Current Catalysis, **XXXX**, *X*, **000-000**

RESEARCH ARTICLE

The Co-catalyst Effects of Mn(II), Zn(II), and Cr(III) Chlorides on Acidic Ionic Liquid Catalyzed Synthesis of Value-added Products from Cellulose in Aqueous Ethanol

Ananda Sarath Amarasekara[1,*], Bernard Wiredu[1] and Moriam Animashaun[1]

[1]*Department of Chemistry, Prairie View A&M University, Prairie View, TX 77446, USA*

ARTICLE HISTORY

Received: October 27, 2022
Revised: January 13, 2023
Accepted: February 01, 2023

DOI:
10.2174/2211544712666230322092202

Abstract: ***Background:*** Catalytic depolymerization and processing of cellulose can be used to produce value-added renewable feedstock chemicals.

Objective: This study aimed to develop an acidic ionic liquid-metal ion chloride catalyst system-based single-reactor method for processing cellulose into value-added products.

Methods: The effect of metal chlorides as co-catalysts on 1-(1-propylsulfonic)-3-methylimidazolium chloride acidic ionic liquid catalyzed degradation of cellulose in 40% (v/v) aq. ethanol was studied by measuring levulinic acid, ethyl levulinate, and 5-hydroxymethylfurfural yields.

Results: In experiments with Mn(II) and Zn(II) chloride co-catalysts at 160 and 170°C for 12 h, the initial yields of ethyl levulinate and 5-hydroxymethylfurfural improved from ~ 7% to ~ 12-15% due to co-catalytic effects. The highest enhancements in ethyl levulinate yields were observed with $CrCl_3$, where the yield increased from 6 to 27% with the addition of a 10 mol% co-catalyst.

Conclusion: All three transition metal chlorides studied caused improvements in yields of secondary products, ethyl levulinate and 5-hydroxymethylfurfural, in acidic ionic liquid catalyzed degradation of cellulose in aqueous ethanol. The most significant enhancements in ethyl levulinate yields were observed with $CrCl_3$ as a co-catalyst.

Keywords: Cellulose, co-catalyst, ethyl levulinate, levulinic acid, 5-hydroxymethylfurfural.

1. INTRODUCTION

Efficient depolymerization of the most abundant biopolymer cellulose to its monomer glucose and conversion to renewable feedstock chemicals and fuels is one of the main challenges in the utilization of renewable biomass in a sustainable carbon-based future. The acid-catalyzed depolymerization of cellulose allows further transformation of glucose to its downstream dehydration and degradation products, such as 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) [1, 2]. There are several innovative approaches tested in recent years for improving acid-catalyzed biomass processing, such as acidic ionic liquids or organic acids in place of traditional mineral acids [3, 4], solid acids [5], immobi-lized acidic ionic liquids [6], mechanical activation methods like ball milling [7] as well as the incorporation of co-catalysts to acid catalyst system [8-10]. The use of metal ions or salts as a co-catalyst is a rational choice as carbohydrate oxygen atoms with lone pairs are well known to interact or complex and possibly enhance the effect of acid-catalyzed hydrolysis of cellulose, as well as further transformations [10-13]. Even though metal complexes and salts are traditionally used as catalysts in countless industrial chemical processes, the application of metal-catalyzed cellulose depolymerization and further transformation of monosaccharides is a relatively unexplored area.

The extended aqueous acid hydrolysis of cellulose at high temperatures is known to give levulinic acid as a result of a series of reactions involving depolymerization of cellu-lose to glucose, dehydration to 5-hydroxymethylfurfural, and then rehydration of levulinic acid; however, many unwanted side reactions, such as humin formation, can affect the le-vulinic acid yield in this acid-catalyzed process [14, 15]. In the last 10-15 years, numerous research groups have ex-plored the potential of levulinic acid-derived compounds, such as 2-methyltetrahydrofuran, γ-valerolactone, levulinate esters [16-19], and 5-methyl-2-pyrrolidone [20] as green solvents [21], polymer and resin precursors [22-24], plasti-cizers [25], as well as building block materials for pharma-ceutical and food industry [26].

---

*Address correspondence to this author at the Department of Chemistry, Prairie View A&M University, Prairie View, TX 77446, USA; Tel: +1 936 261 3107; Fax: +1 936 261 3117; E-mail: asamarasekara@pvamu.edu

2211-5447/XX $65.00+.00

The levulinic acid methyl, ethyl, and butyl esters are particularly attractive groups as blend-in fuels for diesel [27] as well as for gasoline [28]. Ethyl levulinate (EL) is the most widely studied ester. Corn, sugar cane, or cellulose-derived ethanol can be used in esterification [29]. Ghosh et al. have recently suggested that EL would be more suitable as a blend-in fuel for gasoline, rather than as a blend-in for diesel as previously proposed. This proposal was based on their reaction kinetics studies and octane number measurements. Furthermore, they reported a significant enhancement in the octane number of gasoline by blending with ethyl levulinate [30].

Since 2009, we have studied the use of ionic liquid-based catalysts and in particular $-SO_3H$ functionalized Brönsted acidic ionic liquids (BAILs) [31-33] for the hydrolysis of cellulose and cellulosic biomass for biofuel and renewable feedstock applications. During this work, we first reported that BAILs, such as 1-(1-propylsulfonic)-3-methylimidazolium chloride, can be used as an acid catalyst for cellulose hydrolysis in the ionic liquid itself or water as the solvent medium [31, 32]. Moreover, our recent studies have shown that untreated cellulose (DP ~ 450) can be converted to a mixture of levulinic acid, ethyl levulinate, and HMF in a one-pot reaction using BAIL as the catalyst in aqueous ethanol medium [34]. In this procedure, the acidic ionic liquid catalyst is used for multiple processes: such as hydrolysis of cellulose to glucose, conversion of monosaccharide to HMF, LA, and formic acid as well as esterification of LA to ethyl levulinate. The experiment using 1-(1-propylsulfonic)-3-methylimidazolium chloride as the catalyst in ~ 40% water in aqueous ethanol at 170 °C, for 12 h, produced the highest ethyl levulinate yield. However, levulinic acid yield could be enhanced with water content up to about 54% in aqueous ethanol, and the highest LA yield obtained was 23.7%. The BAIL catalyst could be recovered for reuse as well [34]. In attempts to improve the yields of these secondary products, we studied the effects of adding zeolites as co-catalysts on the BAIL-catalyzed cellulose degradation in aqueous ethanol medium [35]. Under this study, the effects of zeolite-β, zeolite-Y and ZSM-5 on BAIL-catalyzed transformation of cellulose to HMF, levulinic acid, and ethyl levulinate in 40% (v/v) aqueous ethanol were studied by measuring the yields of these three products. All three zeolites enhanced the product yields, but the zeolite ZSM-5 co-catalyst was found to be the most effective and a marked effect was reported in ethyl levulinate yields [35]. The highest improvements were observed at 180°C in 24 h experiment and the highest EL yield achieved with ZSM-5 as a co-catalyst was 29.5% [35]. As the continuation of these efforts and an innovative attempt to improve the secondary product yields, in this study, we studied co-catalytic effects of transition metal salts, such as Mn(II), Zn(II), and Cr(III) chlorides, on Brønsted acidic ionic liquid catalyzed degradation of cellulose in aqueous ethanol.

2. EXPERIMENTAL SECTION

2.1. Materials and Instrumentation

Sigmacell cellulose - type 101 (from cotton linter, DP ~ 450), 1,3-propanesultone, 1-methylimidazole, and analytical grade chloride salts, including $MnCl_2.4H_2O$, $ZnCl_2$, and $CrCl_3.6H_2O$, were purchased from Aldrich Chemical Co. Catalyst 1-(1-propylsulfonic)-3-methylimidazolium chloride was prepared by reaction of 1-methylimidazole with 1,3-propanesultone, followed by acidification of the salt produced with 37% concentrated hydrochloric acid according to the literature procedure, as shown in Fig. (**1**) [36, 37]. Stainless steel solvothermal reaction kettles containing Teflon inner sleeves with a volume of 25 mL (Lonsino Medical Products Co., Ltd. Jingsu, China) were used in all cellulose hydrolysis experiments. The reaction kettles were heated in a preheated laboratory oven (Precision Scientific model-28) with an accuracy of ± 1°C. The quantitative analysis of HMF, LA, and EL was carried out by using a Varian 3900 gas chromatography instrument with a 15 m X 0.25 mm WCOT fused silica capillary column, VF-1ms stationary phase. FID detector, injector, and oven temperature were 250, 300, and 200 °C, respectively; flow rate was 2.0 mL/minute. Standard curves for quantitative analysis were generated by means of Varian Star 6.2 Chromatographic Workstation software with the total ion current peak area correlated to the concentration of the compound being used in the quantitative analysis. The HMF, levulinic acid, and ethyl formed were identified and confirmed by co-injection of authentic samples using Varian Saturn 2100T GC-MS.

General procedure for 1-(1-propylsulfonic)-3-methylimidazolium chloride acidic ionic liquid catalyzed the reaction of cellulose in 40% (v/v) aqueous ethanol with and without a metal ion co-catalyst.

Sigmacell cellulose (60 mg, 0.370 mmol of glucose equivalent), 1-(1-propylsulfonic)-3-methylimidazolium chloride (10 mg, 0.042 mmol), and metal chloride co-catalyst (0.042 mmol) were mixed in a stainless steel solvothermal reaction kettle with a volume of 25 mL and then 1.00 mL of 40% (v/v) aqueous ethanol was added. The firmly closed reaction kettle was then heated inside an oven for 6-12 h. The reference experiments without metal chloride co-catalysts were carried out under identical conditions, without adding metal chloride. The kettle was removed from the ov-en at the end of the heating period and cooled to room temperature by running under cold water. The content was dilut-ed with ethyl acetate (10 mL), transferred into a centrifuge tube, and centrifuged at 1700X *g* for 5 minutes. The separat-ed clear ethyl acetate extract was analyzed by gas chroma-tography for HMF, LA, and EL by injecting 2 ∝L samples. The standard curve generated for each compound using Vari-an Star 6.2 GC Workstation software was used in the calcula-tion of the weights of HMF, LA, and EL formed during the reactions. The cellulose degradation reactions were carried out in triplicate and the average percent yields of HMF, levulinic acid, and ethyl levulinate for the reactions carried out for 6 and 12 h were used to draw plots, as shown in Fig. (**2**).

3. RESULTS AND DISCUSSION

1-(1-Propylsulfonic)-3-methylimidazolium chloride was chosen as the homogeneous catalyst for all aqueous ethanol medium cellulose degradation experiments, as our prior studies have shown that this $-SO_3H$ group tethered BAIL is a better catalyst than other pyridinium, triethanol ammonium cation based systems and other imidazolium cation based catalysts [31]. The BAIL catalyst was prepared by a two-step process, as shown in Fig. (**1**), where 1-methylimidazole

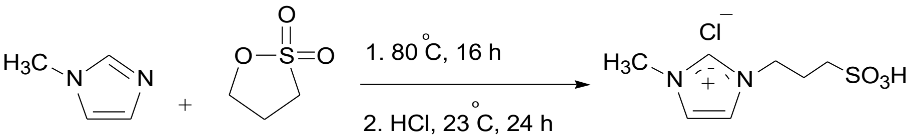


Fig. (1). Synthesis of 1-(propylsulfonic)-3-methylimidazolium chloride catalyst.

was condensed with 1,3-propanesultone to give a zwitterion in the first step. Then, acidification of the resulting salt with 37% concentrated hydrochloric acid and removal of water under vacuum produced the BAIL catalyst in quantitative yield [36, 37].

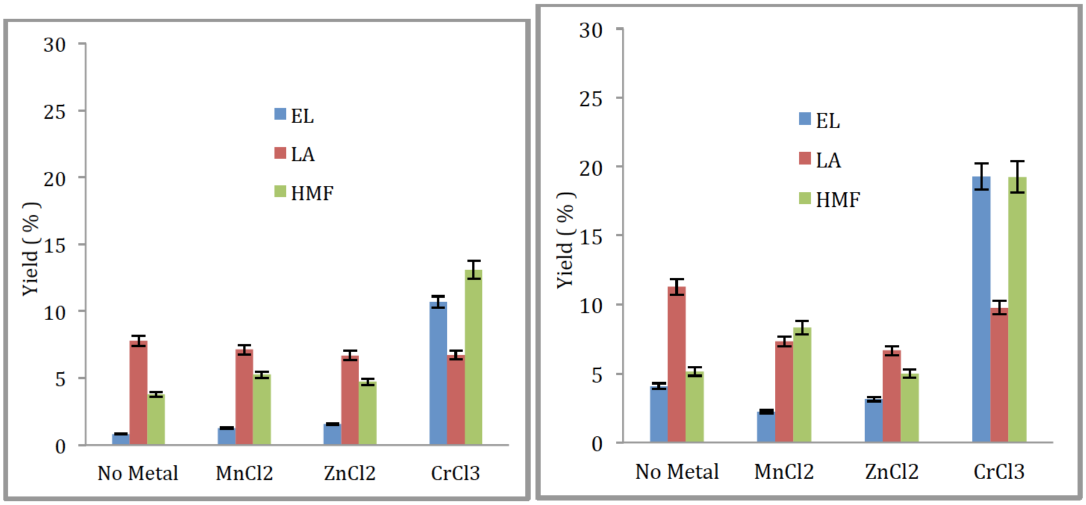
The co-catalyst effects of Mn(II), Zn(II), and Cr(III) chlorides on 1-(1-propylsulfonic)-3-methylimidazolium chloride ionic liquid catalyzed the degradation of cellulose in 40% (v/v) aqueous ethanol were evaluated at four different temperatures 140, 150, 160, and 170 °C and at two different reaction times 6 and 12 h. The composition of the aqueous ethanol medium, temperatures, and reaction times were selected based on our previous experiments on BAIL-catalyzed degradation of cellulose in aqueous ethanol [34, 35]. The Mn(II), Zn(II), and Cr(III) chlorides were chosen as co-catalysts for this study as these transition metals showed significant co-catalytic effects in our previous studies on BAIL catalyzed depolymerization of cellulose to glucose in aqueous medium [38-40]. All experiments were carried out in triplicate, and the average percentage yields of ethyl levulinate (EL), levulinic acid (LA), and 5-hydroxymethylfurfural (HMF) formed with or without Mn(II), Zn(II), and Cr(III) chlorides as co-catalysts under eight different experimental conditions are shown in Fig. (**2**) as plots a-h.

In general, the addition of $CrCl_3$ as a co-catalyst enhanced the combined yields of EL, LA, and HMF in all experiments. In 6 h experiments, the addition of Mn(II) and Zn(II) chloride as co-catalysts had a minimum or no effect on the product yields. However, significant improvements in EL yields and reduction in LA yields could be seen due to the addition of $CrCl_3$ at 160, and 170°C in 6 h experiments in comparison to the sample without a co-catalyst. For example, at 170°C, in the 6 h experiment, EL yield increased from 7.2% to 26.7% and LA yield decreased from 14.1% to 6.2% due to the addition of $CrCl_3$ co-catalyst, as shown in Fig. (**2d**). In longer run (12 h) experiments carried out at 160 and 170°C, Mn(II) and Zn(II) chloride co-catalysts enhanced EL and HMF yields in comparison to samples without co-catalysts. For example, at 160°C, a 12 h experiment without a co-catalyst produced only 6.9 and 7.4% yields of EL and HMF, respectively. The addition of $MnCl_2$ co-catalyst improved EL and HMF yields to 12.4 and 14.8%, respectively. Furthermore, the addition of $ZnCl_2$ improved EL and HMF yields to 14.8 and 11.5%, respectively, as shown in Fig. (**2g**). On the other hand, the addition of Mn(II) and Zn(II) chloride co-catalysts severely reduced the LA yields at 160°C and 170°C in 12 h experiments. This may be due to a positive co-catalytic effect of Mn(II) and Zn(II) chloride in the esterification of LA to EL.

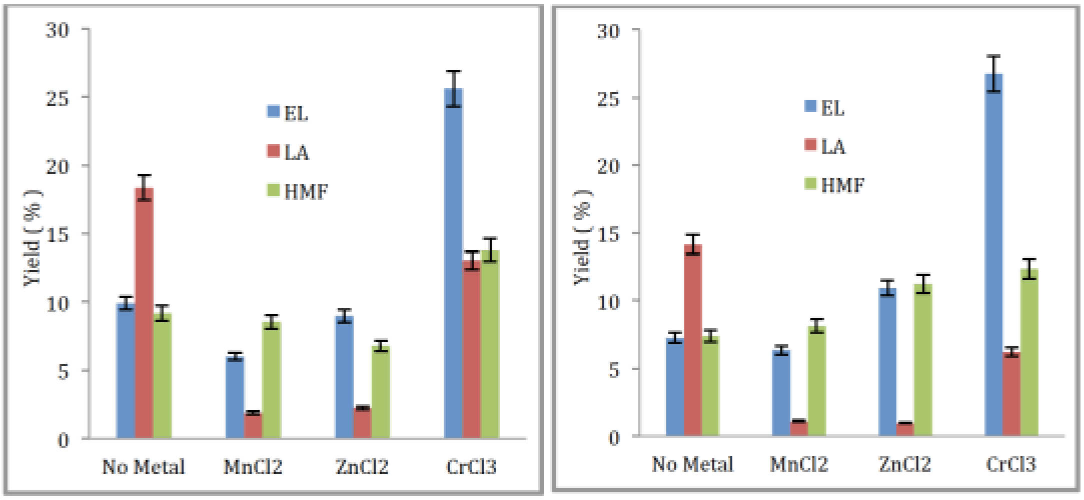
The most significant enhancements in EL yields were seen in 160°C and 170°C, 12 h long run experiments with the addition of $CrCl_3$ as the co-catalyst. As shown in Fig. (**2g**), in the 160 °C, 12 h experiment, EL yield improved from 6.9% to 26.0% due to the addition of $CrCl_3$. Similarly, at 170 °C, in the 12 h experiment (Fig. **2h**), EL yield improved from 6.0% to 27.4% due to the addition of $CrCl_3$, which was a 356% enhancement of EL yield and the highest co-catalytic effect seen in the present study. This is a major improvement in EL yield in a BAIL-catalyzed transformation of cellulose to EL compared to our previous attempts to improve the EL yields by adding different zeolites, such as zeolite-β, zeolite-Y and ZSM-5 as co-catalysts, which produced a maximum enhancement of about 80% [35]. Furthermore, we proposed a reaction pathway for the BAIL-catalyzed cellulose degradation, as shown in Fig. (**3**). In the first step, BAIL-catalyzed depolymerization of cellulose gives glucose and the generally accepted mechanism for dehydration of glucose to HMF involves glucose to fructose isomerization and a stepwise loss of three water molecules, as shown in the scheme [41, 42]. In the series of reactions involved, isomerization is a complex and challenging step, and the addition of a metal chloride co-catalyst may promote this step by chelation with -OH groups and lowering the activation energy for isomerization [43-45]. HMF formed as an intermediate is known to undergo rehydration, followed by fragmentation in aqueous media, producing levulinic acid and formic acid [35].

The co-catalytic effect is particularly significant in using Cr^{3+} chloride, where the highest enhancement in ethyl levulinate yields was reported. Similar catalytic and co-catalytic effects of transition metal salts were reported for dehydration as well as fragmentation transformations of carbohydrates; moreover, these catalytic effects are explained in terms of chelation of metal salts with -OH groups of the carbohydrate [9, 46, 47]. For example, Bali and co-workers studied the mechanism of conversion of glucose to HMF via metal salt catalyzed reactions in 1-ethyl-3-methylimidazolium chloride neutral ionic liquid medium and observed the highest activity with $CrCl_3$ after testing a series of transition metal salts [46]. Furthermore, they explained the catalytic effect of $CrCl_3$ through a mechanism involving the chelation of $CrCl_3$ to the glycosidic -OH and pyranose ring oxygen, followed by ring opening to the open-chain form of glucose, leading to further transformations. In another example, Peng et al. also used a $CrCl_3$-glucose chelation mechanism to explain the catalytic conversion of cellulose to levulinic acid in aqueous medium [9]. Interestingly, none of these previous studies reported oxidation-reduction processes of Cr^{3+} during these catalytic transformations of carbohydrates. Therefore, co-catalytic effects observed in our studies were also likely to be due to similar chelation effects, without oxidation-reduction processes of Cr^{3+} as reported previously [9, 46, 47].

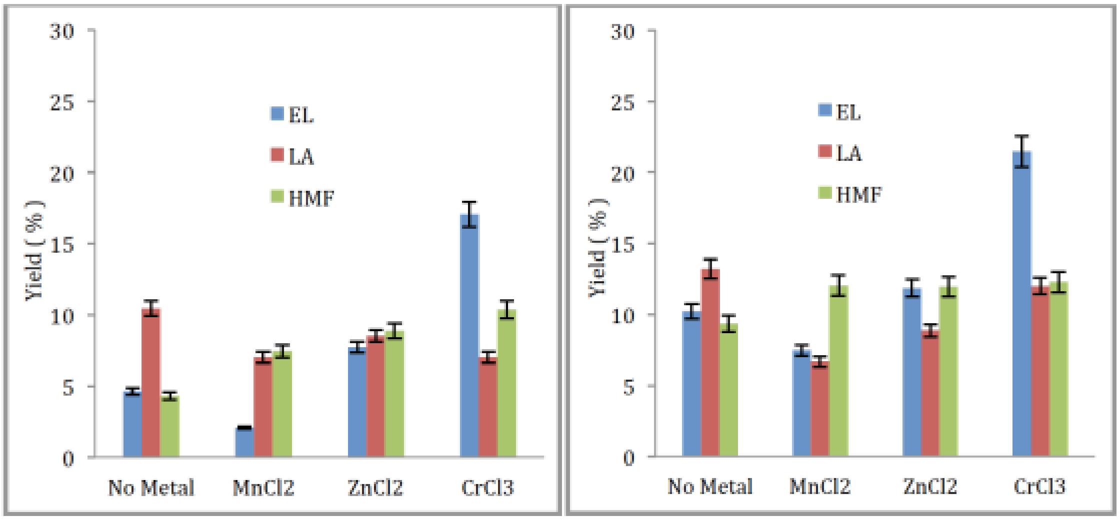
The LA yields are generally higher in experiments carried out without metal salt co-catalysts, as particularly apparent in Figs. (**2c** and **2h**). This may be due to the facile promotion of the esterification of LA to EL by the metal



a. 140°C, 6 h. **b. 150°C, 6 h.**

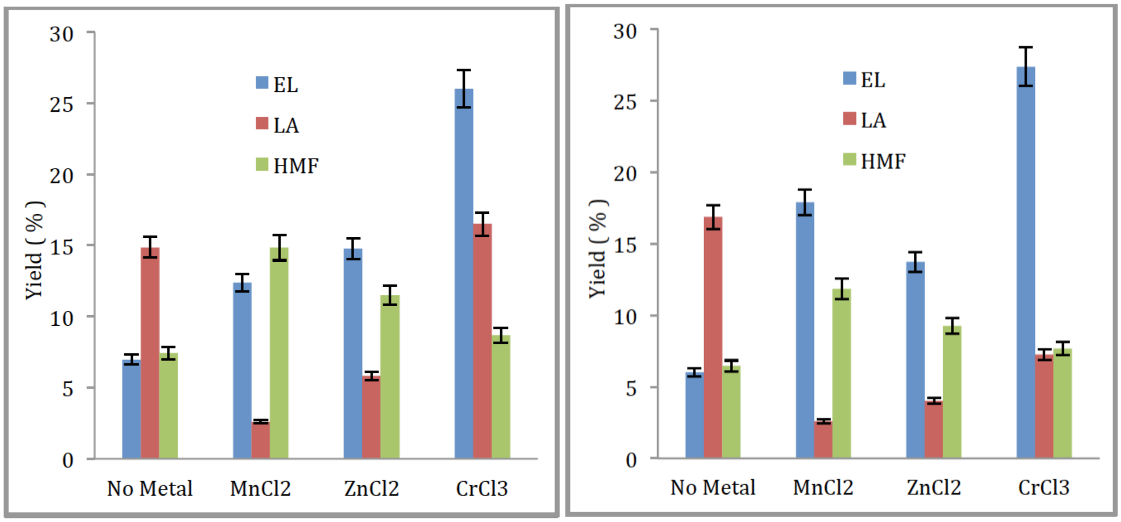


c. 160°C, 6 h. **d. 170°C, 6 h.**



e. 140°C, 12 h. **f. 150°C, 12 h.**

Fig. (2). Contd…



g. 160˚C, 12 h. **h. 170˚C, 12 h.**

Fig. (2). The percentage yields of ethyl levulinate (EL), levulinic acid (LA), and 5-hydroxymethylfurfural (HMF) in Brönsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed conversion of cellulose, with or without Mn(II), Zn(II) and Cr(III) chloride co-catalysts. 60 mg of cellulose (DP ~ 450) and 10 mg of 1-(1-propylsulfonic)-3-methylimidazolium chloride in 1.00 mL of 40% (v/v) aqueous ethanol were used in all experiments. 0.042 mmol of metal chloride was added to the experiments with the co-catalyst. Reaction conditions: **a.** 140˚C, 6h; **b**. 150˚C, 6h; **c**. 160˚C, 6h; **d**. 170˚C, 6h; **e**. 140˚C, 12h; **f**. 150˚C, 12h; **g**. 160˚C, 12h; **h**. 170˚C, 12 h. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

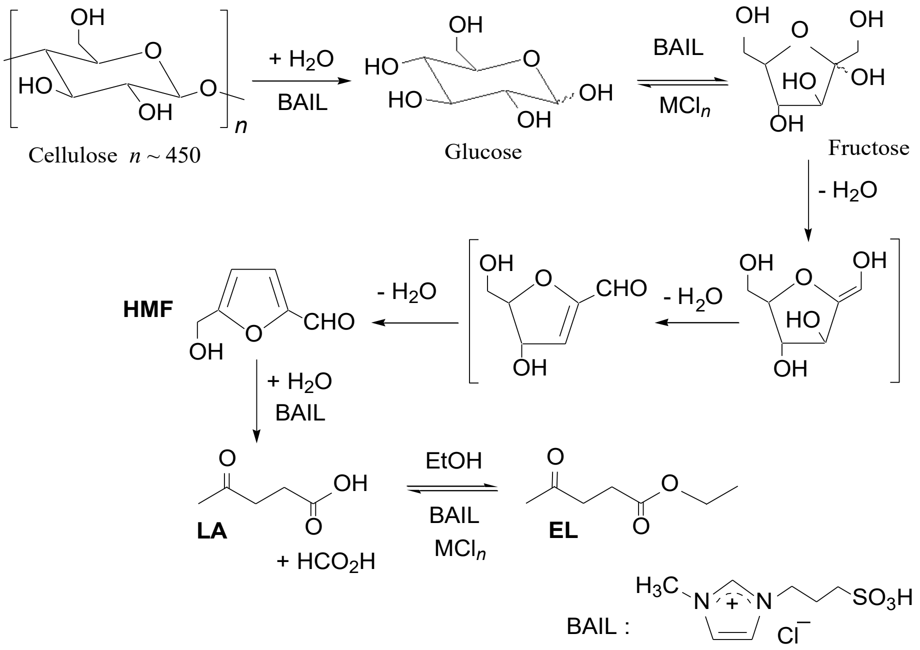


Fig. (3). The proposed reaction pathway for 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyzed reaction of cellulose in 40% (v/v) aqueous ethanol in the presence of Mn(II), Zn(II) or Cr(III) chloride co-catalyst.

catalysts as in the presence of the co-catalysts, the LA formed can further react with ethanol, reducing the LA yield while increasing the EL yields. In most experiments, the addition of co-catalysts caused an increase in EL yield at the expense of LA yield, suggesting that metal catalysts promote the esterification step as well. The addition of $CrCl_3$ has caused significant enhancement in EL yields and it is interesting to note that our earlier experiments on BAIL-catalyzed hydrolysis of cellulose in the presence of $CrCl_3$ demonstrated very low ~ 5-10% yields of glucose [38]. The present results may help to explain this observation, suggesting that glucose may rapidly undergo further transformation to LA and then to EL in the presence of a strongly chelated $CrCl_3$ co-catalyst. It is important to note that most transition metals are toxic to animals and plants and some are toxic at even very low concentrations [48]; therefore, necessary safe-ty precautions are recommended in using and disposal of transition metal salts used as co-catalysts.

CONCLUSION

It was observed that the addition of transition metals, such as Mn(II), Zn(II), and Cr(III) chlorides as a co-catalyst, can be used to improve the yields of secondary products, namely EL, LA, and HMF in acidic ionic liquid catalyzed cellulose degradation in aqueous ethanol. At 160 and 170°C for 12 h, experiments with Mn(II) and Zn(II) chloride co-catalysts improved the initial yields of EL and HMF from ~ 7% to ~ 12-15% due to co-catalytic effect in this one-pot process. The highest enhancements in EL yields were observed with the addition of $CrCl_3$ as the co-catalyst, where 6% to 27% enhancements were noted with the addition of ~ 11 mol% $CrCl_3$ as a co-catalyst. This 356% enhancement of EL yield was found to be much higher than the previously reported 80% co-catalytic yield improvement effect due to zeolites with similar 1-(1-propylsulfonic)-3-methylimidazolium chloride acidic ionic liquid catalyzed degradation of cellulose in aqueous ethanol [38]. The LA and HMF yield improvements may be due to the metal-catalyzed promotion of glucose to fructose isomerization in this multistep process. In addition, Mn(II) and Zn(II) chloride salts appear to promote esterification as well, particularly at higher temperatures and at longer reaction times. Furthermore, considering the number of complex reaction steps involved in producing a tertiary product like ethyl levulinate in a one-pot process from cellulose, the yields achieved are reasonable. We are currently studying the possible recycling of the ionic liquid-metal salt catalyst system for this one-pot process with potential industrial applications.

LIST OF ABBREVIATIONS

LA	=	Levulinic Acid
BAILs	=	Brönsted Acidic Ionic Liquids

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No animals/humans were used in the studies that are the basis of this research.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The authors confirm that the data that support the findings of this study are available within the article.

FUNDING

This study is financially supported by United States National Science Foundation (NSF) grants CBET-1704144, HRD-1036593, United States Department of Agriculture (USDA) grant AFRI 65209-31474, and USDA-SUN grant 3TC 386; Sub-award: 2-569230.

CONFLICT OF INTEREST

Dr. Ananda Amarasekara is an editorial advisory board member of the journal Current Catalysis.

ACKNOWLEDGEMENTS

The authors would like to thank United States National Science Foundation (NSF) grants CBET-1704144, HRD-1036593, United States Department of Agriculture (USDA) grant AFRI 65209-31474, and USDA-SUN grant 3TC 386; Sub-award: 2-569230 for financial support.

REFERENCES

[1] Badgujar, K.C.; Badgujar, V.C.; Bhanage, B.M. A review on catalytic synthesis of energy rich fuel additive levulinate compounds from biomass derived levulinic acid. *Fuel Process. Technol.,* **2020**, *197*, 106213. http://dx.doi.org/10.1016/j.fuproc.2019.106213

[2] Zhao, Y.; Lu, K.; Xu, H.; Zhu, L.; Wang, S. A critical review of recent advances in the production of furfural and 5-hydroxymethylfurfural from lignocellulosic biomass through homogeneous catalytic hydrothermal conversion. *Renew. Sustain. Energy Rev.,* **2021**, *139*, 110706. http://dx.doi.org/10.1016/j.rser.2021.110706

[3] Amarasekara, A.S.; Wiredu, B. Aryl sulfonic acid catalyzed hydrolysis of cellulose in water. *Appl. Catal. A Gen.,* **2012**, *417-418*, 259-262. http://dx.doi.org/10.1016/j.apcata.2011.12.048

[4] Mosier, N.S.; Sarikaya, A.; Ladisch, C.M.; Ladisch, M.R. Characterization of dicarboxylic acids for cellulose hydrolysis. *Biotechnol. Prog.,* **2001**, *17*(3), 474-480. http://dx.doi.org/10.1021/bp010028u PMID: 11386868

[5] Jin, S.; Gong, J.; Yang, C.; Cheng, Y.; Lu, J.; Yang, Q.; Wang, H. A recyclable and regenerable solid acid for efficient hydrolysis of cellulose to glucose. *Biomass Bioenergy,* **2020**, *138*, 105611. http://dx.doi.org/10.1016/j.biombioe.2020.105611

[6] Wiredu, B.; Amarasekara, A.S. Synthesis of a silica-immobilized Brönsted acidic ionic liquid catalyst and hydrolysis of cellulose in water under mild conditions. *Catal. Commun.,* **2014**, *48*, 41-44. http://dx.doi.org/10.1016/j.catcom.2014.01.021

[7] Zhang, Y.; Li, Q.; Su, J.; Lin, Y.; Huang, Z.; Lu, Y.; Sun, G.; Yang, M.; Huang, A.; Hu, H.; Zhu, Y. A green and efficient technology for the degradation of cellulosic materials: Structure changes and enhanced enzymatic hydrolysis of natural cellulose pretreated by synergistic interaction of mechanical activation and metal salt. *Bioresour. Technol.,* **2015**, *177*(0), 176-181. http://dx.doi.org/10.1016/j.biortech.2014.11.085 PMID: 25490099

[8] Liu, L.; Sun, J.; Cai, C.; Wang, S.; Pei, H.; Zhang, J. Corn stover pretreatment by inorganic salts and its effects on hemicellulose and cellulose degradation. *Bioresour. Technol.,* **2009**, *100*(23), 5865-5871. http://dx.doi.org/10.1016/j.biortech.2009.06.048 PMID: 19589672

[9] Peng, L.; Lin, L.; Zhang, J.; Zhuang, J.; Zhang, B.; Gong, Y. Catalytic conversion of cellulose to levulinic acid by metal chlorides. *Molecules,* **2010**, *15*(8), 5258-5272. http://dx.doi.org/10.3390/molecules15085258 PMID: 20714297

[10] Kamireddy, S.R.; Li, J.; Tucker, M.; Degenstein, J.; Ji, Y. Effects and mechanism of metal chloride salts on pretreatment and enzymatic digestibility of corn stover. *Ind. Eng. Chem. Res.,* **2013**, *52*(5), 1775-1782. http://dx.doi.org/10.1021/ie3019609

[11] Li, J.; Xiu, H.; Zhang, M.; Wang, H.; Ren, Y.; Ji, Y. Enhancement of cellulose acid hydrolysis selectivity using metal ion catalysts. *Curr. Org. Chem.,* **2013**, *17*(15), 1617-1623. http://dx.doi.org/10.2174/13852728113179990071

[12] Shrotri, A.; Kobayashi, H.; Fukuoka, A. Cellulose depolymerization over heterogeneous catalysts. *Acc. Chem. Res.,* **2018**, *51*(3), 761-768. http://dx.doi.org/10.1021/acs.accounts.7b00614 PMID: 29443505

[13] Chiappe, C.; Rodriguez Douton, M.J.; Mezzetta, A.; Guazzelli, L.; Pomelli, C.S.; Assanelli, G.; de Angelis, A.R. Exploring and exploiting different catalytic systems for the direct conversion of cellulose into levulinic acid. *New J. Chem.,* **2018**, *42*(3), 1845-1852. http://dx.doi.org/10.1039/C7NJ04707J

[14] Liu, C.; Lu, X.; Yu, Z.; Xiong, J.; Bai, H.; Zhang, R. Production of levulinic acid from cellulose and cellulosic biomass in different catalytic systems. *Catalysts,* **2020**, *10*(9), 1006. http://dx.doi.org/10.3390/catal10091006

[15] Kang, S.; Fu, J.; Zhang, G. From lignocellulosic biomass to levulinic acid: A review on acid-catalyzed hydrolysis. *Renew. Sustain. Energy Rev.,* **2018**, *94*, 340-362. http://dx.doi.org/10.1016/j.rser.2018.06.016

[16] Leal Silva, J.F.; Grekin, R.; Mariano, A.P.; Maciel Filho, R. Making levulinic acid and ethyl levulinate economically viable: A worldwide technoeconomic and environmental assessment of possible routes. *Energy Technol.,* **2018**, *6*(4), 613-639. http://dx.doi.org/10.1002/ente.201700594

[17] Chaffey, D.R.; Bere, T.; Davies, T.E.; Apperley, D.C.; Taylor, S.H.; Graham, A.E. Conversion of levulinic acid to levulinate ester biofuels by heterogeneous catalysts in the presence of acetals and ketals. *Appl. Catal. B,* **2021**, *293*, 120219. http://dx.doi.org/10.1016/j.apcatb.2021.120219

[18] Li, N.; Zhang, X.L.; Zheng, X.C.; Wang, G.H.; Wang, X.Y.; Zheng, G.P. Efficient synthesis of ethyl levulinate fuel additives from levulinic acid catalyzed by sulfonated pine needle-derived carbon. *Catal. Surv. Asia,* **2019**, *23*(3), 171-180. http://dx.doi.org/10.1007/s10563-019-09270-8

[19] Amarasekara, A.S.; Wiredu, B.; Grady, T.L.; Obregon, R.G.; Margetić, D. Solid acid catalyzed aldol dimerization of levulinic acid for the preparation of C10 renewable fuel and chemical feedstocks. *Catal. Commun.,* **2019**, *124*, 6-11. http://dx.doi.org/10.1016/j.catcom.2019.02.022

[20] Amarasekara, A.S.; Lawrence, Y.M. Raney-Ni catalyzed conversion of levulinic acid to 5-methyl-2-pyrrolidone using ammonium formate as the H and N source. *Tetrahedron Lett.,* **2018**, *59*(19), 1832-1835. http://dx.doi.org/10.1016/j.tetlet.2018.03.087

[21] Lomba, L.; Giner, B.; Bandrés, I.; Lafuente, C.; Pino, M.R. Physicochemical properties of green solvents derived from biomass. *Green Chem.,* **2011**, *13*(8), 2062-2070. http://dx.doi.org/10.1039/c0gc00853b

[22] Allaoua, I.; Goi, B.E.; Obadia, M.M.; Debuigne, A.; Detrembleur, C.; Drockenmuller, E. (Co)Polymerization of vinyl levulinate by cobalt-mediated radical polymerization and functionalization by ketoxime click chemistry. *Polym. Chem.,* **2014**, *5*(8), 2973-2979. http://dx.doi.org/10.1039/C3PY01505J

[23] Amarasekara, A.S.; Ha, U.; Okorie, N.C. Renewable polymers: Synthesis and characterization of poly(levulinic acid–pentaerythritol). *J. Polym. Sci. A Polym. Chem.,* **2018**, *56*(9), 955-958. http://dx.doi.org/10.1002/pola.28980

[24] Hayes, G.C.; Becer, C.R. Levulinic acid: A sustainable platform chemical for novel polymer architectures. *Polym. Chem.,* **2020**, *11*(25), 4068-4077. http://dx.doi.org/10.1039/D0PY00705F

[25] Xuan, W.; Hakkarainen, M.; Odelius, K. Levulinic acid as a versatile building block for plasticizer design. *ACS Sustain. Chem.& Eng.,* **2019**, *7*(14), 9b02439. http://dx.doi.org/10.1021/acssuschemeng.9b02439

[26] Kumar, A.; Shende, D.Z.; Wasewar, K.L. Production of levulinic acid: A promising building block material for pharmaceutical and food industry. *Mater. Today Proc.,* **2020**, *29*, 790-793. http://dx.doi.org/10.1016/j.matpr.2020.04.749

[27] Christensen, E.; Williams, A.; Paul, S.; Burton, S.; McCormick, R.L. Properties and performance of levulinate esters as diesel blend components. *Energy Fuels,* **2011**, *25*(11), 5422-5428. http://dx.doi.org/10.1021/ef201229j

[28] Christensen, E.; Yanowitz, J.; Ratcliff, M.; McCormick, R.L. Renewable oxygenate blending effects on gasoline properties. *Energy Fuels,* **2011**, *25*(10), 4723-4733. http://dx.doi.org/10.1021/ef2010089

[29] Amarasekara, A.S. *Handbook of cellulosic ethanol*; John Wiley & Sons: NewYork, **2013**. http://dx.doi.org/10.1002/9781118878750

[30] Ghosh, M.K.; Howard, M.S.; Zhang, Y.; Djebbi, K.; Capriolo, G.; Farooq, A.; Curran, H.J.; Dooley, S. The combustion kinetics of the lignocellulosic biofuel, ethyl levulinate. *Combust. Flame,* **2018**, *193*, 157-169. http://dx.doi.org/10.1016/j.combustflame.2018.02.028

[31] Amarasekara, A.S.; Owereh, O.S. Hydrolysis and decomposition of cellulose in bronsted acidic ionic liquids under mild conditions. *Ind. Eng. Chem. Res.,* **2009**, *48*(22), 10152-10155. http://dx.doi.org/10.1021/ie901047u

[32] Amarasekara, A.S.; Wiredu, B. Degradation of cellulose in dilute aqueous solutions of acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride, and p-toluenesulfonic acid at moderate temperatures and pressures. *Ind. Eng. Chem. Res.,* **2011**, *50*(21), 12276-12280. http://dx.doi.org/10.1021/ie200938h

[33] Amarasekara, A.S.; Shanbhag, P. Degradation of untreated switchgrass biomass into reducing sugars in 1-(Alkylsulfonic)-3-Methylimidazolium brönsted acidic ionic liquid medium under mild conditions. *BioEnergy Res.,* **2013**, *6*(2), 719-724. http://dx.doi.org/10.1007/s12155-012-9291-2

[34] Amarasekara, A.S.; Wiredu, B. Acidic ionic liquid catalyzed one-pot conversion of cellulose to ethyl levulinate and levulinic acid in ethanol-water solvent system. *BioEnergy Res.,* **2014**, *7*(4), 1237-1243. http://dx.doi.org/10.1007/s12155-014-9459-z

[35] Wiredu, B.; Dominguez, J.N.; Amarasekara, A.S. The co-catalyst effect of zeolites on acidic ionic liquid catalyzed one-pot conversion of cellulose to ethyl levulinate and levulinic acid in aqueous ethanol. *Curr. Catal.,* **2015**, *4*, 143-151. http://dx.doi.org/10.2174/2211544704666150727215943

[36] Gui, J.; Cong, X.; Liu, D.; Zhang, X.; Hu, Z.; Sun, Z. Novel Brønsted acidic ionic liquid as efficient and reusable catalyst system for esterification. *Catal. Commun.,* **2004**, *5*(9), 473-477. http://dx.doi.org/10.1016/j.catcom.2004.06.004

[37] Yang, Q.; Wei, Z.; Xing, H.; Ren, Q. Brönsted acidic ionic liquids as novel catalysts for the hydrolyzation of soybean isoflavone glycosides. *Catal. Commun.,* **2008**, *9*(6), 1307-1311. http://dx.doi.org/10.1016/j.catcom.2007.11.023

[38] Wiredu, B.; Amarasekara, A.S. 1-(1-Propylsulfonic)-3-methylimidazolium chloride acidic ionic liquid catalyzed hydrolysis of cellulose in water: Effect of metal ion co-catalysts. *Catal. Commun.,* **2015**, *70*, 82-85. http://dx.doi.org/10.1016/j.catcom.2015.08.004

[39] Wiredu, B.; Amarasekara, A.S. The effect of metal ions as co-catalysts on acidic ionic liquid catalyzed single-step saccharification of corn stover in water. *Bioresour. Technol.,* **2015**, *189*, 405-408. http://dx.doi.org/10.1016/j.biortech.2015.04.030 PMID: 25911191

[40] Amarasekara, A.S.; Wiredu, B. The effect of Manganese (II) chloride as a co-catalyst on cellobiose hydrolysis in dilute aqueous sulfuric acid and acidic ionic liquid mediums. *Catal. Commun.,* **2016**, *81*, 41-44. http://dx.doi.org/10.1016/j.catcom.2016.04.005

[41] Meier, S. Mechanism and malleability of glucose dehydration to HMF: Entry points and water-induced diversions. *Catal. Sci. Technol.,* **2020**, *10*(6), 1724-1730. http://dx.doi.org/10.1039/C9CY02567G

[42] Qian, X. Mechanisms and energetics for acid catalyzed β-D-glucose conversion to 5-hydroxymethylfurfurl. *J. Phys. Chem. A,* **2011**, *115*(42), 11740-11748. http://dx.doi.org/10.1021/jp2041982 PMID: 21916465

[43] Jia, S.; Liu, K.; Xu, Z.; Yan, P.; Xu, W.; Liu, X.; Zhang, Z.C. Reaction media dominated product selectivity in the isomerization of glucose by chromium trichloride: From aqueous to non-aqueous systems. *Catal. Today,* **2014**, *234*, 83-90. http://dx.doi.org/10.1016/j.cattod.2014.02.038

[44] Otomo, R.; Yokoi, T.; Kondo, J.N.; Tatsumi, T. Dealuminated Beta zeolite as effective bifunctional catalyst for direct transformation of glucose to 5-hydroxymethylfurfural. *Appl. Catal. A Gen.,* **2014**, *470*(0), 318-326. http://dx.doi.org/10.1016/j.apcata.2013.11.012

[45] Qi, X.; Watanabe, M.; Aida, T.M.; Smith, R.L., Jr Catalytical conversion of fructose and glucose into 5-hydroxymethylfurfural in hot

compressed water by microwave heating. *Catal. Commun.,* **2008**, *9*(13), 2244-2249.
http://dx.doi.org/10.1016/j.catcom.2008.04.025

[46] Bali, S.; Tofanelli, M.A.; Ernst, R.D.; Eyring, E.M. Chromium(III) catalysts in ionic liquids for the conversion of glucose to 5-(hydroxymethyl)furfural (HMF): Insight into metal catalyst:Ionic liquid mediated conversion of cellulosic biomass to biofuels and chemicals. *Biomass Bioenergy,* **2012**, *42*, 224-227.
http://dx.doi.org/10.1016/j.biombioe.2012.03.016

[47] Wang, S.; Du, Y.; Zhang, W.; Cheng, X.; Wang, J. Catalytic conversion of cellulose into 5-hydroxymethylfurfural over chromium trichloride in ionic liquid. *Korean J. Chem. Eng.,* **2014**, *31*(10), 1786-1791.
http://dx.doi.org/10.1007/s11814-014-0138-8

[48] Stohs, S.; Bagchi, D. Oxidative mechanisms in the toxicity of metal ions. *Free Radic. Biol. Med.,* **1995**, *18*(2), 321-336.
http://dx.doi.org/10.1016/0891-5849(94)00159-H PMID: 7744317