Pretreatments for the continuous production of pyrolytic sugar from lignocellulosic biomass

Sean A. Rollag,[a] Jake K. Lindstrom,[b] and Robert C. Brown[a,b]

a Department of Chemical and Biological Engineering, Iowa State University, Ames, IA, U.S.A.
b Bioeconomy Institute, Iowa State University, Ames, IA, U.S.A.

Abstract

Fast pyrolysis of lignocellulosic biomass yields little sugar or anhydrosugars compared to pyrolysis of pure polysaccharides because naturally abundant alkali and alkaline earth metals (AAEM) in biomass catalyze the fragmentation of pyranose and furanose rings. Sugar yields can be increased dramatically by pretreating the biomass with sulfuric acid prior to pyrolysis, which passivates the catalytic activity of the metals by converting them into thermally stable salts. However, depolymerization of lignin in biomass also depends on the catalytic activity of AAEM. Thus, passivating AAEM has the unintended consequence of slowing the rate of depolymerization and volatilization of lignin, resulting in a transient melt phase that agglomerates and can foul pyrolysis reactors.

To overcome this problem, various non-alkali metal sulfates were tested as replacements for sulfuric acid. Iron in the form of ferrous sulfate proved the most effective in depolymerizing lignin without fragmenting pyranose rings. Conventional nitrogen-blown pyrolysis of ferrous sulfate pretreated corn stover achieved WHSV of 4 h^{-1} compared to only 0.6 h^{-1} for acid pretreated corn stover. Autothermal (air-blown) pyrolysis of ferrous sulfate pretreated corn stover showed even more dramatic improvement, increasing WHSV from 1 h^{-1} to 10 h^{-1} compared to acid pretreated corn stover under autothermal operation. Fermentable sugar yields from the pyrolysis of corn stover increased from 0.9 wt% to 11.8 wt% on a biomass basis, a 13-fold increase as a result of the ferrous sulfate pretreatment. These advantages combine to increase volumetric sugar productivity from 62 g L^{-1} h^{-1} for conventional pyrolysis of untreated corn stover to 2041 g L^{-1} h^{-1} for autothermal pyrolysis of ferrous sulfate treated corn stover.

Keywords: Biomass, pretreatment, pyrolysis, sugars, char agglomeration

1. Introduction

Many biomass wastes consist primarily of lignocellulose, a biocomposite of cellulose, hemicellulose and lignin. Because cellulose represents over 50% of all carbon found in the plant kingdom, its depolymerization and upgrading to biofuels and biobased chemicals has been of particular interest in recent decades.[1,2] Depolymerization via enzymatic hydrolysis has received much of the attention because of its selectivity and opportunities to benefit from advances in biotechnology. A major drawback of enzymatic hydrolysis is the slow rate of volumetric sugar production, requiring large and capital intensive production plants. Thermochemical processing can greatly increase the rate of biomass deconstruction,[3] thereby reducing the scale of biorefineries and enabling modular plant design.

Fast pyrolysis of biomass is a relatively simple method for converting cellulose to anhydrosugars.[4] However, the presence of ash in most lignocellulosic biomass dramatically reduces yields of sugar compared to pure cellulose.[5] Naturally abundant alkali and alkaline earth metals (AAEM) catalyze pyranose and furanose ring breaking of plant polysaccharides.[6] Although this catalytic effect and a method of acid washing to restore anhydrosugar yields was discovered nearly 100 years ago,[7] further development stalled for many years. In the last few decades, researchers have explored thorough leaching of AAEM from biomass with water or dilute acid solutions to dramatically increase yields of anhydrosugars upon drying and pyrolyzing the biomass.[8,9] However, the large quantities of water consumed and discharged makes this approach impractical. Rather than removing AAEM, Kuzhiyil et al.[10] suggested in-situ passivation of its catalytic activity. Several mineral acids were shown to react with AAEM to form thermally stable salts, preventing AAEM cations from interacting with plant polymers. Sulfuric acid pretreatment performed best, with glucose yield from lignocellulose approaching that for pure cellulose (almost 60 wt%).[10,11]

Shortcomings of acid pretreatment were discovered by Zhou et al.[12] in experiments with Douglas fir in continuous auger and fluidized bed reactors. In both cases, acid pretreatment caused the formation of large char agglomerates, which was particularly problematic for stable operation of the fluidized bed reactor.[12] Dalluge et al.[13] found that acid pretreatment of red oak and switchgrass increased sugar yields in an auger pyrolyzer by 105% and 259%, respectively, but also produced significant char agglomeration. Although the auger reactors in these two studies were able to crush and convey agglomerates, this phenomenon represents a daunting challenge for production of sugars in fluidized bed pyrolyzers. Like other friable solid fuels, char agglomerates are subject to attrition and eventual elutriation by the erosive action of sand circulating in a fluidized bed.[14] However, to avoid agglomerate growth from overwhelming agglomerate attrition may require a dramatic reduction in biomass throughput. Mitigating reactor agglomeration rates is paramount to the continuous production of pyrolytic sugar. Notably, char agglomeration has also been observed when pyrolyzing biomass from which AAEM has been leached rather than passivated [8],[9] and when attempting to pyrolyze technical lignin.[15,16]

Kim et al.[17] found that admitting small amounts of oxygen to a fluidized reactor during pyrolysis of acid pretreated biomass substantially reduced char agglomeration, permitting operation at higher biomass feed rates before fouling caused unstable reactor operation. Although pyrolysis is conventionally conducted in the complete absence of oxygen, Polin et al.[18] have recently demonstrated that admission of air at low equivalence ratios (ER) is an effective strategy for intensifying pyrolysis, replacing heat transfer with partial oxidation of pyrolysis products to provide the enthalpy for pyrolysis without significantly affecting yields of the most valuable pyrolysis products. In both of these studies, the introduction of oxygen preferentially consumed char in the reactor, increasing processing rates for untreated and pretreated biomass. While studying pyrolysis of technical lignin, Zhou et al. [15] found calcium hydroxide to be an effective additive in mitigating although not completely preventing agglomeration. Although this might be a useful strategy for lignin pyrolysis, it is of limited use in production of pyrolysis sugars from lignocellulosic biomass since calcium, an alkaline earth metal, is detrimental to the production of pyrolytic sugars.[5] An understanding of the mechanism by which char agglomerates form is important to overcoming this problem.

Char recovered from pyrolysis of acid pretreated biomass is morphologically distinct from char produced from pyrolysis of untreated biomass, which retains much of the cell wall structure of the original biomass.[8,13,17] In contrast, agglomerated char from pretreated biomass has clearly undergone melting before dehydrating into an undifferentiated carbonaceous solid.[8,13,17] We hypothesize that AAEM not only catalyzes pyranose and furanose ring fragmentation in plant polysaccharides but promotes lignin depolymerization. Accordingly, when AAEM are removed or passivated by acid to promote sugar production, lignin decomposes too slowly to prevent melting of the lignin, leading to char agglomeration. We hypothesize that AAEM not only needs to be passivated but replaced by a catalyst that is selective toward lignin depolymerization.

The literature contains relatively little information on catalysts that promote lignin depolymerization. A computational study by Kim et al.[19] suggests a possible mechanism for the interaction of AAEM and lignin during pyrolysis. Studies by Eom et al.,[20] in which potassium, magnesium, and calcium were impregnated in demineralized poplar wood, provides some additional insights. While all three metals influenced the yields of lignin decomposition products in a complex manner, magnesium was distinguished by its ability to increase levoglucosan yields from polysaccharides in the wood. In a later study with acid-washed straw, Eom et al.[21] suggested that inorganic compounds in biomass catalyzed carbonization reactions. In experiments on vacuum pyrolysis, Richards et al.[22] reported ferrous ions (Fe^{2+}) improved levoglucosan yield while lowering the initial temperature for char formation. Di Blasi et al.[23] reported that ammonium ions enhanced production of both anhydrosugar and char. Jakab et al.[24] reported that ammonium ions enhanced production of volatiles from milled wood lignin. The promotion of char formation in lignin by ferrous and ammonium ions indicates that dehydration is accelerated relative to melting, suggesting their potential along with magnesium to selectively catalyze lignin depolymerization without adversely affecting sugar production.

We performed an experimental study to investigate the potential of ferrous, magnesium, and ammonium cations in combination with sulfate anions to prevent agglomeration while promoting sugar formation during pyrolysis of herbaceous biomass. These salts, infused into the biomass as an aqueous solution, are expected to react with AAEM in a manner similar to that already demonstrated for sulfuric acid to form thermally stable AAEM sulfates while the ferrous, magnesium, and ammonium cations are ion exchanged into the biomass where they selectively catalyze lignin depolymerization.

2. Methodology

2.1 Pretreatment methods

Corn stover (*Zea mays* ssp. *mays L.*), was ground in a hammer mill with a 3.175 mm screen followed by knife milling through a 1.5 mm screen. For micropyrolyzer experiments, 2 g of knife-milled biomass was ground in a Retsch planetary ball mill (PM 100) at 400 rpm for 2 hours by alternating 8 minutes of grinding with 12 minutes of cool down to reduce the biomass to a fine powder of less than 50 µm particle size. Pretreatment was performed on 25 mg samples of knife milled or ball milled biomass by placing the sample in a 50 mL beaker and adding 25 mL of 18.2 MΩ ultra-pure deionized water. Either concentrated sulfuric acid, ammonium sulfate, magnesium sulfate, or ferrous sulfate heptahydrate (all purchased from Fisher Scientific) was added to the beaker in an amount based on a correlation developed by Kuzhiyil et al.[10] that expresses the optimum molar ratio of sulfate anions infused into the biomass to AAEM in the biomass. Cations from the sulfuric acid and the three sulfate salts are thought to undergo cation exchange with the AAEM. This mode of action was confirmed by x-ray diffraction tests on biochar formed after pyrolysis of the pretreated biomass, which is further described in the Supplemental Material. The sulfuric acid pretreatment released hydrogen ions, as expected for a Brønsted-Lowry acid (Eq. 1), while the other pretreatments release cations (Eq. 2-4), where *M* represents AAEM cations and *x* equals 3-*n* to balance the electronic charge.

$$H_2SO_4 + nM^x \rightleftharpoons M_nSO_4 + 2H^+ \qquad \text{Eq. 1}$$

$$FeSO_4 + nM^x \rightleftharpoons M_nSO_4 + Fe^{2+} \qquad \text{Eq. 2}$$

$$MgSO_4 + nM^x \rightleftharpoons M_nSO_4 + Mg^{2+} \qquad \text{Eq. 3}$$

$$(NH_4)_2SO_4 + nM^x \rightleftharpoons M_nSO_4 + 2NH_4{}^+ \qquad \text{Eq. 4}$$

Pretreatment levels, summarized in Table 1, were determined by matching the stoichiometry of the optimized sulfuric acid pretreatment for corn stover. Due to the variability in corn stover ash content, the total moles of pretreatment added were adjusted to maintain the correct molar ratio. The mixture of biomass and dissolved salt or acid was stirred at 500 rpm for 4 hours. The mixture was poured onto a watch glass and dried overnight at 105 °C.

Table 1. Pretreatment addition Levels

Pretreatment	Molar addition rate (mmoles/mmoles AAEM)	Mass addition rate (wt% corn stover basis)
Sulfuric acid	0.8	3.25-3.5
Ammonium sulfate	0.8	4.6
Magnesium sulfate	0.8	5.0
Ferrous sulfate	0.8	7.5

For tests requiring a larger amount of pretreated biomass, 1 kg of knife-milled biomass was loaded into an ERWEKA™ paddle mixer. A pretreatment solution of the desired chemical was then prepared for spraying. This solution was produced by dissolving an amount of sulfate as determined by the pretreatment correlation described above in 1 kg of water to achieve a water to biomass ratio of 1:1. Using a syringe pump, the solution was sprayed through an atomizing nozzle at a rate of 75 mL min^{-1} onto the biomass during mixing. The treated biomass was then removed from the mixer, placed in mesh containers and dried at 105 °C in a forced air oven with occasional stirring until moisture content was less than 10 wt%.

2.2 Controlled Pyrolysis Duration-Quench

Effects of pretreatment on the morphology of pyrolyzing biomass was studied using the Controlled Pyrolysis Duration (CPD)-Quench system illustrated in Figure 1, first described by Lindstrom et al.[11] The system, consisting of a furnace-based micropyrolyzer and a computer-controlled actuator, allowed biomass samples to be quickly heated to a prescribed temperature for reaction durations as short as 1 second before ejection into a catch vessel chilled by an ice bath. By removing and cooling samples before pyrolysis was complete, chemical and structural changes in the condensed phase could be examined.

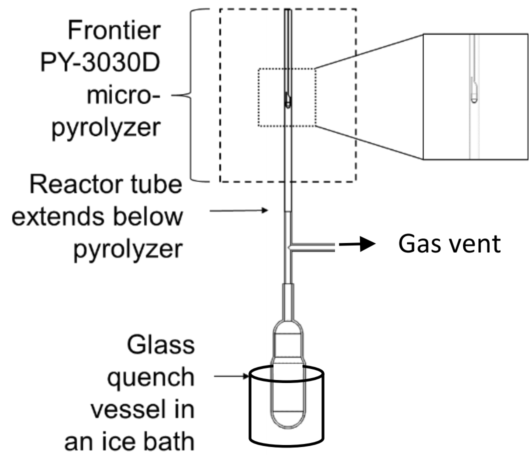


Figure 1. Diagram of Controlled Pyrolysis Duration-Quench originally from Lindstrom et al.[11] Modified by replacement of vapor condenser with direct gas vent and addition of ice bath.

For these tests, knife milling of biomass particles to 150 μm size was performed to prevent damage to the cell structure from ball milling. Milled particles were placed on a strip of aluminum foil. The foil insert was placed in a Frontier Laboratories stainless steel Eco-Cup SF that was then loaded in the micropyrolyzer. The foil insert was necessary to assure the condensed phase product of partial pyrolysis could be laid flat for subsequent analysis by scanning electron microscopy (SEM). The foil insert had negligible effect on particle heating rate when compared to samples not enclosed in foil.[25]

2.3 Continuous Pyrolysis Reactor System

Pyrolysis experiments were performed in a continuous fluidized bed reactor that could be operated either conventionally (nitrogen-blown) or autothermally (air-blown or air and nitrogen-blown). For conventional pyrolysis, thermal energy was provided to the reactor with electric ceramic heaters surrounding the reactor. For autothermal pyrolysis, thermal energy was provided to the process by partial oxidation of pyrolysis products within the reactor, with oxygen provided by mixtures of air and nitrogen that also served to fluidize the reactor. Two Watlow clam-shell ceramic heaters surrounding the reactor were used to heat the system initially and to offset external heat loss as detailed in Polin et al.[18]. Figure 2 shows a schematic of the system, which consists of an injection auger, plenum, fluidized bed, two char cyclones, heavy ends condenser, hot electrostatic precipitator (ESP), light ends condenser, and cold ESP. The reactor, constructed of 3.8 cm diameter, 316 stainless steel pipe, contained 250 g of silica sand to serve as bed media. Fluidizing gas was introduced through a sintered distributor plate and products exited via a 2.3 cm diameter tube at the top of the reactor. All flow rates and temperatures were achieved using a computer-based control system. Feed rate was measured as kilograms per hour but also reported as weight hourly space velocity (WHSV), defined as mass flow rate of biomass divided by mass of bed material (units of h^{-1}). This metric is convenient in assessing the impact of char agglomeration on biomass throughput relative to the working volume of the reactor.

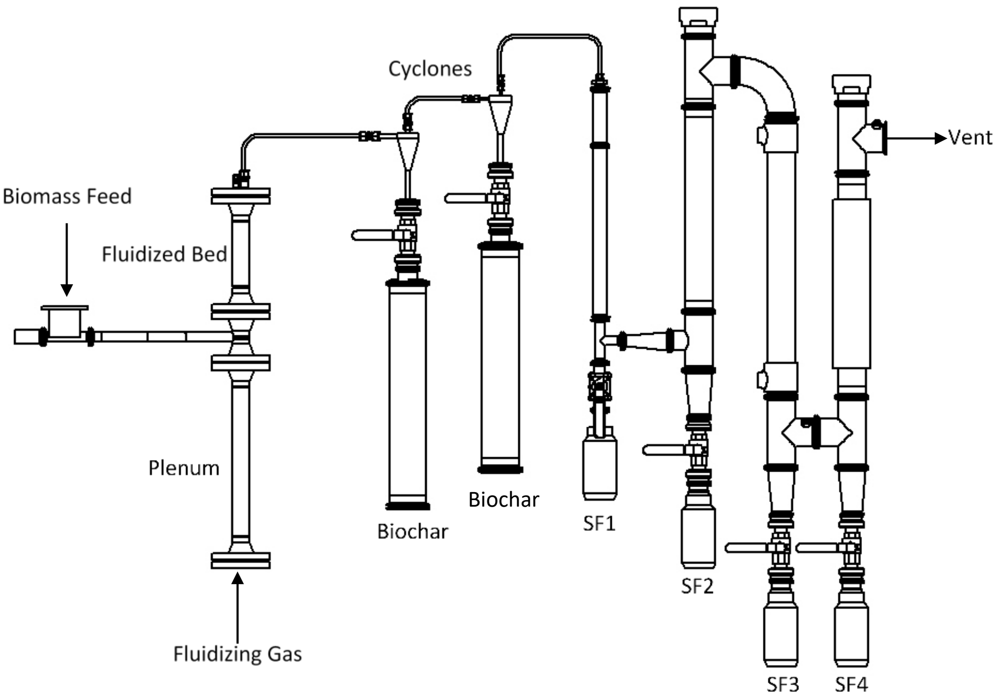


Figure 2. Schematic of the benchtop pyrolyzer and bio-oil collection system.

The reactor was fluidized with 20 standard liters per minute (SLPM) of pure nitrogen, air or a mixture of air and nitrogen regulated by Alicat Scientific mass flow controllers. The ceramic heaters maintained the reactor at 500 °C for conventional pyrolysis. During autothermal pyrolysis the heaters were simply used to overcome parasitic heat losses rather than provide the enthalpy for pyrolysis. The char cyclones were heated by high temperature heat tape to 500 °C to prevent condensation of bio-oil vapors prior to the oil collection system. Stage fraction one (SF1) consisted of a jacketed pipe condenser with the cold side maintained at 90 ºC to cool the vapors from 500 °C to approximately 120 °C. Vapors exiting SF1 entered an ESP representing the second stage fraction (SF2) of bio-oil recovery. This stage fraction was heated to 120 °C by heat tapes and maintained a 15 kV electrical potential to collect heavy aerosols. Liquids collected by SF1 and SF2 constitute the heavy ends of bio-oil and contained the majority of anhydrosugars and phenolic compounds. The light ends condenser (SF3) was a shell and tube heat exchanger with the cold side maintained at 0 °C. A cold ESP (SF4), cooled to -15 °C and operated at 15 kV electrical potential, collected the remainder of the vapors. SF3 and SF4 represent the light ends fraction and consisted mostly of water, organic acids, furans, and other low molecular-weight oxygenated compounds. The gas flow then passed through a desiccant trap to remove any remaining condensable vapors before being vented as non-condensable gases, the mass fraction of which was determined by difference.

2.4 Determination of sustainable throughput

Sustainable throughput, defined as the rate at which biomass could be continuously fed into the reactor while maintaining steady reactor temperatures and pressure drops, was determined for the benchtop pyrolyzer by incrementally increasing biomass feed rate starting at 250 g h^{-1} (WHSV = 1 h^{-1}). If after 30 minutes of continuous operation pressure drop and temperature measurements were stable, the feed rate was increased to 500 g h^{-1} (WHSV = 2 h^{-1}). This procedure was repeated until instabilities in pressure or temperature were observed, indicating unsustainable feed rates and establishing the maximum system throughput. Baseline throughput was established using untreated biomass. For conventional pyrolysis using nitrogen fluidization, the maximum throughput was 1000 g h^{-1} (WHSV = 4 h^{-1}), limited by the rate heat could be supplied to the reactor. In the case of autothermal pyrolysis the maximum throughput was 2500 g h^{-1} (WHSV = 10 h^{-1}), limited by the cooling capacity of the heavy ends collection vessel. Following each test with pretreated biomass, the reactor was opened and inspected for agglomeration to confirm sustainable operation.

2.5 Sugar quantification

Sugar yields were determined by hydrolysis of the heavy ends of bio-oil (combined SF1 and SF2). The hydrolysis method, developed by Bennet et al.[26], mixes 60 mg of bio-oil with 400 mM sulfuric acid followed by heating to 125 °C for 44 minutes. Hydrolyzed samples were then cooled in a freezer to room temperature and syringe filtered using 0.45 μm Whatman filters into 2 mL glass vials. High Performance Liquid Chromatography (HPLC) was performed with a Dionex Ultimate 3000 series HPLC using a water mobile phase and refractive index detector to determine the yield of glucose and xylose.[27]

2.6 Scanning electron microscopy

Char samples from the CPD-Quench were prepared for SEM by mounting them on carbon tape and coating the samples with 5 nm of iridium using a Quorum Q150TS. Imaging was done using a FEI Quanta 250 field emission-SEM with secondary electron, gaseous secondary electron, and backscattered electron detectors. The SEM was coupled with an Oxford Energy Dispersive X-ray Spectroscopy (EDS) system with an X-Max 80 detector. Imaging was done in high vacuum mode with a 10 keV electron beam.

2.7 ICP digestion and analysis

The ash content of biomass was determined using Inductively Coupled Plasma (ICP)-Optical Emission Spectrometry (OES). The samples were first digested in 20 wt% nitric acid via microwave heating in quartz reactor vessels. The digested samples were then diluted 10,000x with 18.2 MΩ water before being analyzed by ICP following the method described by Chi et al.[28]

3. Results and Discussion

3.1 Melt-phase formation in pretreated corn stover

As shown in the SEM images of Figure 3, pyrolysis of untreated corn stover rind (the outer layer of the corn stalk) showed only small structural changes, with the biomass particles initially expanding upon heating followed by contraction as volatiles were released. However, the basic morphology of the plant cells was essentially unchanged.

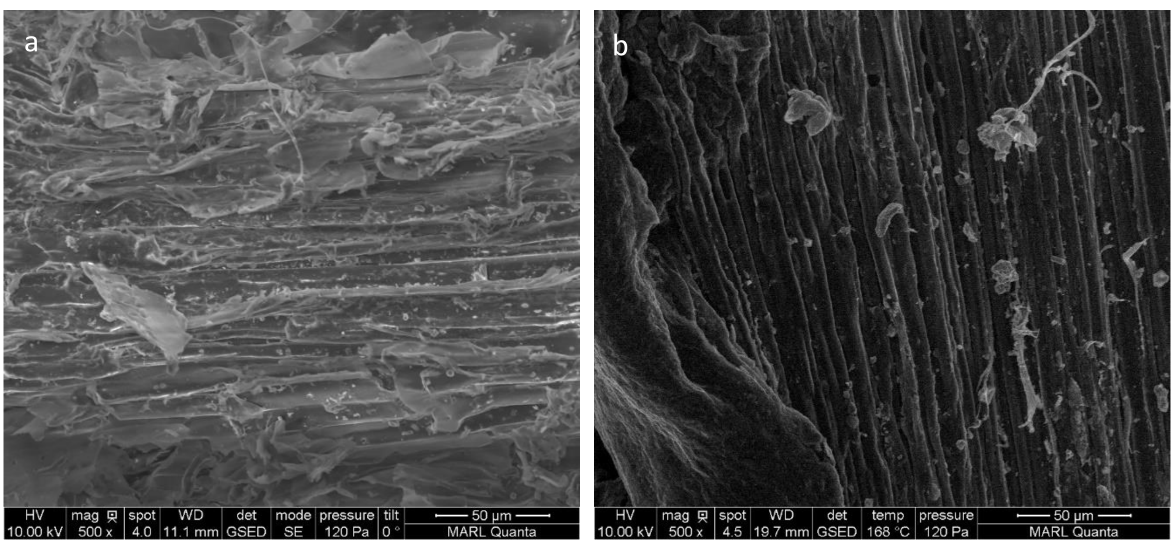


Figure 1. Morphology of plant cells in untreated corn stover show little change during conversion to biochar. SEM micrographs (a) before pyrolysis and (b) after pyrolysis at 500 °C.

Acid pretreatment had different effects on the various components of corn stover. In general, leaves and cobs showed little morphological change. In contrast, the rind showed evidence of melting for pretreatment levels of 3.5 wt% sulfuric acid. This difference might reflect the higher lignin content of the rind compared to other parts of the stover or higher AAEM content in leaves and cobs,[29] which would require higher pretreatment levels to passivate the catalytic activity of AAEM toward lignin depolymerization. As illustrated in Figure 4, formation of a liquid phase became evident on the surface of the rind from pretreated corn stover as pyrolysis temperature increased above 350 °C. At 450 °C rind particles collapsed into a liquid pool in the sample cup. At 500 °C, devolatilization within the melt created bubbles that foamed the liquid, which ultimately dehydrated to form a porous char aggregate.

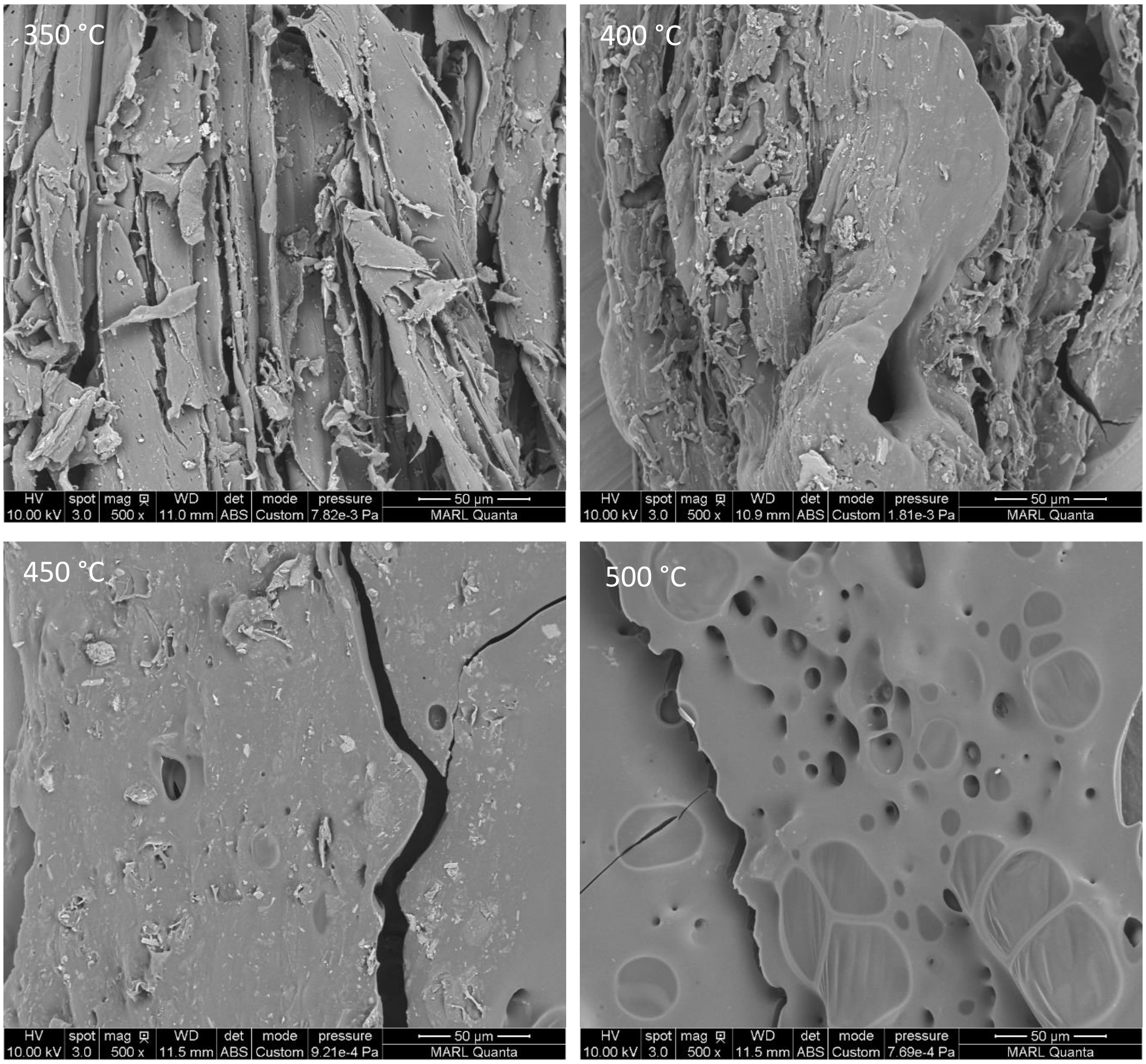
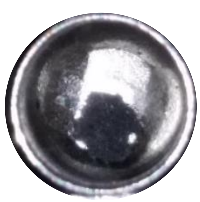
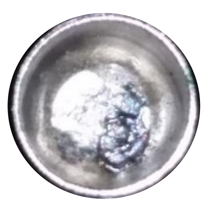
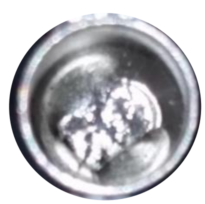
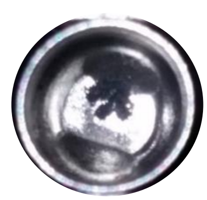
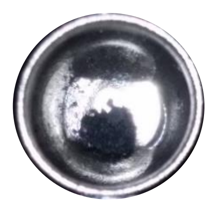
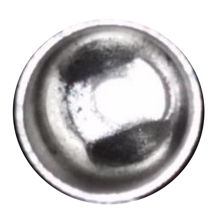


Figure 4. SEM micrographs of partially pyrolyzed corn stover rind pretreated with 3.5 wt% sulfuric acid show increasing evidence of a melt phase as pyrolysis temperature increases.

Clearly, passivation of AAEM causes lignin to melt before substantial vapor or char formation, suggesting the catalytic properties of AAEM need to be replaced to prevent char agglomeration. Testing of various AAEM salts by Patwardhan et al.[5] and Eom et al.[20] found that potassium had a strong negative effect on levoglucosan yields while magnesium had a significantly weaker impact. Dalluge et al.[30] hypothesized this result was associated with the electropositivity of the ions. Based on this theory, ferrous, magnesium, and ammonium cations were selected to evaluate their selectivity in depolymerizing lignin compared to fragmentation of pyranose rings. For each pretreatment, sulfate was the corresponding anion. The goal of this new treatment was twofold: introduce the sulfate anion to produce the same thermally stable salts produced with sulfuric acid pretreatment and add a new lignin depolymerization catalyst to the biomass.

Each of these pretreatments was applied to samples of ball-milled corn stover and subjected to incomplete pyrolysis in the CPD-Quench reactor at 500 ºC for 30 seconds. Table 2 illustrates the char residue in the sample cups for various pretreatments of corn stover including a control with no pretreatment of the corn stover. Shown is both the contents of the sample cups immediately upon removal from the CPD-Quench reactor (as produced) and after inverting the cups and tapping them on a hard surface to remove any loose char residue (after dumping). When biomass melts the resulting agglomerated char adheres to the bottom of the cup and cannot be removed by inverting and tapping the cup. For the untreated stover, the residue is unconsolidated and readily dumped from the cup. In contrast, the acid pretreated stover produces an agglomerated residue that cannot be removed by tapping the inverted sample cup. However, all three alternative treatments (sulfates of ammonia, magnesium and ferrous) produced loose char that was easily dumped from the cups. Based on these results, all three pretreatments were evaluated in continuous pyrolysis tests as described in the next section.

Table 2. Interior of sample cups after partial pyrolysis of ball milled corn stover subjected to various pretreatments.

	Untreated	**3.5 wt% Sulfuric Acid**	**4.6 wt% Ammonium Sulfate**	**5.0 wt% Magnesium Sulfate**	**7.5 wt% Ferrous Sulfate**
Residue – As Produced					
Residue – After Dumping					

3.2 Continuous Pyrolysis in Fluidized Bed

Table 3 summarizes the results of continuous pyrolysis experiments for various pretreatments under conventional (ER=0) and autothermal (ER= 0.09-0.12) including the maximum sustainable WHSV and photographs of biochar recovered from the reactor at the conclusion of the tests. The performance of each pretreatment is detailed below.

Under conventional (nitrogen-blown) pyrolysis, untreated corn stover could be processed at maximum WHSV of 4.0 h^{-1}. The char product was a fine powder without evidence of particle agglomeration. Autothermal (air-blown at ER = 0.11) operation of the reactor, by removing the heat transfer bottleneck of pyrolysis, allowed operation at WHSV up to 10 h^{-1}. Autothermal pyrolysis of untreated corn stover did not produce agglomerated char. As anticipated, conventional (nitrogen-blown) pyrolysis of corn stover pretreated with sulfuric acid at 3.25 wt% was extremely unstable until WHSV was reduced to 0.6 h^{-1}. Operation under autothermal (air-blown) conditions allowed acid pretreated corn stover to be pyrolyzed at WHSV of 1.0 h^{-1}, but this throughput is ten times lower than achieved during autothermal (air-blown) pyrolysis of untreated stover. Heavy agglomeration of char is evident in the photographs of Table 3 for both conventional and autothermal pyrolysis of acid pretreated stover.

Table 3. Operability of continuous fluidized bed reactor for various corn stover pretreatments.

Conventional (ER=0) Pretreatment: None Max WHSV = 4.0	Autothermal (ER=0.11) Pretreatment: None Max WHSV = 10	Conventional (ER=0) Pretreatment: H_2SO_4 Max WHSV = 0.6	Autothermal (ER=0.10) Pretreatment: H_2SO_4 Max WHSV = 1.0
			
Conventional (ER=0) Pretreatment: NH_4SO_4 Max WHSV = 1.0	Autothermal (ER=0.12) Pretreatment: $MgSO_4$ Max WHSV = 10	Conventional (ER=0) Pretreatment: $FeSO_4$ Max WHSV = 4.0 (after auto-ignition in air)	Autothermal (ER=0.09) Pretreatment: $FeSO_4$ Max WHSV = 10
			

The difficulty of pyrolyzing acid pretreated stover at higher throughputs is illustrated in Figure 5, which plots pressure drop across the fluidized bed against time for WHSV of 2 h^{-1}. Small, regular pressure fluctuations (+/- 0.15 kPa) were observed early in the test, associated with the passage of gas bubbles through the bed during steady operation. The disappearance of these regular pressure fluctuations after 7 minutes is the first sign of char agglomeration, corresponding to fouling around the injection auger, which constricts the flow of gas at the bottom of the reactor and causes a transition from bubbling to spouting bed operation. After almost 40 minutes on stream the pressure drop increases to over 140 inches of water in less than 5 minutes making further operation impossible because of severe char agglomeration in the bed.

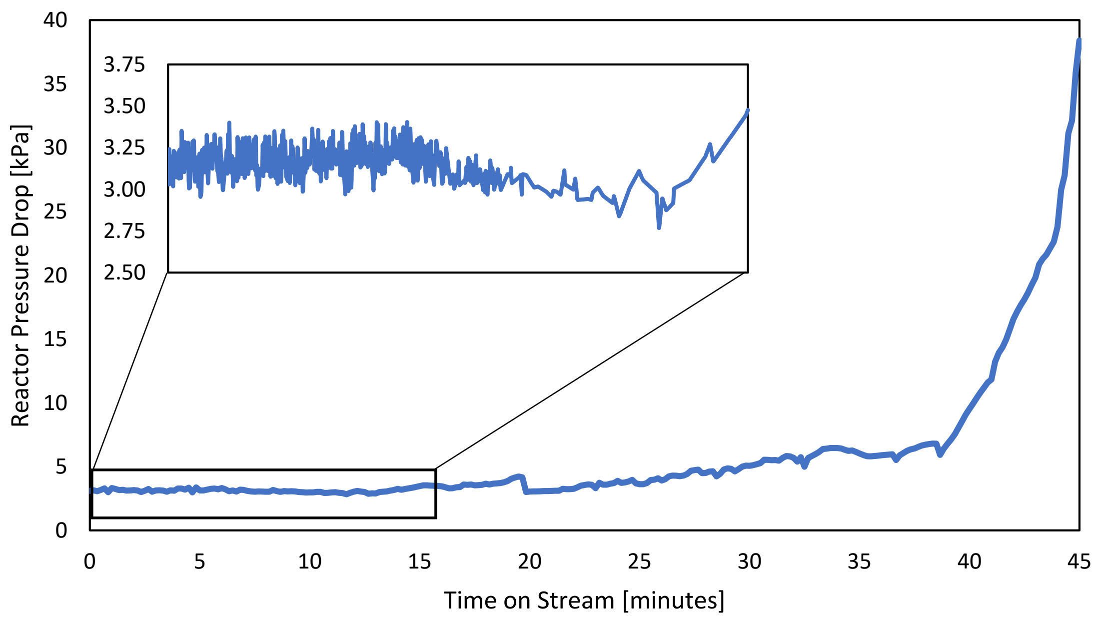


Figure 5. Pressure drop across the fluidized bed reactor under autothermal operation at WHSV of 2 h^{-1} was not steady when feeding corn stover infused with 3.25 wt% sulfuric acid. The initial 15 minutes have been enlarged to better show the transition from bubbling to spouting operation, indicating agglomeration beginning within the reactor. The later substantial increase in pressure drop was caused by extensive char agglomeration.

Upon completion of these tests the reactor was shut down and the internals inspected, which revealed a significant accumulation of agglomerated char especially around the injection auger. These agglomerates ranged in size from less than 1 mm diameter to greater than 20 mm, the latter of which are comparable in size to the diameter of the reactor exit tube.

Although the tests with the CPD-Quench reactor suggested that char agglomeration would not occur for ammonium sulfate pretreated stover, ammonium sulfate pretreatment during nitrogen-blown pyrolysis caused unstable reactor operation at WHSV of 1 h^{-1}. Evident in Table 3, large char agglomerates were formed. Pretreatment with ammonium sulfate was not further pursued because of the combination of char agglomeration and relatively low yields of sugars (4.4 wt%.)

On the other hand, both magnesium sulfate and ferrous sulfate improved operability under air-blown pyrolysis, achieving stable operation at WHSV up to 10 h^{-1}, equaling that achieved with air-blown pyrolysis of untreated stover. Only a single nitrogen-blown test was conducted with ferrous sulfate pretreatment because it was discovered that the anoxic environment of the reactor generated pyrophoric ash, which complicates safe handling of the char, as described in the Safety Note (Section 5) and the Supplemental Material. Magnesium sulfate pretreatment was expected to similarly produce pyrophoric ash under nitrogen-blown conditions and so was not tested. However, this single test achieved WHSV of 4 h^{-1} without formation of agglomerated char, suggesting that both ferrous and magnesium cations depolymerize lignin under both anoxic and oxidizing conditions. The char sample recovered immediately upon conclusion of the ferrous sulfate test was black but upon exposure to air rapidly oxidized to ferric oxide, evident in Table 3 as an orange film on the char.

The impact of pretreatments on product yields (heavy ends, light ends, char, and non-condensable gases) from autothermal pyrolysis of corn stover is illustrated in Figure 6. All tests were performed at comparable WHSV (1-2 h^{-1}) and ER (0.09-0.12). Data for pyrolysis of ammonium sulfate-pretreated stover are not included because stable operation was never achieved. Most notable is the impact of the pretreatments on yields of heavy ends, which consists mostly of sugars from polysaccharides and phenolic oil from lignin depolymerization.[31,32] Pretreatments increased heavy end yields to 21-32 wt% compared to only 17 wt% for untreated stover. Ferrous sulfate pretreatment increased yield of heavy ends from stover an impressive 88% compared to untreated stover. As subsequently described, most of this difference is attributable to sugar production. Corresponding to these increased yields of heavy ends, light ends were reduced by 5-22% as less polysaccharides in the biomass decomposed into light oxygenated compounds. Pretreatments reduced char yields from 23 wt% to 14-17 wt%, suggesting that passivation of AAEM reduced dehydration of plant polymers to char. Pretreatments appeared to produce little change or moderate increases in yields of non-condensable gases.

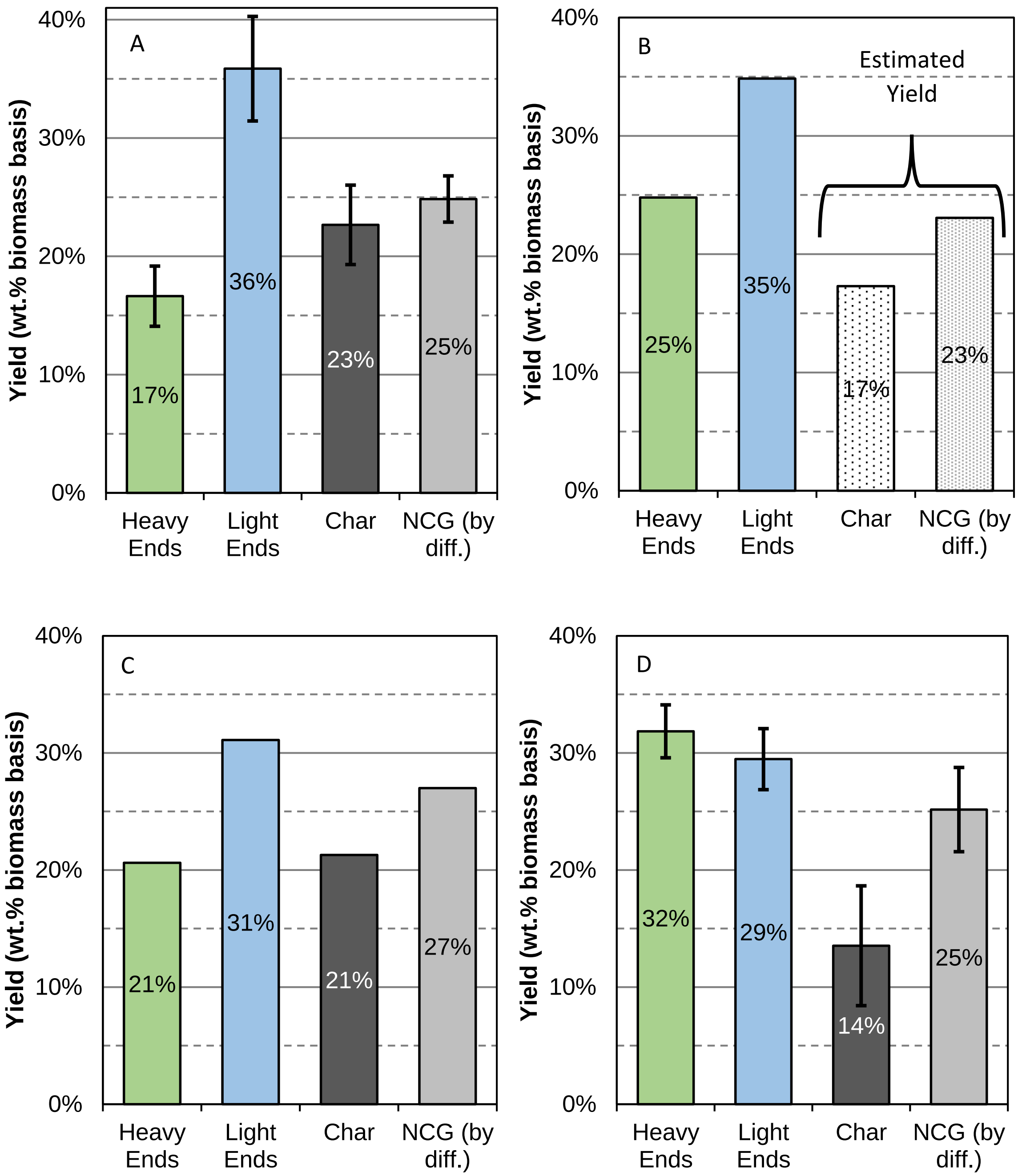


Figure 6. Distribution of heavy ends, light ends, biochar, and non-condensable gases (NCG, by difference) from runs of (A) untreated corn stover; (B) 3.25 wt% sulfuric acid pretreated corn stover; (C) 5 wt% magnesium sulfate pretreated corn stover; and (D) 7.5 wt% ferrous sulfate pretreated corn stover under autothermal conditions at 500 °C and 1-2 h^{-1} WHSV. Control and ferrous sulfate tests were run in triplicate to establish system uncertainty and error bars represent 95% confidence intervals. In (B) the char and NCG yields were estimated from multiple runs due to the significant amount of char agglomeration in the fluid bed and cyclones that could not be recovered.

The sugars and anhydrosugars in the heavy ends from these continuous pyrolysis trials were hydrolyzed and analyzed as monosaccharides. Glucose typically constituted 80% of the total quantified sugars with xylose composing the remainder. Untreated corn stover yielded only 0.9 ± 0.1 wt% sugars due to the catalytic activity of AAEM. Acid pretreatment of corn stover increased sugar yield to 11.9 ± 0.8 wt% for air-blown pyrolysis (12.7 wt% for nitrogen-blown pyrolysis). Interestingly, the absolute increase in sugar yield achieved through acid pretreatment was 11.0 wt% while heavy ends only increased 8 wt%. This result suggests a small loss in lignin-derived content of the heavy ends to either char or non-condensable gases although this loss is within the uncertainly of the data. Magnesium sulfate pretreatment increased sugar yields more modestly than acid pretreatment, achieving 6.6 wt% sugar. Thus, although magnesium was an effective lignin depolymerization catalyst, it also appeared to catalyze pyranose ring fragmentation albeit at rates less than other naturally occurring AAEM in biomass. This result is consistent with observations of Patwardhan et al[6]. who found magnesium decreased levoglucosan yields from cellulose but contrary to claims of Eom et al.[5,20] who claimed magnesium increased levoglucosan yields. The 5.7 wt% increase in sugar yield for the magnesium sulfate pretreatment is higher than the accompanying 4 wt% increase in heavy ends yield, suggesting some loss of lignin-derived compounds to char or non-condensable gases. Ferrous sulfate pretreatment increased sugar yield to 11.8 ± 0.7 wt%, comparable to sugar yield from acid pretreatment. Thus, ferrous ions do not appear to catalyze undesirable pyranose ring fragmentation while acting as an effective lignin depolymerization catalyst. Interestingly, compared to untreated corn stover, ferrous sulfate pretreatment increased sugar yields by 10.9 wt% while heavy ends increased by 15 wt% suggesting that this pretreatment increased both sugar and phenolic oil yields.

The impact of pretreatments that enhance sugar production while avoiding char agglomeration is evident from calculating the volumetric sugar productivity of the fluidized bed reactor for conventional and autothermal pyrolysis of pretreated corn stover. Volumetric sugar productivity (VSP) is defined as the rate of sugar production per unit of active reactor volume ($g\ L^{-1}\ h^{-1}$). This result can be expressed in terms of sugar yield (Y_s) and maximum weight hourly space velocity (WHSV) achieved in the pyrolysis trials where ρ_b is the bulk density of the bed (1730 g L^{-1}):

$$VSP = \rho_b\ Y_s\ WHSV \qquad \text{Eq. 5}$$

These results are plotted as the bubble chart in Figure 7. Sugar productivity for untreated corn stover under conventional pyrolysis is only 62 g L^{-1} h^{-1}, reflecting both the low sugar yield (0.9 wt%) and the modest maximum WHSV (4 h^{-1}). Sugar productivity more than doubled by pyrolyzing untreated corn stover under autothermal conditions. Although acid pretreatment increased yields from less than 1 wt% to over 12 wt%, char agglomeration prevented steady operation above WHSV of 1 h^{-1}, reducing VSP to only 131 h^{-1} for conventional pyrolysis and 206 h^{-1} for autothermal pyrolysis. However, the process intensification advantages of autothermal pyrolysis were regained by replacing acid with magnesium sulfate or ferrous sulfate to pretreat corn stover, achieving five-fold and ten-fold increases in VSP, respectively, compared to acid pretreatment. In fact, this change represents a 400-fold increase in VSP compared to what can be achieved from enzymatic hydrolysis of corn stover[33] despite the more modest sugar yields from pyrolysis, as illustrated in Figure 8.

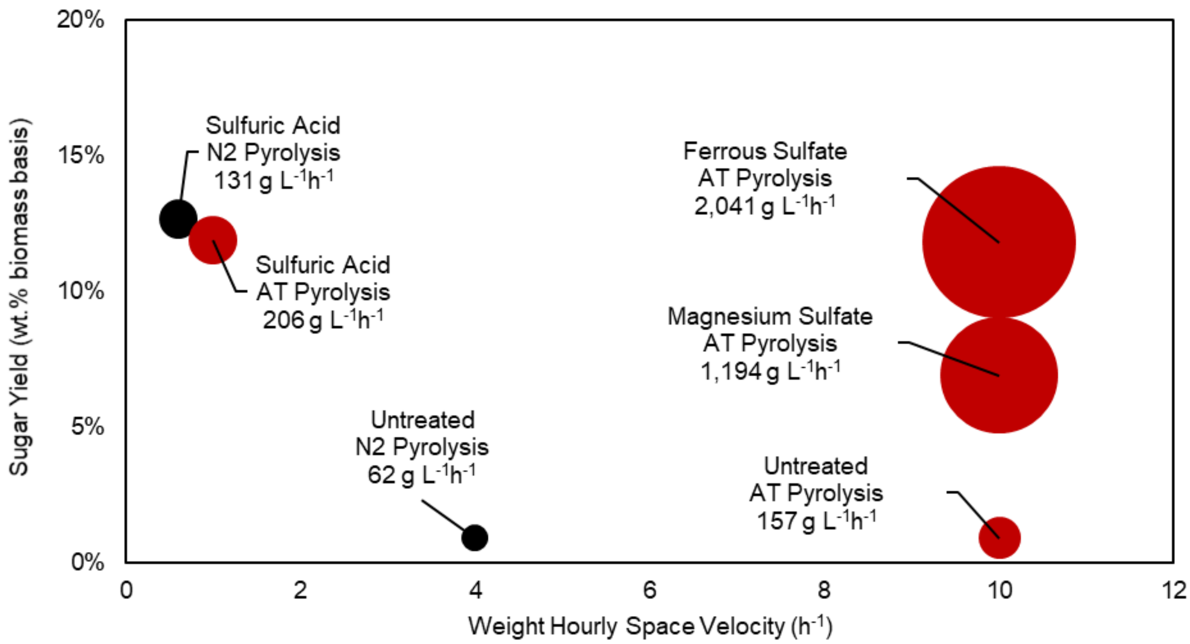


Figure 7. Comparison volumetric sugar productivity for different pretreatments of corn stover pyrolyzed at maximum sustainable feed rate under conventional (N2) and autothermal (AT) operating conditions.

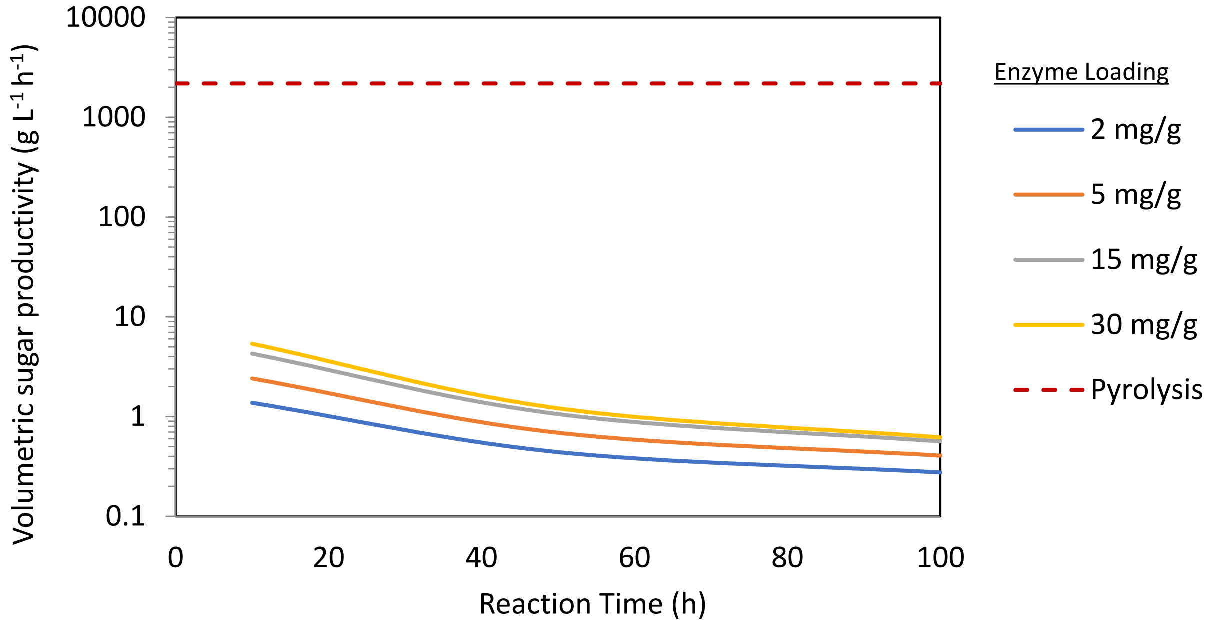


Figure 8. Comparison of sugar productivity via pyrolysis compared to enzymatic hydrolysis (volumetric sugar productivity for pyrolysis based on highest WHSV and sugar productivity achieved in this study with ferrous sulfate pretreated corn stover; volumetric sugar productivity for enzymatic hydrolysis of corn stover based on Reference [33]).

4. Conclusions

Naturally occurring alkali and alkaline earth metals not only catalyze pyranose ring fragmentation in plant polysaccharides during pyrolysis but play an important role in promoting depolymerization and devolatilization of lignin. Attempts to enhance pyrolytic sugar formation by removing or in situ passivating these metals must be accompanied by addition of catalyst selective toward lignin depolymerization if char agglomeration and reactor fouling are to be avoided. This study identified ferrous sulfate as a particularly promising pretreatment of corn stover, producing sugar yields comparable to those from sulfuric acid pretreatment but without char agglomeration. Combining this pretreatment with autothermal operation of the fluidized bed pyrolyzer achieved volumetric sugar productivity of 2041 g L^{-1} h^{-1}, which is 32 times higher than for conventional pyrolysis of untreated corn stover and 10 times higher than autothermal pyrolysis of acid pretreated corn stover. Although sugar yields are modest compared to enzymatic hydrolysis, volumetric sugar productivity for pyrolysis, by virtue of its rapidity, is 400-fold higher than achieved for enzymatic hydrolysis. Whether this advantage translates into attractive economics for cellulosic sugar production is the subject of a future study.

5. Safety note

Some of the char produced under nitrogen-blown pyrolysis with metal sulfate pretreatment formed pyrophoric ash, likely due to the reduction of the salts to fine metal powders. In contrast, char produced under the oxidative environment of autothermal pyrolysis was not pyrophoric. For this reason, we strongly discourage pyrolyzing metal sulfate pretreated biomass under inert gas conditions. In either case, a combustible metals fire extinguisher (Class D) is recommended for the laboratory.

Additionally, thermogravimetric analysis revealed that biomass pretreated with metal sulfate can combust in air at significantly lower temperatures then untreated biomass. These experiments and results are detailed in the Supplemental Material.

Acknowledgments

This work was funded by the U.S. Department of Energy's RAPID Institute administered by the American Institute of Chemical Engineers (AIChE). The authors gratefully acknowledge Preston Gable, Bradley Norman and Zachary Paskach for assistant in performing pyrolysis experiments, Dr. Patrick A. Johnston for assistance with ICP-OES testing and Drs. Warren Straszheim and Dapeng Jing for assistance with the SEM analysis.

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