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Use of metal chlorides during waste wheat straw autohydrolysis to overcome the self-buffering effect

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ABSTRACT

High ash content of waste wheat straw (WWS) is resistant to biorefinery autohydrolysis pretreatment due to its self-buffering effects. In this work, minor addition $FeCl_3$ and $AlCl_3$ were applied to overcome the self-buffering effects of WWS by cationic occupation of the negatively charged sites present on particulate ash's surface. The results showed that with the increasing concentrations (0–20 mM) of $AlCl_3$ and $FeCl_3$, the enzymatic efficiencies of autohydrolyzed WWS were enhanced from 49.7% to 62.1% and 66.6%, respectively. Acid buffer and cation exchange capacity of pretreated WWS were decreased by adding metal chlorides and the reducing results were mainly attributed to cation exchange. Meanwhile, a maximum monosaccharide production (185.3 mg/g-WWS) was achieved with 62.0 mg/g-WWS xylooligosaccharide by using 20 mM $FeCl_3$ during WWS autohydrolysis. The results demonstrated that the implications of $FeCl_3$ and $AlCl_3$ in WWS autohydrolysis were an effective strategy to enhance autohydrolysis efficiency by overcoming self-buffering effects.

1. Introduction

Development and implementation of low-emission and sustainable energy resources has been urgently demanded in the recent decade (Stern et al., 2016). One promising avenue is ethanol production from lignocellulose, which is recognized as a promising alternative to fossil fuel (Anđelković et al., 2017; Jiang et al., 2017). Agricultural and forestry wastes have been presented as potential raw materials for the production of ethanol due to their (current) waste-like nature and enrichment in structural polysaccharides. Regarding their waste-like nature, agricultural and forestry wastes are conventionally burned as fuel, which is a practice recognized for its contribution to air pollution (Chen and Xie, 2014). Because the cost of heavily-studied lignocellulosic feedstocks for ethanol production (wheat straw, corn stover and wood) is estimated as ~30–90 US$ per ton, it is important to develop practices which produce ethanol from lower-cost starting materials (Geng et al., 2015; Lee et al., 2009).

Wheat straw is extensively used in the pulping industry, and it is estimated that about 2×10^5–4×10^5 tons of waste wheat straw ("WWS") are annually produced by wheat straw pulp mills in China alone. WWS itself (consisting of wheat ears, leaves, straw scraps and a large amount of ash) is generated during the crude wheat straw screening operation used in the straw pulping industry. Compared with wheat straw, WWS is not utilizable for pulp production and is thus regarded as waste. However, due to its low value, theoretical availability, and high abundance of polysaccharides (26.5% cellulose and 17.6% xylan), WWS is worthy of investigation as an attractive starting material for the fuel ethanol industry (Huang et al., 2018).

Our previous work on WWS identified that autohydrolysis was an appropriate low-cost and sustainable pretreatment for WWS, but certain concessions had to be made. First, the WWS required a pre-washing operation in order to remove unbound ash. It was found that this ash was causing an unwanted buffering effect on the autohydrolysis liquor, preventing the pH from reaching the values required to facilitate hemicellulose hydrolysis (required for pretreatment). To eliminate the buffering effect of the ash, a 500 times (v/w) water washing step prior to the pretreatment was adopted to remove the unbound ash of WWS effectively, and received significant enhancement of enzymatic hydrolysis efficiency in our previous work (Huang et al., 2016b). However, about 23.0% cellulose and 25.5% hemicellulose were lost after 100 times (v/w) water washing (Huang et al., 2017). Moreover, although water can be recycled, such a huge consumption of water is unpractical for industry. Therefore, it is urgent for researchers to find alternative methods to overcome the self-buffering effect of WWS.

Although it has been reported that implementations of metal chlorides ($AlCl_3$ and $FeCl_3$) during autohydrolysis pretreatment successfully facilitate decomposition of biomass which translates into remarkable enhancements to enzymatic hydrolysis efficiency (Kamireddy

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et al., 2013; Liu et al., 2009; Zhang et al., 2018), there have been no studies which apply these inorganic reagents into the system of autohydrolysis pretreatment of high ash WWS. We chose to investigate the effect of these reagents based on a knowledge of soil science, where ions such as Fe^{3+} & Al^{3+} show stronger cation exchange capacity than H^+ (Charlet and Tournassat, 2005). Thusly, if ash-rich WWS is autohydrolyzed in the presence Fe^{3+} or Al^{3+}, it may be possible for these cations to supersede the interactions problematically occurring between the H^+ generated during autohydrolysis and the ash from WWS. For this reason, $AlCl_3$ and $FeCl_3$ are hypothesized as being capable of eliminating the buffer system resulting from WWS' ash, resulting in monosaccharide gains during subsequent enzymatic hydrolysis. It is worthy to mention that excessive uses of metal chlorides may increase the cost of equipment maintenance due to the low pH values of the prehydrolysate. The aims of adding metal chlorides in autohydrolysis were to make WWS could be pretreated like prewashed WWS under a weakly acid medium (pH around 4). In that pH range, the corrosions of equipment were accessible. Meanwhile, metal chlorides were frequently used in chemical industry (Guisnet et al., 2011). Therefore, implementations of metal chlorides in WWS autohydrolysis showed potential prospects on enhancing the autohydrolysis efficiency by minimizing the self-buffering effects caused by problematic ash.

In the present paper we focus on the effects of metal chloride ($AlCl_3$ and $FeCl_3$) on facilitating autohydrolysis pretreatment efficiency of WWS. The influence of autohydrolysis pretreatment with or without adding metal chloride on the glucan recovery, xylan and lignin removal of the pretreated WWS, and the sequential enzymatic hydrolysis efficiency were studied. The acid buffer capacity changes and cation exchange capacity of pretreated WWS were investigated to show the collapse extent of buffer system and the reducing extents. Cation exchanges during the pretreatment process were estimated by the results obtained by inductively coupled plasma-optical emission spectrometer (ICP-OES).

2. Materials and methods

2.1. Materials and regents

WWS used in this work was provided by a straw pulp mill (Shandong Province, China). Cellulase (Cellic® CTec2) was kindly provided by Novozymes North America (Franklinton, NC, USA), with filter paper activity of 250.0 FPU/mL and cellubiase activity of 2731 U/mL (Ghose, 1987). All other reagents used in this work were analytical grade.

2.2. Autohydrolysis pretreatment

Autohydrolysis pretreatment of WWS was performed in 1.25 L vessels heated by a laboratory oil bath. 50 g (on a dry weight basis) of raw WWS were loaded into reactors and soaked with different concentrations (0–20 mM) of $AlCl_3$, $FeCl_3$, with a final solid to liquid ratio of 1:10 (w/v). The pre-washed WWS produced by 500 times (v/w) water washing was prepared prior to the pretreatment according to our previous work (Huang et al., 2016b) and serves as a control group to be pretreated. For pretreatment, the reactor temperature was raised from 60 °C to 180 °C at a heating rate of 2 °C/min, and maintained at 180 °C for 40 min (Narron et al., 2017; Wu et al., 2018). After pretreatment, reactors were rapidly cooled via submersion into a cold water bath. Pretreated residues were separated from the liquid fraction (prehydrolyzate) using cloth bag filtration. After filtration, the pretreated residues were washed by deionized water until neutral to remove residual metal ions and then stored in sealed plastic bags at 4 °C. Prehydrolyzate was analyzed for pH, and concentrations of inhibitors, monosaccharides, and oligosaccharides (mostly xylo-oligosaccharides, "XOS"). The scheme of metal chlorides assisted WWS autohydrolysis were shown in Fig. 1.

2.3. Cation exchange capacity and acid buffering capacity of pretreated WWS

The cation exchange capacity (CEC) of pretreated material was determined through a method modified from the literature (Hendershot and Duquette, 1986). About 1 g of each sample was milled, and then added to a 30 mL $BaCl_2$ solution to exchange the cations present in ash. Samples were then centrifuged (5000 rpm for 10 min), and the supernatant was discarded. This operation was repeated three times. Next, 50 mL of deionized water was then added to remove Cl^- anions from the solution. This operation was also repeated once more. Resultant samples were then mixed with 25 mL of 0.1 M H_2SO_4 solution to precipitate the adsorbed Ba^{2+} as $BaSO_4$. The mixture was then filtered and the residual acid was collected from the filtrate for titration with 0.1 M NaOH solution. The CEC was calculated from the amount of H^+ adsorbed by the sample during the precipitation of $BaSO_4$.

The acid buffering capacity (ABC) of pretreated WWS samples were determined using a procedure reported in literature (Lloyd and Wyman, 2005). For each sample, 10 g (on a dry weight basis) pretreated WWS was put into a polytetrafluoroethylene crucible and burned in Muffle furnace at 575 °C for 12 h. After combustion and cooling to room temperature, the remainder ash was dried to constant weight for 4 h at 105 °C. Next, the dried ash was mixed with 50 mL deionized water in a beaker. The ash & water mixture was then titrated with 0.1 M H_2SO_4 solution at a flow rate of 0.05 mL/min using a multi-water quality meter (MM-60R, TOADKK, Tokyo, Japan). The terminal pH value was set at 3.0, and the volume of titration was recorded. ABC was calculated from said results.

2.4. Element analysis

Quantification of metal cations was performed using a procedure modified from the literature (Souza et al., 2018). For quantification in solids samples, solid ash was obtained through incineration of pretreated WWS at 575 °C for 12 h. Next, ~0.01 g ash or 1 mL liquid prehydrolyzate liquid (liquid samples) were inserted into a reaction vessel. Following sample addition, 5 mL HNO_3 (65% $m\,m^{-1}$) and 1 mL H_2O_2 (30% $m\,m^{-1}$) was added into the reaction vessel for analyzing metal cations. However, for detecting Si contents, 2.5 mL HF (48% $m\,m^{-1}$), 3 mL HNO_3 (65% $m\,m^{-1}$), 1 mL HCl (12 M) and 1.25 g granular boric acid was loaded into the reaction vessel (Bernas, 1968). A closed-vessel microwave system (MARS6, CEM, USA) was then used to acid digest the materials. Digestion was conducted at 165 °C for 5 min, followed by a ramp up to 185 °C for 20 min. After digestion, acid removal was performed at 160 °C for 1 h to evaporate nitric acid and resulting in ~ 1 mL of residual liquids following digestion. The remaining liquid was then mixed with de-ionized water to the constant volume 30 mL for cation measurement. Analytical blanks (deionized water) were also subjected to the same digestion procedure. After sample preparation, Fe, Al, Ca, Mg, K and Na concentrations were determined by ICP-OES (Optima 8000, Perkin-Elmer).

2.5. Enzymatic hydrolysis

Enzymatic hydrolysis of WWS samples was performed in 0.05 M citrate buffer (pH 4.8) at 50 °C with a substrate loading of 5% (w/v), with the reaction slurry agitated using a thermostat shaker at 150 rpm. The enzyme loading during all hydrolysis experiments was maintained at 25 FPU/g-glucan. Samples were withdrawn during the course of hydrolysis at 2, 4, 6, 12, 24, 48 and 72 h. The obtained enzymatic hydrolyzates were centrifuged at 10000 rpm for 10 min to remove residual suspended solids. As compared to autohydrolyzed WWS, no residual metal cations (Al and Fe) were found in the enzymatic hydrolysate of metal chloride pretreated residues. To quantify monosaccharides in enzymatic hydrolyzate, the supernatants were diluted and subsequently filtered through a 0.22 μm syringe filter for HPLC (high performance