Carbohydrate Polymers 117 (2015) 569–576

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Selective and recyclable depolymerization of cellulose to levulinic acid catalyzed by acidic ionic liquid

Huifang Ren[a], Buana Girisuta[c], Yonggui Zhou[a], Li Liu[b,*]

[a] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*
[b] *Dalian University of Technology, Dalian 116024, China*
[c] *Institute of Chemical and Engineering Sciences, Jurong Island 627833, Singapore*

ARTICLE INFO

Article history:
Received 17 March 2014
Received in revised form 1 July 2014
Accepted 26 September 2014
Available online 15 October 2014

Keywords:
Biomass
Cellulose
Depolymerization
Ionic liquids
Levulinic acid

ABSTRACT

Cellulose depolymerization to levulinic acid (LA) was catalyzed by acidic ionic liquids (ILs) selectively and recyclably under hydrothermal conditions. The effects of reaction temperature, time, water amount and cellulose intake were investigated. Dilution effect becomes more pronounced at lower cellulose intake, dramatically improving the yield of LA to 86.1%. A kinetic model has been developed based on experimental data, whereby a good fit was obtained and kinetic parameters were derived. The relationships between IL structure, polymeric structure and depolymerization efficiency were established, shedding light on the in-depth catalytic mechanism of IL, inclusive of acidity and hydrogen bonding ability. The LA product can be readily separated through extraction by methyl isobutyl ketone (MIBK) and IL can be reused over five cycles without loss of activity. This environmentally friendly methodology can be applied to selective production of LA from versatile biomass feedstocks, including cellulose and derivatives, glucose, fructose and HMF.

1. Introduction

Exploring how to produce chemicals and fuels from biomass alternatively has come to prominence due to diminishing fossil resources and increasing concern about sustainable development, for biomass is the only sustainable source of organic carbon. As analogous to petrochemical refinery, biorefinery strategy has been proposed by US National Renewable Energy Laboratory (NREL) as a facility that integrates conversion processes and equipments to produce fuels, power, and chemicals from biomass (Kamm, Gruber, & Kamm, 2006). Moreover, 12 platform chemicals have been identified by the US Department of Energy (Werpy & Petersen, 2004), which could be major outputs from an integrated biorefinery. As one of the platform chemicals, levulinic acid (LA) is a versatile building block for fuel additives, solvents, resin and polymer precursors, flavor substances, pharmaceutical agents and chemical intermediates (Rackemann & Doherty, 2011). Recent work further demonstrated that LA can serve as initial feedstock for existing petrochemical processing operations, bridging the biomass and petroleum processing together (Bozell, 2010). Thereby production of LA from biomass has become one of the key steps for biorefinery.

As the most abundant biomass and sustainable raw materials, cellulose consists of D-glucopyranoside units linked together by β-1,4 glycosidic bonds. Cellulose is generally regarded as a difficult material to work with due to its densely packed structure and insolubility in water (Jarvis, 2003). Alternative media capable of dissolving cellulose are required to facilitate biomass processing, whereas the attribute has been demonstrated by ionic liquids (ILs), which has been widely recognized as green media due to their non-flammability and non-volatility. Swatloski, Spear, Holbrey, and Rogers (2002) firstly found out [C_4mim]Cl was able to dissolve up to 25% of cellulose under microwave irradiation, which opened up vast possibilities to biomass utilization, taking advantage of the remarkable designability and functionality of ionic liquids (Welton, 1999). A number of studies have been reported on depolymerization of cellulose using ionic liquids ever since (Amarasekara & Owereh, 2009; Binder & Raines, 2009; Dee & Bell, 2011; Kim et al., 2011; Kuo, Suzuki, Yamauchi, & Wu, 2013; Li & Zhao, 2007; Liu, Zhang, & Zhao, 2013; Rinaldi, Palkovits, & Schüth, 2008; Song, Fan, Ma, & Han, 2013; Su et al., 2009; Tao, Song, & Chou, 2010; Vanoye, Fanselow, Holbrey, Atkins, & Seddon, 2009; Xiong, Zhang, Wang, Liu, & Lin, 2014). Li and Zhao (2007) firstly applied ionic liquids in cellulose conversion towards glucose, where sulphuric acid in [C_4mim]Cl resulted in a yield of 43% for glucose. Later Su et al. (2009) applied ionic liquids in cellulose conversion towards 5-hydroxymethylfurfural (HMF), where copper chloride

---

* Corresponding author. Tel.: +86 411 84795945; fax: +86 411 84795945.
E-mail address: lliu@dlut.edu.cn (L. Liu).

http://dx.doi.org/10.1016/j.carbpol.2014.09.091
0144-8617/© 2014 Published by Elsevier Ltd.

and chromium chloride in $[C_2mim]Cl$ led to a yield of 55% for HMF. In contrast, application of ionic liquids as catalysts in recycle fashion has been far less explored in cellulose conversion.

Depolymerization of cellulose to LA has been attempted by various catalysts, including mineral acids (Girisuta, Janssen, & Heeres, 2007; Szabolcs, Molnar, Dibo, & Mika, 2013; Tabasso, Montoneri, Carnaroglio, Caporaso, & Cravotto, 2014), metal chlorides (Seri, Sakaki, Shibata, Inoue, & Ishida, 2002), solid acid catalysts (Alonso, Gallo, Mellmer, Wettstein, & Dumesic, 2013; Zakzeski, Grisel, Smit, & Weckhuysen, 2012; Zuo, Zhang, & Fu, 2014) and acidic polymers (Vyver et al., 2011), whereas the challenging issues were focused on improving the selectivity of LA and developing efficient strategies for product separation and catalyst recovery. Acidic ionic liquids have large potentials in replacing conventional acidic catalysts for they are flexible, recyclable, and could be used as dual solvents and catalysts (Cole et al., 2002). Applications of acidic ionic liquids as catalysts for cellulose conversion have been reported with 62% (Amarasekara & Owereh, 2009) and 99% (Liu, Xiao, Xia, & Ma, 2013) yields towards total reducing sugar (TRS) product; 37% (Tao, Song, Yang, & Chou, 2011), 53% (Zhou, Liang, Ma, Wu, & Wu, 2013), 66.5% (Shi et al., 2013), and 69.7% (Ding et al., 2012) yields towards HMF product, in the presence of metal chloride as co-catalyst or IL as solvent. Recently, we employed SO_3H-functionalized acidic ionic liquids in the direct conversion of cellulose to LA under microwave irradiation, whereas 55% of LA has been obtained (Ren, Zhou, & Liu, 2013). Alternatively, hydrothermal conditions have attracted increasing attentions due to the unique inherent properties of high-temperature water, which provides environmentally friendly reaction medium (Jin & Enomoto, 2011). In this work, we developed selective and recyclable methodology under hydrothermal conditions, dramatically improving the yield of LA to 86.1%. Continued efforts were devoted to understand the basic nature of cellulose depolymerization towards LA.

2. Experimental

2.1. Materials and equipments

Microcrystalline cellulose (average particle size 50 μm, DP = 237, which was used in cellulose experiments unless otherwise specified) and HMF (98%) were purchased from Acros Organics (USA). α-Cellulose (Cat. No. C8002, DP = 100) and sigmacell cellulose (Cat. No. S6790, DP = 400–500) were purchased from Sigma (St. Louis, USA). Carboxymethylcellulose (MW 90,000, DS = 0.7, viscosity 50–100 mPa s; MW 250,000, DS = 0.7, viscosity 1500–3100 mPa s; MW 250,000, DS = 1.2, viscosity 1500–3100 mPa s) were supplied by Aladdin Reagent Co., Ltd. (Shanghai, China). Cellulose and derivatives were dried under vacuum at 80 °C for 24 h to diminish trace amount of moisture prior to use. Fructose (99%) and glucose (p.a.) were purchased from local suppliers. 1,3-Propane sultone and 1-methylimidazole were purchased from Wuhan Fengfan Chemical Co., Ltd. (Wuhan, China) and freshly distilled before use. Nine ionic liquids including 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate ($[C_3SO_3Hmim]HSO_4$), 1-methyl-3-(4-sulfobutyl)imidazolium hydrogen sulfate ($[C_4SO_3Hmim]HSO_4$), *N*-(3-sulfopropyl)pyridinium hydrogen sulfate ($[C_3SO_3HPy]HSO_4$), *N*,*N*,*N*-triethyl-*N*-(3-sulfopropyl)ammonium hydrogen sulfate ($[C_3SO_3HN_{222}]HSO_4$), triphenyl(3-sulfopropyl)phosphonium hydrogen sulfate ($[C_3SO_3HPPh_3]HSO_4$), 1-methyl-3-(3-sulfopropyl)imidazolium dihydrogen phosphate ($[C_3SO_3Hmim]H_2PO_4$), 1-methyl-3-(3-sulfopropyl)imidazolium methanesulfonate ($[C_3SO_3Hmim]CH_3SO_3$), 1-methyl-3-(3-sulfopropyl)imidazolium 1-naphthalenesulfonate ($[C_3SO_3Hmim]$1-NS), and 1-methyl-3-(3-sulfopropyl)imidazolium chloride ($[C_3SO_3Hmim]Cl$) were prepared according to literature and characterized by NMR prior to use (Supplementary data) (Cole et al., 2002). The NMR spectra were recorded on Bruker Avance III 500 MHz and Bruker DRX 400 MHz spectrometers. UV–vis spectra were recorded on Jasco UV-550 spectrophotometer. The infrared spectra were recorded on Bruker Equinox 55 infrared spectrometer. Scanning electron microscopy images were obtained on Nova NanoSEM 450 field emission scanning electron microscopy, where samples were coated with a thin Aurum film.

2.2. General procedure for cellulose conversion

In a typical procedure, cellulose, ionic liquid and de-ionized water were mixed in a stainless steel autoclave with Teflon lining and heated in an oil bath maintained at the desired temperature for a specified length of time with magnetic stirring. The reaction was quenched in an ice bath. After filtration of insolubles and removal of water by rotary evaporation at 50 °C for 5 min, the crude product was analyzed by ^1H NMR using ionic liquid as internal standard. The yields of products were calculated from the equation: yield (%) = (mol of the product)/(mol of glucose unit in cellulose) × 100%. All the results were replicated at least three times. The analytical error was evaluated to be within 5% based on standard samples of known concentrations. The insoluble humins were collected from the reaction mixture by filtration, oven-dried, and weighed, whereby the yields of humins in weight percentage were calculated relative to cellulose.

2.3. Reuse of IL

In the first run, the reaction of cellulose (550 mg), $[C_3SO_3Hmim]HSO_4$ (1.000 g) and de-ionized water (6.000 g) were heated in a 20 mL autoclave at 170 °C for 5 h. After filtration of insolubles and removal of water by rotary evaporation at 50 °C for 5 min, the crude product was analyzed by ^1H NMR using ionic liquid as internal standard. The aqueous solution of ionic liquid was extracted by MIBK 60 mL × 3, and dried under high vacuum. Afterwards, the IL was adjusted to 1.000 g by adding fresh IL of no more than 5% and reused in the next cycle as above.

3. Results and discussion

3.1. The effects of reaction temperature and time on cellulose depolymerization

The experiments for determining the effects of reaction temperature and time on cellulose conversion were carried out in 10 mL autoclaves at temperatures ranging from 160 to 180 °C, during the reaction course of 0.5–5 h, with 1.000 g of IL 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate ($[C_3SO_3Hmim]HSO_4$), 2.000 g of H_2O and 250 mg of cellulose. As shown in Fig. 1a, the yield of LA increased with the rise of reaction temperature from 160 to 180 °C within 2 h. Then the yield of LA reached *ca.* 50% at 170 and 180 °C, slightly higher than 160 °C, suggesting higher reaction temperature is favorable to LA formation during short reaction time. When the reaction time was prolonged over 4 h, the yield of LA increased to 53.7% at 160 °C and levelled off afterwards, surpassing 170 and 180 °C. It can be learnt that through extending the reaction time, the yield of LA can be further improved at lower temperature. Therefore the cellulose conversion is sensitive to the effects of reaction temperature and time in the presence of 2 g of water, which

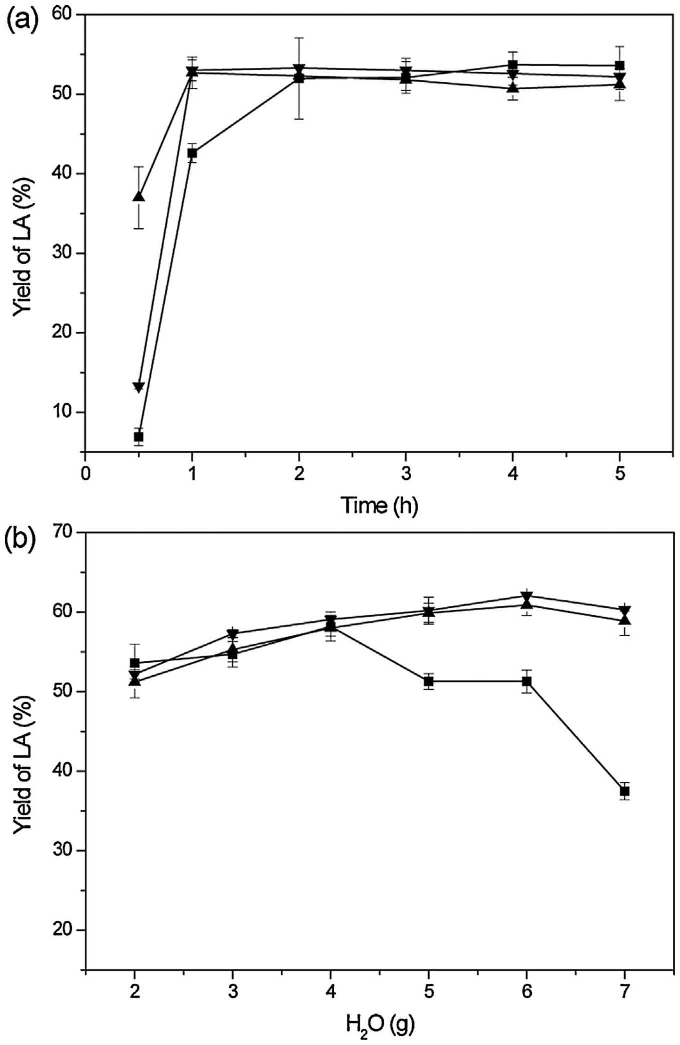

Fig. 1. The effects of time and water amount at different temperatures: (■) 160 °C; (▼) 170 °C; (▲) 180 °C. Conditions: 250 mg cellulose, 1.000 g [C_3SO_3Hmim]HSO_4, (a) 2.000 g H_2O, (b) 5 h.

seems to proceed faster initially at higher temperature and result in higher yield eventually at lower temperature.

3.2. *The effect of water amount on cellulose depolymerization*

As green solvent, water plays a crucial role in the hydrothermal conversion of cellulose to LA. Fig. 1b shows the effect of water amount on the yield of LA at different temperatures. The yield of LA varied in analogous tendency at 170 and 180 °C, different from 160 °C. When the water amount ranged from 2 g to 6 g, the yield of LA increased from 52.2% to 62.1% at 170 °C, and from 51.5% to 60.8% at 180 °C, which decreased slightly to 60.3% and 58.7% in the presence of 7 g of water, respectively. With water amount increased, dilution effect suppresses the formation of dark colored solid byproducts, known as humins, leading to higher yield of LA. However at 160 °C, the yield of LA increased first and then decreased from 58.3% to 37.5% with increasing water amount from 4 g to 7 g, ascribing to severely lowered catalytic activity which could not be compromised by the dilution effect. Meanwhile, 15.4% of glucose was observed in the presence of 7 g of water at 160 °C. Apparently, the temperature has dramatic effect on cellulose conversion. With water amount enlarged, higher reaction temperature is needed to convert the glucose intermediate completely to LA, suggesting substantial catalytic activity is necessary to reflect the positive dilution effect.

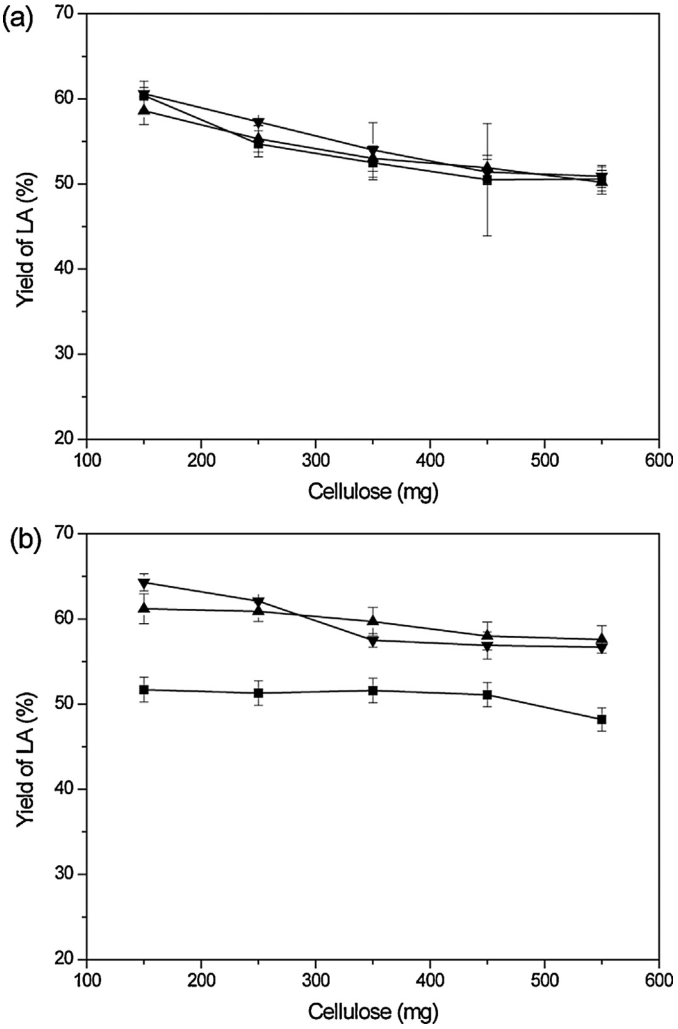

Fig. 2. The effect of cellulose intake at different temperatures: (■) 160 °C; (▼) 170 °C; (▲) 180 °C. Conditions: 1.000 g [C_3SO_3Hmim]HSO_4, 5 h, (a) 3.000 g H_2O, (b) 6.000 g H_2O.

3.3. *The effect of cellulose intake on cellulose depolymerization*

From an economical point of view, the cellulose digestibility is an important perspective of the conversion process. Fig. 2 shows the effect of cellulose intake on the yield of LA with the addition of 3 g (Fig. 2a) and 6 g of water (Fig. 2b), respectively. In the presence of 3 g of water, the yield of LA decreased slightly from 60% to 50% in similar trends with increasing cellulose intake from 150 mg to 550 mg at explored temperatures, attributing to that higher cellulose dosage induces humin formation and consequently restrains LA production. In the presence of 6 g of water, the yield of LA decreased from 51.7% to 48.1% at 160 °C, from 64.3% to 56.4% at 170 °C, and from 61.2% to 57.6% at 180 °C, with increasing cellulose intake from 150 mg to 550 mg. In contrast, 160 °C is not high enough to convert cellulose efficiently to LA when 6 g of water was added. While higher temperatures of 170 and 180 °C resulted in higher yields of LA with the addition of 6 g of water rather than 3 g of water, confirming that water can restrain the side products of humins to considerable extent. It confirms that dilution effect shows up in combination with higher temperature especially

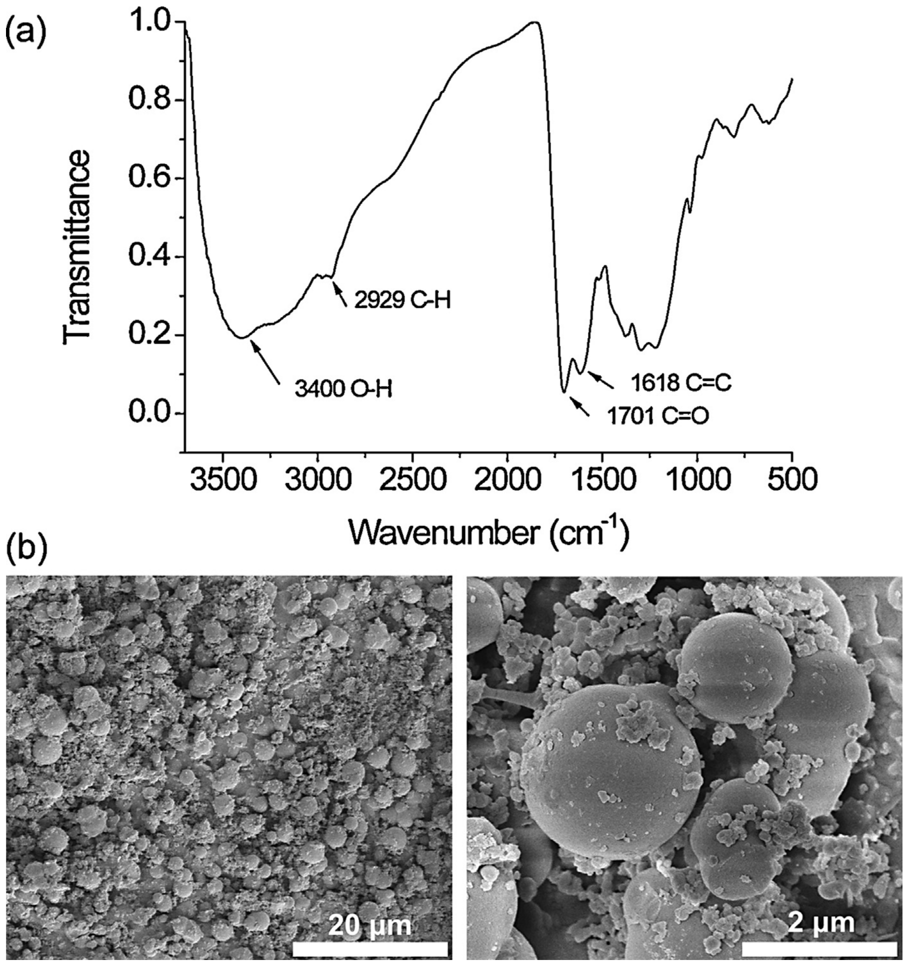

Fig. 3. (a) IR spectrum and (b) SEM images of humins after complete conversion of cellulose. Conditions: 150 mg cellulose, 1.000 g [C_3SO_3Hmim]HSO_4, 6.000 g H_2O, 170 °C, 5 h.

170 °C for substantial activation, which becomes more pronounced at lower cellulose intake.

To further look into the distinctive dilution effect on the yield of LA observed at low cellulose intake, the cellulose conversion was subjected to a broad range of cellulose intake under the same condition (1.000 g IL, 6.000 g H_2O, 170 °C, 5 h). With cellulose intake reduced to 20 mg, the yield of LA improved up to 86.1% (Table A.1, Supplementary data). It verified that low cellulose intake can spur the transformation of cellulose to LA effectively. On the other hand, with increase of cellulose loadings, the yield of LA decreased. Nevertheless, when the ratio of cellulose to IL enhanced to 220%, 49.7% yield of LA could still be reached, demonstrating improved cellulose digestibility of IL. Nowadays, for applications of ionic liquids in cellulose conversion, increasing cellulose digestibility is highly demanding. When ionic liquids act as solvent (Binder & Raines, 2009; Dee & Bell, 2011; Kim et al., 2011; Kuo et al., 2013; Li & Zhao, 2007; Rinaldi et al., 2008; Su et al., 2009; Vanoye et al., 2009; Xiong et al., 2014), the cellulose/IL ratio is usually in the range of 5–10 wt%, whereas additional catalysts of acid or metal chloride are needed. When ionic liquids act as catalyst (Amarasekara & Owereh, 2009; Liu, Xiao, et al., 2013; Tao et al., 2010), the cellulose/IL ratio is mostly in the range of 20–50 wt%, however normally co-catalyst or IL as solvent is required to improve the selectivity of the desired product. Herein, cellulose has been converted to LA in high selectivity with [C_3SO_3Hmim]HSO_4 acting as catalyst, exclusive of co-catalyst and [C_4mim]Cl as solvent, whereas *ca.* 50% yield of LA could be obtained at cellulose/IL ratio up to 220%. The current methodology thus provides simple and efficient paradigm for IL application in biorefinery.

3.4. Mechanism and kinetics of cellulose depolymerization to LA

In fact, it is a complicated multistep process of cellulose conversion into LA, which involves several important intermediates. As generally recognized, cellulose depolymerizes to glucose first, and glucose transforms to 5-hydroxymethylfurfural (HMF), which further rehydrates to form LA. In our catalytic process towards the target product of LA, other than glucose, only tract amount of HMF was observed under incomplete conversion of cellulose. Since all our experiments were carried out at temperatures <180 °C, this observation is in line with the previous study (Girisuta et al., 2007), which has shown that significant amount of HMF would form only at reaction temperatures >200 °C.

As mentioned before, we observed the parallel formation of byproduct humins, which are suggested to proceed through the cross-polymerization or condensation of glucose and HMF (Patil, Heltzel, & Lund, 2012; Sievers et al., 2009). The infrared spectrum of humins from cellulose (Fig. 3a) shows the absorbance bands at 3400 cm^{-1} attributed to O—H stretching vibrations, 2929 cm^{-1} attributed to aliphatic C—H stretching vibrations, 1701 and 1618 cm^{-1} corresponding to C=O and C=C vibrations, respectively. The bands in the 1000–1450 cm^{-1} region are assigned to C—O stretching and O—H bending vibrations. The bands at 750–875 cm^{-1} are ascribed to aromatic C—H out-of-plane bending vibrations. No

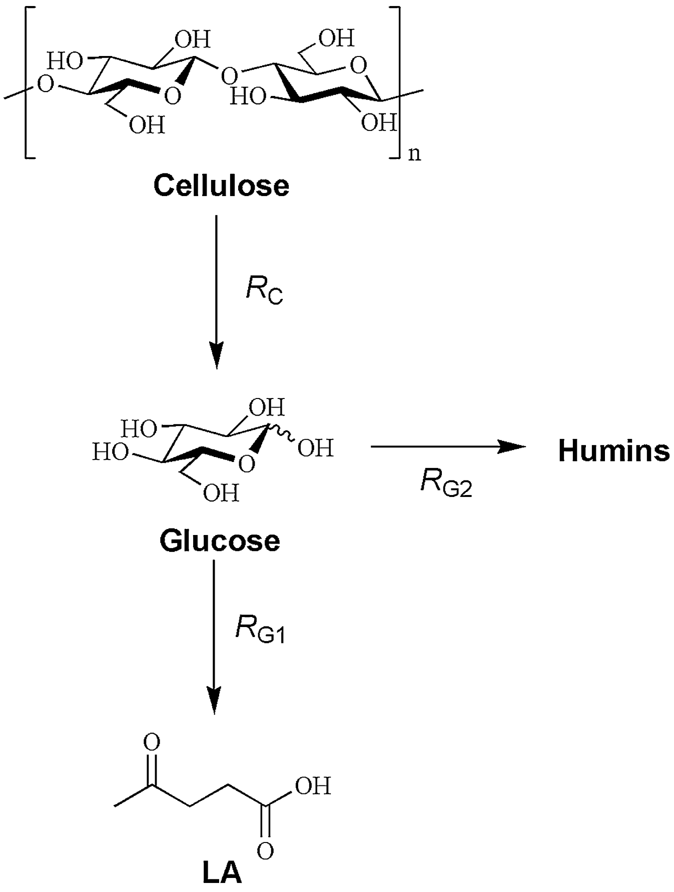

Fig. 4. Reaction pathway of cellulose depolymerization to LA catalyzed by IL.

absorbance peaks ascribed to IL were observed, indicating no IL remained in humin byproduct, which was confirmed by the elemental analysis of humins (C, 64.560; H, 4.421; N, 0.000). The scanning electron microscopy (SEM) images of humins show two types of particles, including big isolated spherical particles (*ca.* 2 µm) and small agglomerated particles less than 1 µm (Fig. 3b). In our catalytic system, the yields of humins, in the range of 14–22 wt%, decreased with increase of water amount after complete conversion of cellulose at 170 and 180 °C (Fig. A.1, Supplementary data), whereas the quantification of humins seemed unlikely at 160 °C due to the mixing with unconverted cellulose starting material. Furthermore, the dilution effect at 170 °C is more notable than that at 180 °C, confirming 170 °C is the optimum reaction temperature.

A kinetic study was carried out to gain an in-depth insight on the cellulose depolymerization to LA catalyzed by ionic liquid. The first systematic kinetic study on biomass hydrolysis to glucose was developed by Saeman (1945). Afterwards, kinetic studies on H_2SO_4-catalyzed hydrolysis of cellulose to LA have been reported by Girisuta et al. (2007). In this work, we proposed the following kinetic model for the IL-catalyzed cellulose depolymerization to LA, including the depolymerization of cellulose to glucose and the subsequent conversion of glucose to LA and humins (Fig. 4), whereas the reaction rates were approximated using the pseudo-first-order approach.

The first step in the depolymerization of cellulose was the cleavage of β-(1 → 4)-glycosidic bond to glucose. The reaction rate for this depolymerization step (R_C) was expressed by Eq. (1), whereas the concentration of cellulose (C_{CEL}) was defined as the number of available anhydroglucose units:

$$R_C = k_C C_{CEL} \tag{1}$$

Table 1
The kinetic parameters of cellulose depolymerization to LA.

Reaction	k_R (min^{-1})[a]	E (kJ/mol)
Cellulose → Glucose	0.134 ± 0.013	121.78 ± 7.19
Glucose → LA	0.258 ± 0.016	202.55 ± 5.34
Glucose → Humins	0.206 ± 0.014	166.85 ± 6.51

[a] The reference temperature was set at 170 °C.

As only trace amount of HMF was observed throughout our kinetics experiments, the formation reaction of HMF and its subsequent decomposition reactions were not included in the kinetic model. Accordingly, we proposed that glucose was converted directly to LA and simultaneously decomposed to the undesired product humins, whereby their reaction rates were defined as Eqs. (2) and (3), respectively:

$$R_{G1} = k_{G1} C_{GLC} \tag{2}$$

$$R_{G2} = k_{G2} C_{GLC} \tag{3}$$

The following equation was used to define the reaction rate constants given in Eqs. (1)–(3):

$$k_i = k_{R,i} \exp\left[\frac{E_i}{R}\left(\frac{T - T_R}{T_R T}\right)\right] \quad i \equiv \text{C, G1, G2} \tag{4}$$

The kinetic parameters defined in Eq. (4) were estimated by minimizing the sum of square error between the experimental data and the predicted values obtained from the solution of these differential Eqs. (5)–(7):

$$\frac{dC_{CEL}}{dt} = -R_C \tag{5}$$

$$\frac{dC_{GLC}}{dt} = R_C - R_{G1} - R_{G2} \tag{6}$$

$$\frac{dC_{LA}}{dt} = R_{G1} \tag{7}$$

A MATLAB optimisation routine *fminsearch* was used to obtain the best estimates of the kinetic parameters, which are given in Table 1. A good fit between the experimental data and kinetic model was obtained, as shown in Fig. 5.

The slowest reaction rate constant at the reference temperature (k_R) was observed for the depolymerization of cellulose to glucose (0.134 min^{-1}), which suggests that this reaction could be the rate-limiting step in the whole steps of cellulose conversion to LA. The highest reaction rate constant was observed in the reaction of glucose to LA (0.258 min^{-1}), which indicates that the conversion of glucose to LA was the fastest reaction compared to the other reactions. Based on the value of k_R for glucose to humins reaction (0.206 min^{-1}), it can be calculated that about 55.6% of the glucose converted would form LA as the desired product selectively, which is very close to our experimental data using glucose as the starting material (60.0%). The depolymerization reaction of cellulose to glucose catalyzed by IL has the lowest activation energy (121.78 kJ/mol), which is relatively lower than 151.5 kJ/mol reported for H_2SO_4 catalyst (Girisuta et al., 2007). This result indicates that depolymerization of cellulose catalyzed by IL is more favored energetically.

3.5. *The effect of IL structures on cellulose depolymerization*

One of the advantages of ionic liquid is designability, whereas the desired properties can be obtained through adjusting the cationic and anionic structures of ionic liquids. Some insights were put into the effect of IL structures on cellulose conversion to LA, whereby the Brønsted acidities of ILs were determined by Hammett method (Gu, Zhang, Duan, & Deng, 2005) using UV–vis spectrophotometer with 4-nitroaniline as indicator. The maximal absorbance

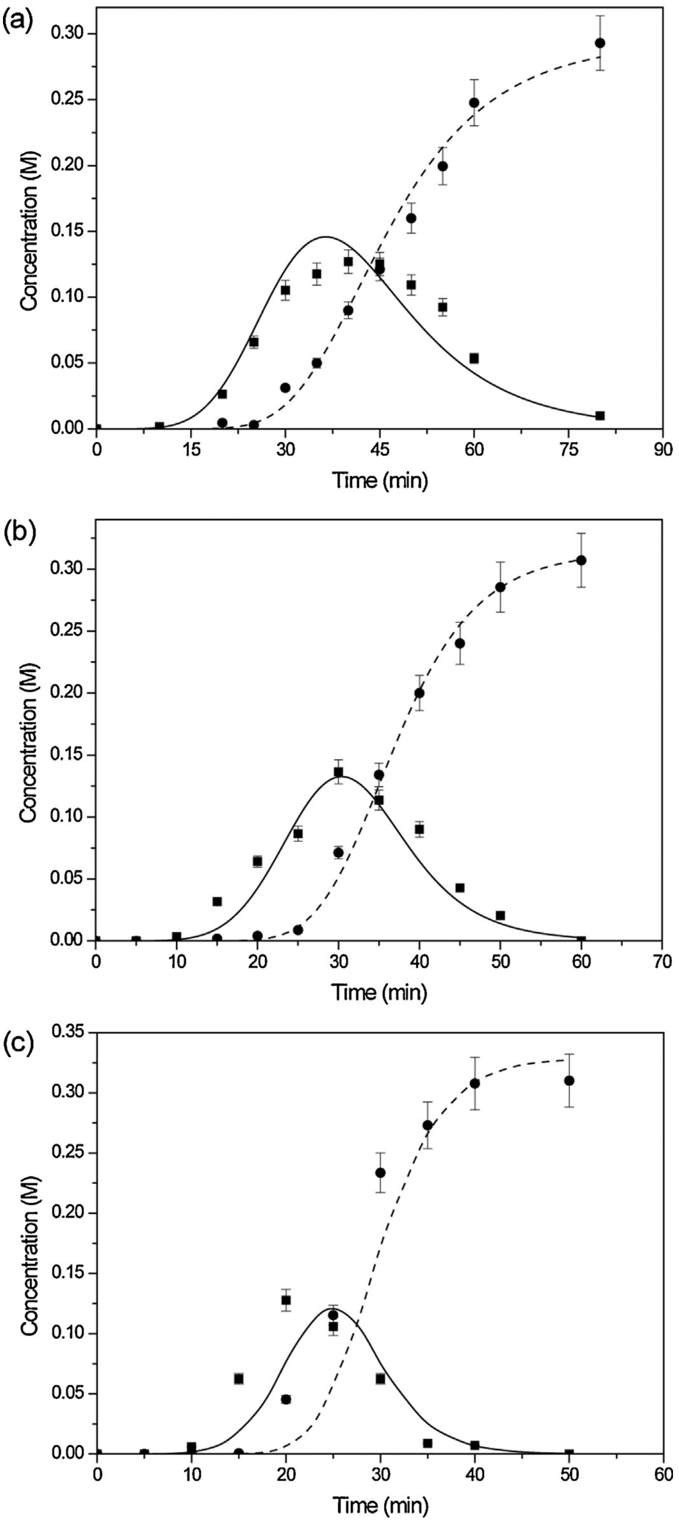

Fig. 5. Comparison of experimental data (■: Glucose concentration; ●: LA concentration) and kinetic model (solid and dashed lines). Conditions: 250 mg cellulose, 1.000 g [C_3SO_3Hmim]HSO_4, 2.000 g H_2O, (a) 160 °C, (b) 170 °C, (c) 180 °C.

Table 2
Cellulose conversion to LA catalyzed by acidic ionic liquids.[a]

IL	A_{max}	[I] (%)	[IH^+] (%)	H_0	Y_{LA} (mol%)
–	0.401	100	0	–	0
[C_3SO_3Hmim]HSO_4	0.249	62.1	37.9	1.204	63.0
[C_4SO_3Hmim]HSO_4	0.266	66.4	33.6	1.285	57.6
[$C_3SO_3HN_{222}$]HSO_4	0.270	67.4	32.6	1.305	54.5
[C_3SO_3HPy]HSO_4	0.259	64.6	35.4	1.251	56.9
[$C_3SO_3HPPh_3$]HSO_4	0.264	65.8	34.2	1.273	55.2
[C_3SO_3Hmim]H_2PO_4	0.370	92.2	7.8	2.063	16.7
[C_3SO_3Hmim]CH_3SO_3	0.267	66.6	33.4	1.289	53.9
[C_3SO_3Hmim]1-NS	0.323	80.6	19.4	1.607	53.8
[C_3SO_3Hmim]Cl	0.354	88.2	11.8	1.863	66.2

[a] All the experiments were conducted at 170 °C for 5 h with 150 mg of cellulose, 3.31 mmol of IL and 6.000 g of H_2O.

of the unprotonated form of the indicator was observed at 381 nm in H_2O, which decreased after adding acidic ionic liquid. Under the same concentration of 4-nitroaniline (4 mg/L) and ionic liquids (50 mmol/L) in H_2O, Hammett acidity functions (H_0) of ILs with different cations and anions were calculated and compared thereafter. As summarized in Table 2, the type of cations has slight effect on the acidities of ILs which decrease in the order: imidazolium > pyridinium > triphenylphosphonium > triethylammonium, whereas elongating the alkyl chain linked with the sulfonic acid group from propyl to butyl also causes small decrease of acidity. In contrast, for ILs with the same cationic structure of [C_3SO_3Hmim], the acidities of ILs are more dependent on the anions and decrease in the order: $HSO_4^- > CH_3SO_3^-$ > 1-NS > $H_2PO_4^-$. Consequently, the stronger the acidity of ILs, the higher yield of LA was obtained, indicating the essential role of the acidity in the catalytic cleavage of cellulose, possibly through protonation of glycosidic oxygen. Surprisingly, when [C_3SO_3Hmim]Cl was tested, the highest yield of LA (66.2%) was achieved, although its acidity is much lower than that of [C_3SO_3Hmim]HSO_4. Rogers and co-workers (Remsing, Swatloski, Rogers, & Moyna, 2006; Swatloski et al., 2002) reported that hydrogen bonding exists between the carbohydrate hydroxyl protons and the IL Cl^-, which helps to break the extensive hydrogen bonding network of cellulose and facilitate its dissolution. Herein, it shed light on that stronger hydrogen bond acceptors as IL anions could presumably increase accessibility of the polymer to the acid sites and then promote the catalytic performance of IL in cellulose conversion, apart from acidity factor.

3.6. *Application to versatile biomass feedstocks*

The catalytic methodology of IL can be applied to produce LA product from versatile biomass feedstocks. When organic molecules such as glucose, fructose and HMF were used as starting materials instead of cellulose under the same reaction conditions, as shown in Table 3, the yields of LA increase in the order glucose (60.0%, entry 1) < fructose (76.7%, entry 2) < HMF (93.4%, entry 3). Furthermore, by using a variety of cellulose and derivatives as starting materials, the relationship between polymeric structure and yield of LA was established for the first time. The results are summarized in Table 3.

Firstly, the effect of degree of polymerization (DP) of cellulose on the yield of LA was investigated, ranging from 100 to 500. The yield of LA reached the highest of 65.6% for sigmacell cellulose

Table 3
Conversion of different biomass feedstocks into LA.[a]

Entry	Feedstock	DP	DS	Y_{LA} (mol%)
1	Glucose	–	–	60.0
2	Fructose	–	–	76.7
3	HMF	–	–	93.4
4	Cellulose	100	0	56.4
5	Cellulose	237	0	63.0
6	Cellulose	400–500	0	65.6
7	CMC (MW 90,000)	–	0.7	44.0
8	CMC (MW 250,000)	–	0.7	43.9
9	CMC (MW 250,000)	–	1.2	40.1

[a] All the experiments were conducted at 170 °C for 5 h with 0.925 mmol of feedstock, 1.000 g of [C_3SO_3Hmim]HSO_4 and 6.000 g of H_2O.

(DP = 400–500, entry 6), followed by 63.0% for microcrystalline cellulose (DP = 237, entry 5) and 56.4% for α-cellulose (DP = 100, entry 4) in order. It seems that the yield of LA increases slightly with higher DP. The depolymerization efficiency towards LA is hindered by the parallel formation of humins. The higher DP, the harder and slower hydrolysis of cellulose (Fig. A.2, Supplementary data). Accordingly there were less glucose and HMF accumulated in the conversion process of cellulose with higher DP than lower DP, which may reduce the polymerization and condensation reactions to form humins, hence leading to higher yield of LA.

Secondly, the effect of degree of substitution (DS) of cellulose derivatives on the yield of LA was evaluated. Three kinds of carboxymethylcellulose (CMC) with different DS and molecular weight (MW) were compared under the same conditions. CMC (MW 90,000) and CMC (MW 250,000) with the same DS of 0.7 gave similar yields of LA (entry 7 and 8), whereas CMC (MW 250,000) with DS of 0.7 gave a higher yield of LA than CMC (MW 250,000) with DS of 1.2 (entry 9), indicating DS has a more perceptible effect than DP. The more hydroxyl groups were substituted, the more difficultly the cellulose derivatives were depolymerized to LA, highlighting the key role of hydroxyl groups during the breakdown of polymeric backbones. It is likely due to hydrogen bonding between hydroxyl protons and IL anions increasing accessibility of the polymer to acid sites and promoting the catalytic process, also in line with the result that IL with stronger hydrogen bond acceptor as anion led to higher yield of LA.

3.7. Separation of LA and reuse of IL

The recyclability of IL was investigated with 550 mg of cellulose, 1.000 g of [C_3SO_3Hmim]HSO_4 and 6.000 g of H_2O at 170 °C for 5 h. After the reaction, a variety of organic solvents were screened to extract LA product from the aqueous solution of IL and methyl isobutyl ketone (MIBK) proved to be optimum extraction solvent, where the extraction efficiency was as high as 98% and over 95% of the IL can be recovered. The yield of LA did not decrease during the recycle, but increased gradually from 58.5% to 65.7% after five cycles (Fig. A.3, Supplementary data), demonstrating that the IL maintained high catalytic activity. Through comparison of ^{1}H NMR spectra among IL recycled after five times, fresh IL and its zwitterionic precursor, it can be seen that the IL catalyst remains stable under the reaction conditions and does not decompose to the corresponding zwitterion (Fig. A.4, Supplementary data). It is assumed that the increase of LA yield was attributed to the residual oligomers of cellulose dissolved in the reaction mixture which can further transform to LA in the subsequent cycle. Moreover, LA can be routinely distilled as pure product from MIBK which is reusable too.

4. Conclusions

A highly selective and recyclable approach to depolymerize cellulose to levulinic acid was developed by catalysis of acidic ionic liquids under hydrothermal conditions. The optimum reaction conditions were 1 g of IL and 6 g of water at 170 °C for 5 h, whereas dilution effect becomes more pronounced at lower cellulose intake of 20 mg, dramatically improving the yield of LA up to 86.1%. Nevertheless, at a higher cellulose/IL ratio of 220%, *ca.* 50% yield of LA could be reached, demonstrating improved cellulose digestibility of IL. The catalytic mechanism of IL was in-depth explored, inclusive of acidity and hydrogen bonding ability, which mostly depend on anions. The acidic IL-catalyzed methodology provides green and simple paradigm to selective production of LA from versatile biomass feedstocks.

Acknowledgments

This project was supported by the Fundamental Research Funds for the Central Universities. L. L. acknowledges DICP-100-Talents Program for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.09.091.

References

Alonso, D. M., Gallo, J. M. R., Mellmer, M. A., Wettstein, S. G., & Dumesic, J. A. (2013). Direct conversion of cellulose to levulinic acid and gamma-valerolactone using solid acid catalysts. *Catalysis Science and Technology*, *3*, 927–931.

Amarasekara, A. S., & Owereh, O. S. (2009). Hydrolysis and decomposition of cellulose in brönsted acidic ionic liquids under mild conditions. *Industrial and Engineering Chemistry Research*, *48*, 10152–10155.

Binder, J. B., & Raines, R. T. (2009). Simple chemical transformation of lignocellulosic biomass into furans for fuels and chemicals. *Journal of the American Chemical Society*, *131*, 1979–1985.

Bozell, J. J. (2010). Connecting biomass and petroleum processing with a chemical bridge. *Science*, *329*, 522–523.

Cole, A. C., Jensen, J. L., Ntai, I., Tran, K. L. T., Weaver, K. J., Forbes, D. C., et al. (2002). Novel brønsted acidic ionic liquids and their use as dual solvent-catalysts. *Journal of the American Chemical Society*, *124*, 5962–5963.

Dee, S. J., & Bell, A. T. (2011). A study of the acid-catalyzed hydrolysis of cellulose dissolved in ionic liquids and the factors influencing the dehydration of glucose and the formation of humins. *ChemSusChem*, *4*, 1166–1173.

Ding, Z.-D., Shi, J.-C., Xiao, J.-J., Gu, W.-X., Zheng, C.-G., & Wang, H.-J. (2012). Catalytic conversion of cellulose to 5-hydroxymethyl furfural using acidic ionic liquids and co-catalyst. *Carbohydrate Polymers*, *90*, 792–798.

Girisuta, B., Janssen, L. P. B. M., & Heeres, H. J. (2007). Kinetic study on the acid-catalyzed hydrolysis of cellulose to levulinic acid. *Industrial and Engineering Chemistry Research*, *46*, 1696–1708.

Gu, Y., Zhang, J., Duan, Z., & Deng, Y. (2005). Pechmann reaction in non-chloroaluminate acidic ionic liquids under solvent-free conditions. *Advanced Synthesis and Catalysis*, *347*, 512–516.

Jarvis, M. (2003). Cellulose stacks up. *Nature*, *426*, 611–612.

Jin, F., & Enomoto, H. (2011). Rapid and highly selective conversion of biomass into value-added products in hydrothermal conditions: Chemistry of acid/base-catalysed and oxidation reactions. *Energy and Environmental Science*, *4*, 382–397.

Kamm, B., Gruber, P. R., & Kamm, M. (2006). *Biorefineries—Industrial processes and products*. Weinheim: Wiley-VCH.

Kim, B., Jeong, J., Lee, D., Kim, S., Yoon, H.-J., Lee, Y.-S., et al. (2011). Direct transformation of cellulose into 5-hydroxymethyl-2-furfural using a combination of metal chlorides in imidazolium ionic liquid. *Green Chemistry*, *13*, 1503–1506.

Kuo, I-J., Suzuki, N., Yamauchi, Y., & Wu, K. C.-W. (2013). Cellulose-to-HMF conversion using crystalline mesoporous titania and zirconia nanocatalysts in ionic liquid systems. *RSC Advances*, *3*, 2028–2034.

Li, C., & Zhao, Z. K. (2007). Efficient acid-catalyzed hydrolysis of cellulose in ionic liquid. *Advanced Synthesis and Catalysis*, *349*, 1847–1850.

Liu, B., Zhang, Z., & Zhao, Z. K. (2013). Microwave-assisted catalytic conversion of cellulose into 5-hydroxymethylfurfural in ionic liquids. *Chemical Engineering Journal*, *215*, 517–521.

Liu, Y., Xiao, W., Xia, S., & Ma, P. (2013). SO_3H-functionalized acidic ionic liquids as catalysts for the hydrolysis of cellulose. *Carbohydrate Polymers*, *92*, 218–222.

Patil, S. K. R., Heltzel, J., & Lund, C. R. F. (2012). Comparison of structural features of humins formed catalytically from glucose, fructose, and 5-hydroxymethylfurfuraldehyde. *Energy and Fuels*, *26*, 5281–5293.

Rackemann, D. W., & Doherty, W. O. S. (2011). The conversion of lignocellulosics to levulinic acid. *Biofuels Bioproducts and Biorefining*, *5*, 198–214.

Remsing, R. C., Swatloski, R. P., Rogers, R. D., & Moyna, G. (2006). Mechanism of cellulose dissolution in the ionic liquid 1-n-butyl-3-methylimidazolium chloride: A ^{13}C and $^{35/37}$Cl NMR relaxation study on model systems. *Chemical Communications*, 1271–1273.

Ren, H., Zhou, Y., & Liu, L. (2013). Selective conversion of cellulose to levulinic acid via microwave-assisted synthesis in ionic liquids. *Bioresource Technology*, *129*, 616–619.

Rinaldi, R., Palkovits, R., & Schüth, F. (2008). Depolymerization of cellulose using solid catalysts in ionic liquids. *Angewandte Chemie International Edition*, *47*, 8047–8050.

Saeman, J. F. (1945). Kinetics of wood saccharification—Hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature. *Industrial and Engineering Chemistry*, *37*, 43–52.

Seri, K., Sakaki, T., Shibata, M., Inoue, Y., & Ishida, H. (2002). Lanthanum (III)-catalyzed degradation of cellulose at 250 °C. *Bioresource Technology*, *81*, 257–260.

Shi, J., Gao, H., Xia, Y., Li, W., Wang, H., & Zheng, C. (2013). Efficient process for the direct transformation of cellulose and carbohydrates to 5-(hydroxymethyl) furfural with dual-core sulfonic acid ionic liquids and co-catalysts. *RSC Advances*, *3*, 7782–7790.

Sievers, C., Musin, I., Marzialetti, T., Olarte, M. B. V., Agrawal, P. K., & Jones, C. W. (2009). Acid-catalyzed conversion of sugars and furfurals in an ionic-liquid phase. *ChemSusChem*, *2*, 665–671.

Song, J., Fan, H., Ma, J., & Han, B. (2013). Conversion of glucose and cellulose into value-added products in water and ionic liquids. *Green Chemistry*, *15*, 2619–2635.

Su, Y., Brown, H. M., Huang, X., Zhou, X., Amonette, J. E., & Zhang, Z. C. (2009). Single-step conversion of cellulose to 5-hydroxymethylfurfural (HMF), a versatile platform chemical. *Applied Catalysis A: General*, *361*, 117–122.

Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellulose with ionic liquids. *Journal of the American Chemical Society*, *124*, 4974–4975.

Szabolcs, A., Molnar, M., Dibo, G., & Mika, L. T. (2013). Microwave-assisted conversion of carbohydrates to levulinic acid: An essential step in biomass conversion. *Green Chemistry*, *15*, 439–445.

Tabasso, S., Montoneri, E., Carnaroglio, D., Caporaso, M., & Cravotto, G. (2014). Microwave-assisted flash conversion of non-edible polysaccharides and post-harvest tomato plant waste to levulinic acid. *Green Chemistry*, *16*, 73–76.

Tao, F., Song, H., & Chou, L. (2010). Hydrolysis of cellulose by using catalytic amounts of $FeCl_2$ in ionic liquids. *ChemSusChem*, *3*, 1298–1303.

Tao, F., Song, H., Yang, J., & Chou, L. (2011). Catalytic hydrolysis of cellulose into furans in $MnCl_2$-ionic liquid system. *Carbohydrate Polymers*, *85*, 363–368.

Vanoye, L., Fanselow, M., Holbrey, J. D., Atkins, M. P., & Seddon, K. R. (2009). Kinetic model for the hydrolysis of lignocellulosic biomass in the ionic liquid, 1-ethyl-3-methyl-imidazolium chloride. *Green Chemistry*, *11*, 390–396.

Vyver, S. V., Thomas, J., Geboers, J., Keyzer, S., Smet, M., Dehaen, W., et al. (2011). Catalytic production of levulinic acid from cellulose and other biomass-derived carbohydrates with sulfonated hyperbranched poly(arylene oxindole)s. *Energy and Environmental Science*, *4*, 3601–3610.

Welton, T. (1999). Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chemical Reviews*, *99*, 2071–2083.

Werpy, T., & Petersen, G. (2004). Top value-added chemicals from biomass, volume I: Results of screening for potential candidates from sugars and synthesis gas.

Xiong, Y., Zhang, Z., Wang, X., Liu, B., & Lin, J. (2014). Hydrolysis of cellulose in ionic liquids catalyzed by a magnetically-recoverable solid acid catalyst. *Chemical Engineering Journal*, *235*, 349–355.

Zakzeski, J., Grisel, R. J. H., Smit, A. T., & Weckhuysen, B. M. (2012). Solid acid-catalyzed cellulose hydrolysis monitored by in situ ATR-IR spectroscopy. *ChemSusChem*, *5*, 430–437.

Zhou, L., Liang, R., Ma, Z., Wu, T., & Wu, Y. (2013). Conversion of cellulose to HMF in ionic liquid catalyzed by bifunctional ionic liquids. *Bioresource Technology*, *129*, 450–455.

Zuo, Y., Zhang, Y., & Fu, Y. (2014). Catalytic conversion of cellulose into levulinic acid by sulfonated chloromethyl polystyrene solid acid catalyst. *ChemCatChem*, *6*, 753–757.