



## Short Communication

# The effect of metal ions as co-catalysts on acidic ionic liquid catalyzed single-step saccharification of corn stover in water



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## HIGHLIGHTS

- $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$  co-catalysts enhances TRS yields in the corn stover hydrolysis.
- Hydrolysis using  $\text{Mn}^{2+}$  co-catalyst gave the highest TRS yield of 90.2% at 160 °C.
- Except  $\text{Cr}^{3+}$ , all other metal chloride co-catalysts improved the glucose yields.

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## ABSTRACT

The effects of adding  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{La}^{3+}$  chlorides as co-catalysts to 1-(1-propylsulfonic)-3-methylimidazolium chloride acidic ionic liquid catalyzed saccharification of corn stover in aqueous medium was studied at 140–170 °C, by measuring the total reducing sugar (TRS) and glucose yields. The samples with  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$  as co-catalysts produced higher TRS yields compared to the sample without the metal ions. The  $\text{Mn}^{2+}$  produced the highest catalytic effect enhancements and produced TRS yields of 68.0%, 72.9%, 90.2% and 87.9% at 140, 150, 160 and 170 °C respectively; whereas the corn stover samples without the  $\text{Mn}^{2+}$  produced TRS yields of 42.9%, 52.3%, 54.4% and 53.5% at the same four temperatures. At higher temperatures of 160 and 170 °C, all metal ions studied produced significant enhancements in glucose yields, except  $\text{Cr}^{3+}$ . The addition of  $\text{La}^{3+}$  as a co-catalyst produced the highest glucose yield improvement.

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## 1. Introduction

The conversion of the biomass to fermentable sugars or saccharification is a critical step in the cellulosic ethanol process and heating in the presence of dilute aqueous acid catalysts is an alternative method to widely practiced enzymatic hydrolysis. In recent times a number of researchers have attempted to revive this classical method by improving on simple aqueous sulfuric acid high temperature–pressure treatments (Amarasekara, 2013). Some of the new directions taken in enhancing sugar yields include the use of organic acids such as malic acid, aryl/alkyl sulfonic acids in place of sulfuric acid (Mosier et al., 2001; Amarasekara and Wiredu, 2012) mechanical activation such as ball milling (Zhang et al., 2015) as well as incorporation of co-catalysts to acid catalyst system (Liu et al., 2009; Peng et al., 2010; Kamireddy et al., 2013). The addition of metal ions as a co-catalyst for enhancing the effect of an acid is a logical choice as one can expect the chelation of

certain metal ions with hydroxyl group may facilitate the action of the Brønsted acid (Liu et al., 2009; Peng et al., 2010; Kamireddy et al., 2013). In most studies transition metals have been tested as co-catalysts, for example, Monavari and co workers have shown that the utilization of a small amount of ferrous sulfate during the  $\text{SO}_2$ – $\text{H}_2\text{SO}_3$  pretreatment of spruce wood chips could produce a slight increase in overall glucose yield from 74% to 78% (Monavari et al., 2011). In another recent study Zhao et al. have examined the effects of addition of  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  as co-catalysts in the acid hydrolysis of corn stover under microwave irradiation conditions (Zhao et al., 2013). Where they observed enhancements in reducing sugar yields in the order  $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$ . Furthermore, a 3.0% concentration of ferrous sulfate as a co-catalyst produced the highest reducing sugar yield of 35.10% (Zhao et al., 2013). In another recent report the effects of six metal ions:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  on dilute hydrochloride acid catalyzed hydrolysis of bamboo biomass in ionic liquid *n*-butylmethylimidazolium chloride was investigated (Wang et al., 2014). In this study, Wang et al. reported a total reducing sugar yield of 67.1%, using  $\text{CuCl}_2$  as the co-catalyst, after

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4 h at 100 °C. In addition, they noticed an increase in the total reducing sugar yield by about 7% when the reaction time was decreased to 3 h (Wang et al., 2014). The pretreatment and saccharification with metal ion itself acting as a Lewis acid without the use of a Brønsted acid is also known. In this example sugarcane bagasse was pretreated with different metal chlorides: CrCl<sub>3</sub>, FeCl<sub>3</sub>, FeCl<sub>2</sub>, ZnCl<sub>2</sub> and AlCl<sub>3</sub> before the enzymatic hydrolysis and FeCl<sub>3</sub> pretreatment produced the highest sugar yield (Chen et al., 2014). In addition halide salts of alkali and alkali earth metals are also known to improve the hydrothermal saccharification of cellobiose under microwave heating conditions (Tsubaki et al., 2012).

Since 2009 we have been exploring the use of alkyl/aryl sulfonic acids (Amarasekara and Wiredu, 2012), as well as sulfonic acid group functionalized acidic ionic liquids (Amarasekara and Owereh, 2009; Amarasekara and Wiredu, 2011) as catalysts for the saccharification of cellulose and lignocellulosic biomass for cellulosic ethanol process and other biofuel applications. Where we first reported that sulfonic acid group functionalized imidazolium type Brønsted acidic ionic liquid like 1-(1-propylsulfonic)-3-methylimidazolium chloride can be used as an acid catalyst at temperatures below 100 °C and at atmospheric pressure for the hydrolysis of cellulose dissolved in the ionic liquid itself (Amarasekara and Owereh, 2009). In the follow up work we found that these acidic ionic liquids can be used as homogeneous catalysts in aqueous phase as well (Amarasekara and Wiredu, 2011). For example, a dilute aqueous solution 0.0321 mol H<sup>+</sup>/L 1-(1-propylsulfonic)-3-methylimidazolium chloride was shown to be a better catalyst than aqueous sulfuric acid of the same H<sup>+</sup> ion concentration for the hydrolysis of cellulose in water at 140–160 °C temperature range (Amarasekara and Wiredu, 2011).

This superior catalytic activity of the Brønsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride when compared to sulfuric acid was explained as a result of an interaction or binding of the imidazolium chloride ionic moiety on the cellulose surface, which assisted the approach of the acidic functionality for the hydrolysis of the glycosidic link in the polysaccharide. Since a number of recent studies on using transition metal ions like Cu<sup>2+</sup> and Fe<sup>3+</sup> have shown to improve the mineral acid catalyzed saccharification of biomass, we hypothesized that even better catalytic effect enhancements can be expected for Brønsted acidic ionic liquid catalyzed saccharification of lignocellulosic biomass. Therefore, in an attempt to test this hypothesis and to develop a simple cellulase enzyme mimic type homogeneous acid catalysts for cellulosic ethanol and other biorefinery processes as well as an extension of our earlier work (Amarasekara and Owereh, 2009) we have studied the effects of eight metal ions as co-catalysts on acidic ionic liquid catalyzed single step saccharification of corn stover in water.

## 2. Experimental

### 2.1. Materials and instrumentation

Corn stover used in this study is a gift sample from National Renewable Energy Laboratory, Boulder, CO, USA. Air-dried corn stover was pulverized in a blender to obtain a homogenous powder and sieved through a brass mesh (Aldrich mini-sieve set, Z 675415, size 25, particle size 0.7 mm). The powder was then dried (~15 h) in an oven maintained at 70 °C, to a constant weight, and stored in a tightly sealed plastic bottle. 1-Methylimidazole, 1,3-propanesultone, analytical grade chloride salts of Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and La<sup>3+</sup> were purchased from Aldrich Chemical Co. Single step corn stover saccharification experiments in water were carried out in 25 mL stainless steel solvothermal reaction kettles with Teflon inner sleeves, purchased from Lonsino Medical

Products Co. Ltd. Jingsu, China. These reaction kettles were heated in a preheated Precision Scientific model-28 laboratory oven with temperature accuracy ±1 °C. Total reducing sugars (TRS, total of glucose and glucose oligomers with reducing groups) produced during the corn stover saccharification was measured using 3,4-dinitrosalicylic acid (DNS) method (Breuil and Saddler, 1985). The glucose produced in the saccharification was measured using glucose oxidase–peroxidase enzymatic assay (Bergmeyer and Bernt, 1974). The absorption readings in the DNS method and oxidase–peroxidase enzymatic assay were recorded using a Thermo Scientific GENESYS 10S UV/Vis spectrophotometer and 1.00 cm quartz cells.

### 2.2. Synthesis of 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyst

1-(1-Propylsulfonic)-3-methylimidazolium chloride was prepared by condensation of 1-methylimidazole with 1,3-propanesultone and acidification of the resulting salt with conc. HCl, following the previously published procedure (Gui et al., 2004).

### 2.3. General experimental procedures for the saccharification of corn stover samples using aqueous 1-(1-propylsulfonic)-3-methylimidazolium chloride solutions with and without metal ions

A stock solution of the 1-(1-propylsulfonic)-3-methylimidazolium chloride acidic ionic liquid in water was prepared by dissolving appropriate amount in deionized water to give an acid concentration of 0.0321 mol H<sup>+</sup>/L. The accuracy of the concentration was checked by titration with standardized aqueous NaOH solution using phenolphthalein as the indicator. Corn stover powder (0.050 g) was suspended in 2.50 mL of the aqueous acidic ionic liquid solution and metal chloride (20 mol% of glucose equivalent in corn stover) was added to the stainless steel reaction kettle with a Teflon inner sleeve. The reaction kettle was firmly closed and heated in a thermostated oven maintained at the desired temperature for 3.0 h. Then reaction kettle was removed from the oven and immediately cooled under running cold water to quench the reaction. The contents were transferred into a centrifuge tube and diluted to 10.0 mL with deionized water, neutralized by drop wise addition of 0.5 M aq. NaOH, and centrifuged at 1700g for 6 min to precipitate the solids. The clear supernatant was used for the total reducing sugar (TRS) determination by 3,4-dinitrosalicylic acid (DNS) method and the glucose formed was measured using glucose oxidase/peroxidase enzymatic assay as described in our earlier work (Amarasekara and Wiredu, 2012). A similar experiment without the metal salt was used as the reference. The total C5 and C6 polysaccharides (cellulose + xylan + arabinan + mannan + galactan) in corn stover was taken as 65% (w/w) for the theoretical yield calculations as described in the analysis elsewhere (Amarasekara, 2013; Huang et al., 2009). The TRS and glucose % yields produced during the saccharification of corn stover in aqueous 1-(1-propylsulfonic)-3-methylimidazolium chloride solution at 140, 150, 160 and 170 °C, using Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and La<sup>3+</sup> chlorides as co-catalysts, as well as the reference samples are shown in Figs. 1 and 2.

## 3. Results and discussion

Our earlier studies have shown that imidazolium type sulfonic acid group functionalized 1-(1-alkylsulfonic)-3-methylimidazolium chloride ionic liquids are a better catalysts than pyridinium and triethanol ammonium cation based acidic ionic liquids with built-in sulfonic acid groups for the cellulose hydrolysis (Amarasekara and Owereh, 2009). Therefore 1-(1-

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