Carbohydrate Polymers 115 (2015) 439–443

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

In situ NMR spectroscopy: Inulin biomass conversion in $ZnCl_2$ molten salt hydrate medium—$SnCl_4$ addition controls product distribution

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ARTICLE INFO

Article history:
Received 18 April 2014
Received in revised form 18 August 2014
Accepted 9 September 2014
Available online 18 September 2014

Keywords:
Inulin biomass
5-HMF
Levulinic acid
Molten salt hydrate medium
In situ NMR

ABSTRACT

The dehydration of inulin biomass to the platform chemicals, 5-hydroxymethylfurfural (5-HMF) and levulinic acid (LA), in $ZnCl_2$ molten salt hydrate medium was investigated. The influence of the Lewis acid catalyst, $SnCl_4$, on the product distribution was examined. An *in situ* ^1H NMR technique was employed to follow the reaction at the molecular level. The experimental results revealed that only 5-HMF was obtained from degradation of inulin biomass in $ZnCl_2$ molten salt hydrate medium, while the LA was gradually becoming the main product when the reaction temperature was increased in the presence of the Lewis acid catalyst $SnCl_4$. *In situ* NMR spectroscopy could monitor the reaction and give valuable insight.

1. Introduction

The deterioration of environment and diminishing fossil resources have given rise to a universal interest in sustainable resources exploration and utilization (Bai, Xiao, & Sun, 2014; He et al., 2014; Liu et al., 2014; Omari, Besaw, & Kerton, 2012; Pan et al., 2013; Siankevich et al., 2014; Tao, Song, Yang, & Chou, 2011; Yao et al., 2014; Zhang, Liu, & Zhao, 2012). Biomass has received great interests recently because of their potential applications for producing valuable liquid fuel and platform chemicals, such as 5-hydroxymethylfurfural (5-HMF) or levulinic acid (LA) (Climent, Corma, & Iborra, 2014; Shi et al., 2014; Song, Fan, Ma, & Han, 2013; van Putten et al., 2013).

Inulin, which is also called α-D-glucopyranosyl-[β-D-fructo furanosyl]$_{(n-1)}$-D-fructofuranoside or D-fructofuranoside-[β-D-fructo furanosyl]$_{(n-1)}$-D-fructofuranoside, is a natural linear polyfructan, and can be obtained in large quantities from plants of the *Compositae* family such as Jerusalem artichoke, chicory and dahlia (Barclay, Ginic-Markovic, Johnston, Cooper, & Petrovsky, 2012). Due to its high D-fructose content, inulin is considered to be an ideal source of preparing D-fructose derived chemicals (*i.e.* 5-HMF). Owing to its strong intra- and inter-molecular hydrogen bonds between —OH groups, it is difficult to dissolve and hydrolyze inulin under mild conditions in aqueous solution. It is therefore important to develop an environmentally benign medium for dissolving inulin in order to effectuate the hydrolysis to D-fructose and D-glucose, as well as the dehydration of the monosaccharides into 5-HMF and/or LA in a “one pot” fashion.

Recently, molten salt hydrate medium, *i.e.* $ZnCl_2{\cdot}4H_2O$ (65 wt% $ZnCl_2$ solution), has been disclosed as an efficient reaction medium for transforming lignocellulosic biomass (de Almeida et al., 2010; Deng et al., 2012; Li, Spina, Moulijn, & Makkee, 2013) and chitin biomass (Wang, Pedersen, Deng, Qiao, & Hou, 2013) into value-added fine chemicals, such as 5-HMF and isosorbide. Compared with dipolar aprotic organic solvents, ionic liquids or other reaction media, the $ZnCl_2{\cdot}4H_2O$ system might be more promising due to its low price, recyclable and the efficient downstream separation of 5-HMF (Deng et al., 2012; Shi et al., 2014; Song et al., 2013; Wang et al., 2013).

Precise product distribution control, for example of the well-known platform chemicals, 5-HMF and LA, is a challenge for biomass conversion. This is mainly due to the fact that the

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http://dx.doi.org/10.1016/j.carbpol.2014.09.011
0144-8617/

reaction pathway and 5-HMF rehydration into LA is effected profoundly by the following factors, including the properties of extensively utilized Lewis acid catalysts (Pagán-Torres, Wang, Gallo, Shanks, & Dumesic, 2012), the concentration of Lewis acid or Brønsted acid concentration (Omari et al., 2012), the synergetic effect of these two type of acid catalyst (Yang, Fu, Mo, & Lu, 2013), and even the intrinsic Brønsted acidity originated from the hydrolysis of Lewis acid cation (Choudhary et al., 2013). So, it is an interesting job to disclose the influence of Lewis acid catalyst addition on the product distribution of biomass degradation in $ZnCl_2$ molten salt hydrate medium. It is will be benefited to the higher product yields and efficient separation.

According to previous experimental results, $SnCl_4$ played a completely different role in the degradation of chitin biomass and cellulose biomass (Hu, Zhang, Song, Zhou, & Han, 2009; Omari et al., 2012; Wang et al., 2013). For chitin biomass-$ZnCl_2$ molten salt hydrate reaction system, the reaction was seriously inhibited by Sn^{4+} due to the strong chelation between $—NH_2$ groups of D-glucosamine and Sn^{4+} (Wang et al., 2013). However, the degradation of glucose was promoted by this Lewis acid catalyst (unpublished results). Hence, in order to investigate whether a control of the distribution of products including 5-HMF and LA could be achieved, the conversion of inulin biomass in $ZnCl_2$ molten salt hydrate with and without $SnCl_4$ as a co-catalyst was investigated systematically.

2. Experimental

2.1. Materials

Inulin (Practical grade, degree of polymerzation is ∼9, capped with glucose at reducing end of polyfructosyl chain, the ^1H and ^{13}C NMR were measured and listed in Figs. S1 and S2), sucrose (analytical grade, 99.8%), glucose (analytical grade, 99.5%) and fructose (analytical grade, 99.5%) were obtained from Shanghai crystal pure Co., Ltd. $ZnCl_2$, $SnCl_4{\cdot}5H_2O$ and maleic acid were purchased from Beijing Chemical Reagent Company. Deuterium oxide (D_2O, 99.9 atom% D) was supplied by Cambridge Isotope Laboratory. Double distilled water was used in all experiments. All reagents utilized in this work were used as received without further purification.

2.2. General reaction procedure

In a typical dehydration experiment, the reaction mixture was prepared by 5.6 mmol monosaccharide unit and 30 g $ZnCl_2$ molten salt hydrate medium with or without 2.8 mmol $SnCl_4$. This reaction mixture was heated in an oil bath under continuous stirring. At certain times during the reaction period, aliquot of the reaction mixture was taken out from the reaction flask and immediately emerged in an ice bath to quench the reaction. A gradually darkening of the initial clear solution to black slurry was usually observed under the applied conditions. The yields of 5-HMF and LA, as well as the rate of substrate consumption during the reaction, were quantitatively analyzed by ^1H NMR spectroscopy using maleic acid as internal standard substance, following the procedure described by Rundlöf et al. (2010) Maleic acid with concentration of 1.0574 mg/mL in D_2O was prepared as a standard solution, then 0.1 mL of reaction mixture was mixed with 0.4 mL this standard solution to give the ^1H NMR sample. 5-HMF and LA yields were determined by the following formula: yield = (moles of 5-HMF or LA)/(moles of monosaccharide unit) × 100%.

2.3. Procedure for in situ NMR study

The reaction was followed by *in situ* NMR using a Bruker AV-III 400 with a ^1H frequency of 400.13 MHz. The chemical shift for ^1H NMR was referenced to 4.77 ppm of deuterated solvent residual proton, HDO. A reaction mixture of sucrose in $ZnCl_2{\cdot}4D_2O$ (65 wt% $ZnCl_2$ in deuterium oxide solution) was prepared in a 5 mm heavy wall tube, with the same concentration of substrate and catalyst ($SnCl_4$) as in the general reaction procedure. Before it was transferred into the NMR spectrometer, which was already preheated to 100 °C, the solution was kept at room temperature for 10 min to reach equilibrium. When the temperature inside the NMR spectrometer probe was stabilized at 100 °C again after sample loading, ^1H NMR (ns = 8) spectra were recorded at certain times during the measurement.

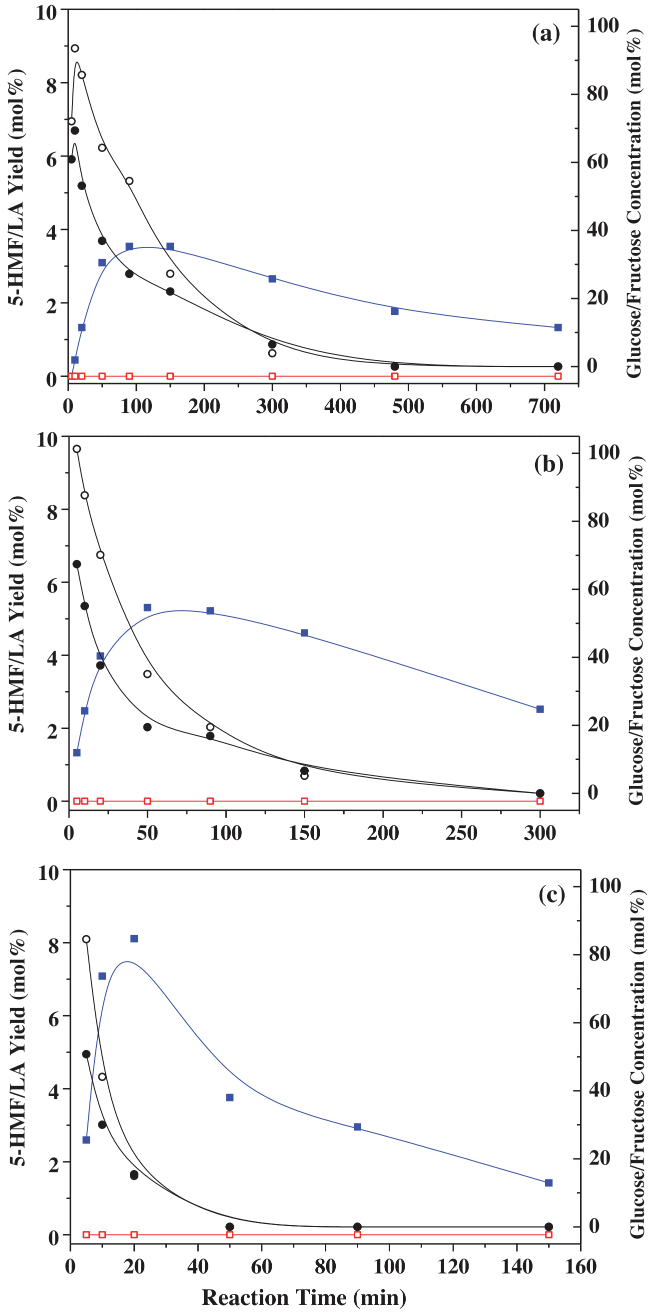

Fig. 1. Product and substrate concentrations as a function of the reaction time at different temperatures for sucrose degradation. Concentration: 1 g sucrose in 30 g $ZnCl_2$ molten salt hydrate medium ($ZnCl_2{\cdot}4H_2O$). (a) 80 °C; (b) 100 °C; (c) 120 °C. 5-HMF yield ■; LA yield □; fructose concentration ●; glucose concentration ○.

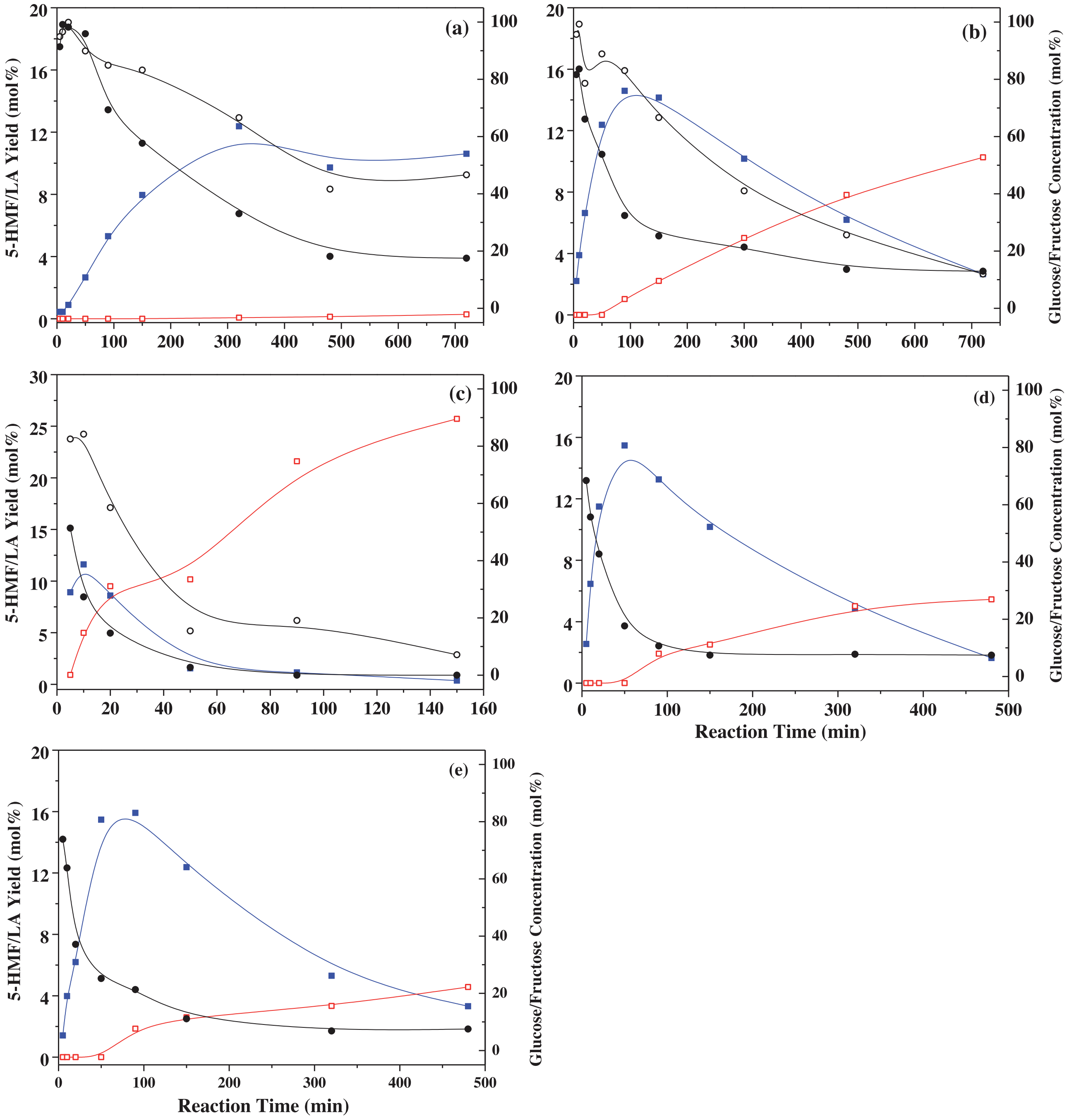

Fig. 2. Product and substrate concentrations as a function of the reaction time at different temperatures for inulin biomass degradation. Concentration: 1 g substrate in 30 g $ZnCl_2$ molten salt hydrate medium ($ZnCl_2·4H_2O$), $SnCl_4$/substrate unit = 0.5 (mol/mol). (a) sucrose, 80 °C; (b) sucrose, 100 °C; (c) sucrose, 120 °C; (d) fructose, 100 °C; (e) inulin, 100 °C. 5-HMF yield ■; LA yield □; fructose concentration ●; glucose concentration ○.

3. Results and discussion

3.1. Sucrose degradation in $ZnCl_2$ molten salt hydrate medium

Initially, the $ZnCl_2$ molten salt hydrate was preferred for dissolving inulin according to our previous work, (Deng et al., 2012; Wang et al., 2013) and it showed that $ZnCl_2·4H_2O$ acts as good solvent for inulin as well as being an acidic reaction medium (Fig. S3).

Sucrose can be considered as the smallest inulin (Barclay et al., 2012), so the hydrolysis and dehydration of sucrose were investigated as a model system under various reaction conditions. The quantitative ^1H NMR technique was employed to follow the substrate consumption rate and to quantify product yields.

If the reaction of sucrose was performed at 80 °C (Fig. 1(a)) in $ZnCl_2·4H_2O$ without $SnCl_4$ added, the hydrolysis of sucrose was finished within 5 min. and the highest concentrations of D-glucose and D-fructose during the reaction process were reached (the chemical structure identification for sucrose, glucose and fructose during reaction are presented in Section 3.3). When reaction time was prolonged from 10 min to 300 min, the concentration of D-glucose and D-fructose decreased from 93.5% and 69.3% to 3.9% and 6.5%, respectively. Moreover, the 5-HMF yield increased gradually during the first 90 min of reaction time, the highest 5-HMF yield of 3.5% was achieved at 90 min; 5-HMF yield decreased gradually when reaction time was prolonged from 90 min to 600 min. The trend of 5-HMF yield over reaction time is quite similar to our previous report with D-glucose and D-glucosamine as substrates. (Deng et al., 2012; Wang et al., 2013) When the temperature was increased to 100 °C and 120 °C (Fig. 1(b) and (c)), the hydrolysis of sucrose finished immediately (in less than 5 min), and the yield of 5-HMF increased from 3.5% at 80 °C to 5.3% at 100 °C, and 8.1% at 120 °C.

One important thing should be addressed, *i.e.* only 5-HMF was observed within the investigated reaction time and temperature range in the $ZnCl_2{\cdot}4H_2O$ sucrose system, and no LA was observed (Deng et al., 2012; Wang et al., 2013). LA is the rehydration product of 5-HMF under acidic condition (van Putten et al., 2013).

3.2. *Inulin biomass degradation in $ZnCl_2$ molten salt hydrate medium with $SnCl_4$*

If $SnCl_4$ (0.5 equiv.), as a Lewis acid catalyst, was added into the reaction mixture, the yields of 5-HMF at each reaction temperature were consistently higher than the corresponding reactions without Sn^{4+}. For example, at 100 °C, the yield of 5-HMF was 14.6% with Sn^{4+} added (Fig. 2(b)), while it was 5.3% for the reaction without Sn^{4+} added when reaction temperature is 100 °C.

Unexpectedly, the 5-HMF rehydration product LA was also detected in this reaction system with Sn^{4+}. Correspondingly, formic acid (FA), which is the widely utilized hydrogen resource for transfer hydrogenation reaction, was also observed. Surprisingly, the main product was switched from 5-HMF to LA gradually when the reaction temperature was increased from 80 °C to 120 °C. At 80 °C, the maximum yield for 5-HMF and LA were 12.4% and 0.28%, respectively, with 5-HMF being the main product (Fig. 2(a)). When the reaction temperature was increased to 120 °C, the highest yields were 11.6% and 25.7% for 5-HMF and LA, respectively, with LA being the main product (Fig. 2(c)). An apparent reaction time and temperature dependence were observed for the sucrose hydrolysis, monosaccharide consumption, 5-HMF formation and LA yields. Thus, the above experiments demonstrate that in the $ZnCl_2$ molten salt hydrate medium, the Lewis acid catalyst Sn^{4+} is not only effective for the conversion of substrate to 5-HMF, but it also promote the 5-HMF rehydration to LA and FA (Omari et al., 2012).

Other model compounds, *i.e.* D-fructose and the biopolymer inulin, were also used as feedstock for producing 5-HMF and LA in $ZnCl_2$ molten salt hydrate medium with the Lewis acid co-catalyst $SnCl_4$. The highest 5-HMF yields obtained from D-fructose and inulin at 100 °C were 15.5% (Fig. 2(d)) and 15.9% (Fig. 2(e)), respectively. The highest LA yields from fructose and inulin were 5.4% and 4.6%, respectively. The results above clearly demonstrate that substrate consumption, 5-HMF and LA yields, approximately follow the same trend in the reactions for bothD-fructose and inulin. This suggests that the conversion of biopolymer into monosaccharides through breaking the glycosidic bond was faster than the dehydration of monosaccharide. The rate determining step for the inulin degradation is therefore the dehydration step, and not the glycosidic bonds hydrolysis.

3.3. *In situ NMR characterization of the sucrose dehydration using $SnCl_4$*

To gain insights into the reaction pathways at the molecular level, and elucidate the role of Lewis acid catalyst, Sn^{4+}, during the inulin biomass degradation in $ZnCl_2$ molten salt hydrate, molecular level monitoring was performed by *in situ* ^1H NMR technology. The sucrose dehydration reaction was carried out in $ZnCl_2{\cdot}4D_2O$ with a catalytic amount of $SnCl_4$ at 100 °C, and the obtained time-progression ^1H NMR spectra were stacked and presented in Fig. 3.

According to the ^1H NMR spectrum at the initial stage of the reaction, and 1D ^1H NMR, ^{13}C NMR, and 2D ^1H-^1H COSY, ^1H-^{13}C HSQC spectra of authentic samples, the following proton signals of sucrose (Figs. S4–S7), fructose (Figs. S8–S11) and glucose (Figs. S12–S15) could be assigned (there are chemical shift differences for these experimental samples and authentic samples due to the solvent effect). A peak with chemical shift of 5.51 ppm is assigned to α-H_1 of D-glucose. The signal at 3.70 ppm belongs to the β-H_1 of D-fructose. The peak at 4.27 ppm is the typical signal of the glucosyl-attached fructosyl H_3 of sucrose, which can be utilized for showing if the glycosidic bond of sucrose still remains or not during the reaction. All NMR signals ($\delta = 5.51$, 3.70 and 4.27 ppm) mentioned above were selected to indicate the formation of intermediate monosaccharides and the consumption of all substrates including sucrose, D-glucose and D-fructose. According to the ^1H NMR, 2D ^1H-^1H COSY, ^1H-^{13}C HSQC spectra of reaction mixture contains of 5-HMF and mixture rich of FA and LA (Figs. S16–S23), the characteristic peaks found at $\delta = 9.50$, 8.45 and 2.40 ppm are signals owing to 5-HMF, FA and LA, respectively, and they are designated to follow the product formation of these compounds.

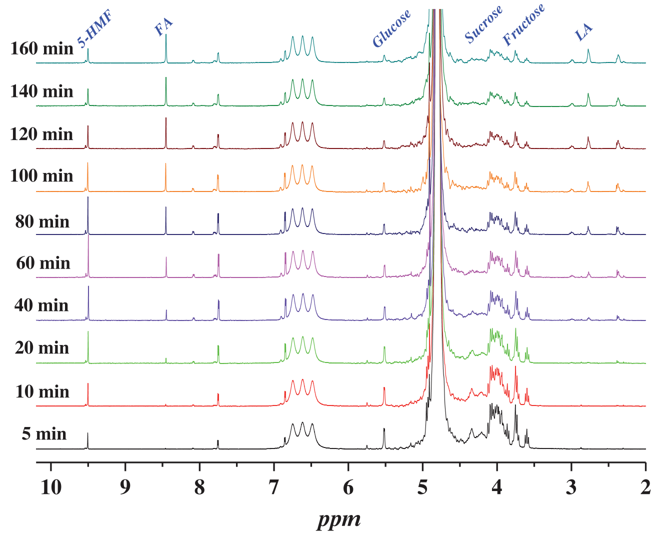

Fig. 3. Stacked ^1H NMR spectra of *in situ* NMR study. Solvent: $ZnCl_2{\cdot}4D_2O$ with $SnCl_4$; substrate: sucrose; reaction temperature: 100 °C.

As shown in Fig. 3, the intensity for signal of sucrose at 4.27 ppm decreased quickly and became almost negligible after 20 min, and the peaks of D-glucose ($\delta = 5.51$ ppm), D-fructose ($\delta = 3.70$ ppm), 5-HMF ($\delta = 9.50$ ppm), FA ($\delta = 8.45$ ppm) and LA ($\delta = 2.40$ ppm) appeared simultaneously. Moreover, the signals of by-products, for instance, the soluble oligomers, were not strong enough to be detected during the reaction. It was revealed that the hydrolysis of the substrate in the present reaction using the reaction medium containing the co-catalyst $SnCl_4$ is highly efficient. With the reaction proceeding, the H_1 signals of intermediate monosaccharides including D-glucose ($\delta = 5.51$ ppm) and D-fructose ($\delta = 3.70$ ppm) became weaker and finally negligible. Meanwhile, the intensity of 5-HMF signals ($\delta = 9.50$ ppm) increased constantly until 80 min where after it then decreased gradually, but the intensity of signals attribute to FA ($\delta = 8.45$ ppm) and LA ($\delta = 2.40$ ppm) were increasing constantly all the time. These data suggested that the rate of formation of 5-HMF is slower than 5-HMF rehydration into LA and FA.

The signals earlier reported for reaction intermediates in the conversion of D-glucose and D-fructose into 5-HMF, such as 3-deoxy-glucosone and (4*S*,5*R*)-4-hydroxy-5-hydroxymethyl-4,5-dihydrofuran-2-carbaldehyde, are not observed from the *in situ* spectra (Jadhav, Pedersen, Soiling, & Bols, 2011). Presumably, these possible intermediate compounds are too unstable or with too short life time in this $ZnCl_2$ molten salt hydrate medium to be observed. As a result, the observation and identification of the reaction intermediate compounds are difficult within the NMR time resolution (Akien, Qi, & Horvath, 2012; Kimura, Nakahara, & Matubayasi, 2011). These results are in agreement with reports of hexose monosaccharide dehydration in the aqueous medium (Kimura et al., 2011).

4. Conclusions

Our results show that the degradation of inulin biomass in $ZnCl_2$ molten salt hydrate medium can selectively afford the 5-HMF; whereas the ratio between LA and 5-HMF can be controlled precisely by taking advantage of the Lewis acid catalyst ($SnCl_4$) in combination with the reaction temperature. *In situ* NMR spectroscopy was demonstrated to be a convenient method to follow the reaction pathways of inulin biomass degradation. The results of this study will pave the way for improved control of the biomass degradation products and support the possible industrial application for platform molecular production.

Acknowledgements

The authors would like to acknowledge the financial support from the Major State Basic Research Development Program of China (973 Program) (no. 2012CB215305), the National Natural Science Foundation of China (no. 21106172), and the Natural Science Foundation for Youths of Shanxi (2012021009-2, 2013021008-7).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.09.011.

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