5 g/L/h.[42]

These improvements in reactor operability and volumetric sugar productivity were accompanied by changes in char yield. Char yields from pretreated red oak decreased by 27% while char yields from pretreated Southern yellow pine increased 20%. For red oak, a hardwood composed primarily of S lignin [34], ferrous cations catalyzed a shift toward vapor products. For Southern yellow pine, a softwood composed almost exclusively of G lignin,[34] ferrous cations appear to have increased condensation and/or dehydration reactions to produce char. The yield of gases on a mass basis remained unchanged between the control and pretreated red oak, while a substantial decrease was observed for southern yellow pine.

### **3.5 Improved autothermal operation from ferrous acetate treatment**

The sustained operation of an autothermal pyrolyzer relies upon the generation of energy from partial oxidation of pyrolysis products. We observed during the testing of ferrous pretreated biomass a reduction in the equivalence ratio, oxygen consumed over stoichiometric oxygen requirements, required to maintain reactor operation. During autothermal pyrolysis the equivalence ratio decreased, from 10.1% to 8.7% for untreated and ferrous pretreated red oak, respectively. Likewise, the equivalence ratio was observed to decrease from 9.6% to 8.3% for untreated and ferrous pretreated southern yellow pine, respectively. These reductions in oxygen demand stem from two separate phenomena.

Ideally during autothermal pyrolysis the majority of the oxygen introduced into the reactor reacts preferentially with the biochar to form carbon dioxide.[28] This is due to biochar being low value and the production of carbon dioxide releasing 3.6 times more energy than carbon monoxide. This is what was observed for red oak pretreated with ferrous iron. The yield of biochar was reduced and figure 6 shows a significant shift from carbon monoxide to carbon dioxide. The addition of iron generates the same catalytic oxidation effect Peterson et al.[28] observed for native biomass AAEM, higher levels of AAEM catalyst in biochar increased the CO<sub>2</sub> to CO ratio. This shift in red oak gas products represents a 19% increase in energy released

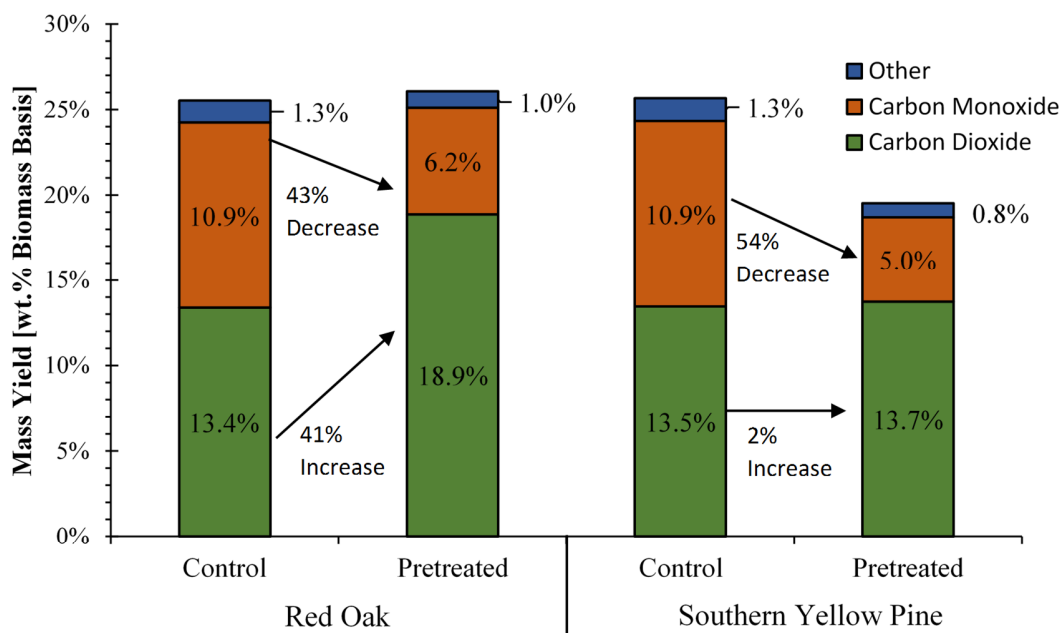


Figure 6. Yield of NCG produced during autothermal pyrolysis of (A) untreated red oak, (B) ferrous treated red oak, (C) untreated southern yellow pine and (D) ferrous treated southern yellow pine. Other represents the sum of other detected gases primarily methane and ethylene with trace amounts of ethane and oxygen. Biomass basis indicates the pretreatment mass has been removed from the feed mass.

from the improved oxidation of iron treated biochar.

The ferrous pretreatment of southern yellow pine produced a reduction in carbon monoxide yields without a corresponding increase in carbon dioxide. This resulted in a 13%

reduction in energy from oxidation reactions. We believe this energy deficit is likely balanced by the increase in char yield associated with pretreated southern yellow pine, since the formation of char is an exothermic process.[43] The 20% increase in char production for southern yellow pine generated the additional energy required to sustain autothermal pyrolysis.

Changes to the equivalence ratio have important implications for designing commercial scale autothermal pyrolyzers. Process intensification of autothermal pyrolysis is currently limited by the amount of oxygen fed to the reactor. Ferrous iron pretreatment improves the efficiency of oxygen utilization leading to greater process intensification. Employing full air blown autothermal pyrolysis a commercial scale system could process approximately 15% more low ash biomass when pretreated with ferrous iron than when left untreated.

#### **4. Conclusions**

The discovery that simple acid infusions into biomass can passivate the catalytic activity of AAEM cations opened the way for intensifying pyrolytic sugar production. However, this required substituting ferrous cations as lignin depolymerization catalyst to prevent char agglomeration. A previous study[23] demonstrated that ferrous sulfate pretreatment was effective in intensifying sugar production from herbaceous biomass without char agglomeration. This study revealed that insufficient ferrous cation was exchanged into low ash woody biomass to be effective in preventing char agglomeration. As an alternative, we found that ferrous acetate, which decomposes at pyrolysis temperatures, could provide the shortfall in ferrous cations enabling intensified sugar production from woody biomass. The rules dictating ferrous catalyst requirements for several biomass types appear to depend upon the S-lignin content. Adaptation of the ferrous sulfate and ferrous acetate blend proved successful for biomass of varied lignin composition and AAEM content.

The iron-rich biochar resulting from autothermal pyrolysis of wood pretreated with ferrous sulfate and ferrous acetate is preferentially oxidized compared to the more valuable pyrolysis vapors. Furthermore, while non-catalytic oxidation of char yields a considerable fraction of carbon monoxide, iron-catalyzed oxidation yields predominantly carbon dioxide, releasing more energy for less carbon. Accordingly, the pretreatment of biomass with ferrous compounds for the intensification of volumetric sugar production also has the unanticipated benefit of reducing oxygen demand for autothermal operation of a fast pyrolyzer. Challenges to implementing this new pretreatment at a commercial scale remain, particularly in generating ferrous acetate. The use of acetic acid recovered from pyrolysis to produce ferrous acetate is an intriguing prospect. Regardless of the potential challenges, ferrous pretreatment of biomass remains a promising technology.

## **5. Acknowledgments**

This work was funded by the American Institute of Chemical Engineers as part of the Department of Energy sponsored RAPID Institute (subcontract #138846). The authors gratefully acknowledge Preston Gable, Bradley Norman, and Zachary Paskach for helping with continuous pyrolysis tests, Dr. Patrick A. Johnston for assistance with ICP testing and Dr. Warren Straszheim for assistance with SEM analysis.

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