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The promotion effect of NaCl on the conversion of xylose to furfural

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Summary of main observation and conclusion In this work, the promotion effect of NaCl on the conversion of xylose to furfural in H_2O was studied. It was found that xylose conversion and furfural yield increased with NaCl concentration. NaCl decreased the pH of the solution providing H^+ for the acid catalytic dehydration of xylose. The formation of oligomers was determined by GPC and ESI-MS in the initial stage of reaction, especially at low temperature. Excess NaCl promoted the formation of humins in the late stage of the reaction. NaCl could also change the decomposition route of formic acid. Meanwhile, NaCl had the ability to phase separation. Combining these effects with organic solvent during the reaction could inhibit the formation of humins and increase the yield of furfural. In NaCl-H₂O-THF biphasic system without other catalyst, the optimal furfural yield of 76.7% and selectivity of 77.6% were achieved at 463 K in 2 hours.

1. Introduction

With the depletion of fossil resources and the enhancement of people's awareness of environmental protection, the use of agricultural waste has received much attention. The conversion of lignocellulose into valuable platform chemicals becomes one of the research hotspots.¹⁻³ Hemicellulose is one of the three major components in lignocellulosic biomass, which contains mainly xylose.⁴ Furfural is a typical dehydration product of xylose and one of the most important bio-based platform chemicals, capable of being used to synthesize furfuryl alcohol, γ-valerolactone (GVL), tetrahydrofuran (THF), and resin, which are widely used as fuel additives and industrial materials.⁵⁻⁹ Hence, study on xylose to furfural with high selectivity, which provides way to use biomass to its fullest while simplifies the further separation.

There are lots of methods for directly converting biomass to furfural. Industrially, homogenous mineral acids such as HCl and n_{25} D_4 were used as catalysts in aqueous solution for transforming hemicellulose in biomass to furfural, resulting in a yield of 40% - 50%.^{6, 10-12} Nevertheless, HCl and H_2SO_4 are strong acids, which would corrupt equipment and are difficult to separate, recycle and handle after catalyzed process.¹³ Alternatively, the production of furfural from hemicellulose might also be realized via two steps: hemicellulose is firstly hydrolyzed to pentoses such as xylose, and secondly the pentoses are dehydrated to form furfural.²

Wu *et al.* achieved high yield of xylose (95.5 mol%) from corn stover by using maleic acid as a catalyst at 140 °C.¹⁴ Jiang *et al.* found that high concentration chloride ions significantly accelerated the depolymerization process of xylo-oligomers to xylose.¹⁵ Marcotullio *et al.* considered that chloride ions enhanced furfural formation from xylose in dilute aqueous acidic solution.¹⁶ The results indicated that chloride ions promoted the formation of the 1,2-enediol from the acyclic form of xylose, and thus the subsequent acid catalyzed dehydration to furfural. Enslow *et al.* investigated the role of metal halides in enhancing dehydration of xylose to furfural.¹⁷ Fulmer *et al.* found that NaCl decreased the pH of hydrochloric acid solution. They proposed that the salt likewise increased the activity of the acid.¹⁸

There were also plenty of work developing water-organic biphasic system to inhibit the formation of humins.² Morais *et al.*

reported benefits by using a H₂O/THF/MIBK biphasic system with which they obtained 56.6 mol% of furfural yield from xylose with 5 MPa initial high-pressure CO₂ at 180 °C for 60 min.¹⁵ [°] Guenic *et* al. reported the maximum furfural yield of 80% from xylose at 170 $^{\circ}\!C$ for 60 min in a microwave-assisted $H_2O\text{-}CPME$ biphasic system in the presence of Nafion NR50 and NaCl.²⁰ NaCl was also used to enhance the ability of forming a water-organic biphasic system. Zhao et al. added appropriate amount of NaCl into CO_2 -water-isopropanol system, increasing the yield of furfural from 55.81% to 69.20%.²¹ No doubt, as a common salt in life, NaCl had a certain ability to enhance the conversion of carbohydrates. However, most researches studied NaCl as an additive rather than studying individually. Kammoun et al. found that NaCl promoted the conversion of xylose to furfural, and the maximum furfural yield was 44 mol% in 1.63 mol/L NaCl-H₂O solution.²² The effect of chloride and sodium ions on xylose conversion required further studv.

In this study, we discussed the effect of NaCl by using a single NaCl-H₂O system without other catalyst to convert xylose. The regulating effects of NaCl on the reaction kinetics were comparatively elaborated by using H₂O and NaCl-H₂O as the reaction solvent. The roles of NaCl on the conversion of xylose were studied by gel permeation chromatography (GPC) and electrospray ionization mass spectrometry (ESI-MS). The effect of formic acid produced in the process was discussed.

2. Results and Discussion

2.1 The effect of NaCl concentration

Usually, the reaction temperature of xylose conversion to furfural (FF) was $433 - 493 \text{ K.}^{2, 16, 23-24}$ In this section, 463 K was chosen as the reaction temperature firstly. Figure 1 showed the results of xylose conversion in NaCl-H₂O solution with different concentration of NaCl at 463 K. The concrete data were shown in Table S1. In H₂O system, it needed 4 hours to achieve complete xylose conversion in the absence of NaCl. The yield of furfural increased first with reaction time, and reached the highest (55.4%) at 3 hours, and then decreased. The decrease of furfural yield to 52.6% at 4 hours could be ascribed to the formation of humins.

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Table 1		The decomposition of FF and FA at 463 K for 4 hours ^{<i>a</i>} .						
Entry		Substrates	Solvents	Conversion	Gaseous products			
	1	FA	H ₂ O	19.5%	H ₂ , CO ₂ , CO			
	2	FA	NaCl-H ₂ O	20.4%	H ₂ , CO ₂ , CO			
	3	FF	H ₂ O	13.2%	CO ₂			
	4	FF	NaCl-H ₂ O	28.9%	CO ₂			
	5	FA+FF	H ₂ O	13.0%	H ₂ , CO ₂ , CO			
	6	FA+FF	NaCl-H ₂ O	47.6%	H ₂ , CO ₂ , CO			

 a The concentration of FA and FF in the solution were 0.0411 mol/L and 0.0673 mol/L, respectively. 50 mL H₂O, the amount of NaCl was 18 g in Entries 2, 4 and 6, 463 K, 4 hours, 2 MPa (Ar), 400 r/min.

According to the color change, excess NaCl promoted more humins formed in the late stage of the reaction. In order to figure out why the yield of FF and FA decreased in the late stage of the reaction, six control experiments were conducted at 463 K for 4 hours (Table 1). When FF was used as substrate, the repolymerization and decomposition of FF was remarkably increased in 36wt% NaCl-H₂O system. Liquid products in the two systems were both FA and humins. There was only a trace amount of CO₂ of gas products both in the two systems. When FA was used as substrate, the decomposition of FA was slightly increased in 36wt% NaCl-H₂O system. None of liquid product was detected. Compared with H₂O, the amount of CO increased while the amount of H₂ and CO₂ decreased in 36wt% NaCl-H₂O system. When FF and FA were both used as substrates, the degradation of FF was more remarkable in 36wt% NaCl-H₂O system. The amount of CO in 36wt% NaCl-H₂O system was about 3 times larger than that in H₂O. In conclusion, NaCl changed the decomposition route of FA. NaCl favored the formation of humins from furfural with prolonged reaction time, especially in the presence of FA.



Figure 2. The impacts of pH and added organic solvent on xylose conversion (A), yield of FF (B) and FA (C), carbon balance (D), selectivity of FF (E) and FA (F). Reaction conditions: 0.5 g xylose, 50 mL H_2O or dilute sulphuric acid solution, 0-18 g NaCl, 463 K, 0.5-4 h, 2 MPa(N₂), 400 r/min.

The promotion of NaCl on xylose conversion might be ascribed to the change of pH value by NaCl.¹⁸ The pH of water was 6.43. When adding 5wt% NaCl, the value of pH rapidly decreased to 5.64. Subsequently, constantly adding quantitative NaCl until it was saturated, the pH of the solution gradually decreased to 5.29 (Table S1). The concentration of H^{+} increased from 3.7*10⁻⁷ mol/L (H₂O) to 5.1*10⁻⁶ mol/L (saturated NaCl-H₂O solution). In order to figure out the effect of pH on the conversion of xylose, the pH of the reaction system was adjusted to 5.29 by adding H₂SO₄. When reaction time was less than 2 hours, xylose conversion in H₂SO₄ solution (Figure 2, blue line) was slightly lower than that in 36wt%-NaCl solution (red line), carbon balance, yield and selectivity of furfural were higher, respectively. This indicated that pH was not the only factor working in NaCl-H₂O systems. Lots of researches reported that chloride anions promoted the dissolution of saccharides, caused by the interaction of chloride anions with xylose via Cl...H-O hydrogen bonding. $^{\rm 25\text{-}29}$ In other words, the promotion of NaCl on xylose conversion might be also caused by the interaction between xylose and NaCl.^{16, 3}



Scheme 1. The proposed conversion routes of xylose to furfural.

According to experimental results and combined with literatures, the proposed conversion routes of xylose to furfural was shown in Scheme 1. Xylose could form xylofuranose through xylulose by route 1, and then xylofuranose could directly or stepwise dehydrated to furfural. Xylose could also form xylopyranose and stepwise dehydrate to form furfural. NaCl decreased the pH of the solution providing H^+ for the acid catalytic dehydration of xylose. Meanwhile, Cl⁻ interacted with hydroxyl groups (hydrogen-bonding), being conducive to the formation of the intermediates thus accelerating the conversion of xylose.



Figure 3. The effect of temperature on: Conversion of xylose (A), yield of furfural (B) and formic acid (C), carbon balance (D) in H_2O ; conversion of xylose (E), yield of furfural (F) and formic acid (G), carbon balance (H) in saturated NaCl- H_2O , respectively. Reaction conditions: 50.0 mL H_2O , 0.5 g Xylose, without or with 18.0 g NaCl, 403-463 K.

2.2 The effect of temperature on the dehydration

Figure 3 showed the conversion of xylose to furfural in pure water and in saturated NaCl-H₂O solution over the temperature range from 403 K to 463 K. With the reaction temperature increased, the promotion of NaCl on the conversion of xylose became more and more obvious. At 403 K, the conversion of xylose was merely 12.8% and 20.6% at 300 min, respectively in the H₂O and 36wt% NaCl-H₂O system. At 463 K, the conversion of xylose increased to 59.1% and 90.4% at 75min in the two systems, respectively. The effect of temperature was more remarkable in 36wt% NaCl-H₂O solution than in water. In the initial stage of the reaction, the selectivity of FF in the NaCl-H₂O system was less than that in H₂O. In the middle stage of the reaction, the selectivity of FF in the NaCl-H₂O system was higher than that in H₂O. As can be seen, raising temperature could greatly shorten reaction time to get a higher selectivity of furfural.

The reaction rate constant k calculated by furfural yield at different temperatures in the two systems were summarized in Table S2. With temperature increased (403-463 K), the difference of k between 36wt%NaCl-H₂O and H₂O increased. Increasing temperature enhanced the promotion effect of NaCl on the reaction.

Table 2 The effect of temperature on formic acid (FA) formation at the beginning of the reaction^a.

Entry	System	Temp. (K)	t ^b (min)	Con. (Xyl)	Y. (FA)	S. (FA)
1		403	180	10.4%	1.6%	15.4%
2		418	60	10.1%	2.3%	22.5%
3	H ₂ O	433	30	14.3%	3.5%	24.1%
4		448	15	11.1%	2.9%	25.6%
5		463	5	15.4%	5.3%	34.3%
6		403	120	10.9%	0.4%	3.4%
7	NaCl-H ₂ O	418	30	10.4%	0.7%	7.1%
8		433	15	15.0%	1.7%	11.5%
9		448	15	19.5%	3.2%	16.4%
10		463	5	25.8%	4.4%	17.1%

 a Reaction conditions: 0.5 g xylose, 50 mL H₂O, where the amount of NaCl was 18 g in Entry 6-10, 2 MPa (N₂), 400 r/min. b t refers to reaction time.

The apparent activation energy (Ea) was calculated according to the reaction rate constant (Figure S1). Although the Ea of xylose conversion in 36wt% NaCl-H₂O system was a little higher than that in H₂O system, the pre-exponential factor of reaction in 36wt% NaCl-H₂O system was 78 times larger than that in H₂O system. The larger Ea is, the more influence of temperature on the reaction will have. In other words, raising the temperature is more beneficial to the dehydration of xylose in 36wt% NaCl-H₂O than in H₂O.



Figure 4. The relationship between FA yield and xylose conversion in the three systems. Reaction conditions: 0.5g Xylose, 50 mL H_2O , 0-18g NaCl, 418 K, 15 – 300 min.

The effect of temperature on formic acid formation at the beginning of the reaction was listed in Table 2. In H₂O system, the yield and selectivity of FA increased with elevating temperature in the case of low xylose conversion. For instance, at 403 K, the conversion of xylose, yield and selectivity of FA were 10.4%, 1.6% and 15.4% at 180 min, respectively. While at 418 K, the values were respectively 10.1%, 2,3% and 22.5% at 60 min. The similar conclusion could be obtained in 36wt% NaCl-H₂O system. It could be concluded that higher temperature favored the formation of FA in the initial stage of reaction. Analysis of the FA yield as a function of xylose conversion revealed that NaCl could decrease the yield and selectivity of formic acid (Figure 4).

2.3 The effect of added FA

In the process of xylose conversion to furfural, formic acid was

the main byproduct. In addition to be generated from xylose, formic acid could also be generated from the destruction of furfural.³¹ Previous studies also used FA as catalyst to catalyze the conversion of xylose.³²⁻³⁴ We conducted two sets of control experiments with or without FA at 463 K for 0.5 h. The amount of FA used was almost equal to that produced during the reaction. By calculating and simulating the amount of FA generated in H₂O and NaCl-H₂O systems, we chose 0.02 mol/L as the concentration of FA for control experiment, which was less than other studies.³²⁻³⁴ At the beginning of the reaction, prepared FA solution vas added into H₂O and NaCl-H₂O system, respectively (Table 3), ensuring that the concentration of FA was 0.02 mol/L in aqueous solution. The addition of FA increased the furfural selectivity and arbon balance both in H₂O and NaCl-H₂O system. After adding FA, the yield of furfural increased from 23.5% to 25.0% and the electivity of furfural increased from 59.3% to 75.4% in H_2O system for 30 min at 463 K. At the same reaction temperature and time, the yield of furfural increased from 43.1% to 63.1% and he selectivity of furfural increased from 69.3% to 76.8% in NaCl-H₂O system.

The addition of FA increased the furfural yield and selectivity by restraining the occurrence of side reactions. It makes sense that, arge amount of FA was generated at the beginning of the reaction, which catalyzed the formation of furfural. NaCl promoted the ionization of FA, increasing the H⁺ concentration of the solution.

table 3 The influence of formic acid on xylose conversion and furfural yield^a.

Entry		Condition	Con. / %	Yield / %		Selectivity / %		Carbon
			Xylose	FF	FA	FF	FA	balance (%)
	1	H ₂ O	39.6	23.5	8.1	59.3	20.3	91.9
D	2	36wt%NaCl	62.2	43.1	7.5	69.3	12.1	88.4
	3	FA-H ₂ O	33.1	25.0	6.9	75.4	20.7	98.7
	4	FA-36wt%NaCl	82.3	63.1	5.9	76.8	7.2	86.8

Reaction conditions: 463 K, 0.5 h, 2 MPa (N_2), 400 r/min, the oncentration of FA was 0.0206 mol/L in aqueous phase.

he analysis of oligomers

In all the experiments, carbon balance was less than 100% alculated by identified small molecular products. The value of carbon balance decreased with time under all the reaction conditions tested, as shown in Figure 1(D) and Figure 3(D, H). In he case of similar xylose conversion, higher temperature was beneficial to furfural selectivity and carbon balance in shorter reaction time, especially in 36wt% NaCl-H₂O system (Table 4).

able 4 Comparation of carbon balance in the two systems^a.

Ī	Entry	System	Temp. (K)	t ^b (min)	Con. (Xyl)	S. (FF)	Carbon balance
	1	, H₂O	433	90	20.4%	51.1%	94.3%
1	2	H ₂ O	418	300	20.3%	49.6%	92.8%
	3	NaCl-H ₂ O	433	30	19.8%	27.7%	91.1%
	4	NaCl-H₂O	418	90	20.5%	20.6%	89.0%
	5	NaCl-H ₂ O	433	300	64.4%	58.1%	84.5%
	6	NaCl-H ₂ O	463	30	62.2%	69.3%	88.4%
	7	H₂O	463	75	59.1%	61.2%	87.2%

 a Reaction conditions: 0.5 g xylose, 50 mL H₂O, where the amount of NaCl was 18 g in Entries 3 to 6, 2 MPa (N₂), 400 r/min. b t refers to reaction time.



Figure 5. The molecular distribution of four reactions (a, b, in H_2O system, 15min, 90min, respectively; c, d, in 36wt% NaCl- H_2O system, 15min, 90min, respectively). The refers to molecular weight (Mw) that was less than 200 Da, refers to Mw that was between 200 and 350 Da, refers to Mw that was between 200 and 350 Da, refers to Mw that was more than 500 Da. Reaction conditions: 50.0 mL H_2O , 0.5 g Xylose, in the absence or presence of 18.0 g NaCl, 433K

In order to figure out what generated at the beginning of the reaction, gel permeation chromatography (GPC) and ESI-MS tests were carried out. After adding NaCl, the percentage of larger molecules increased in molecular weight distribution of reaction liquid (Figure 5). NaCl promoted the formation of trimers (350-500), and larger oligomers (>500). In the initial stage of the reaction, the low furfural selectivity was caused by NaCl promoted formation of oligomers.

The ESI-MS results of incompletely converted xylose reaction solution were analyzed in both H₂O and NaCl-H₂O system (Figure S2). ESI-MS results showed besides remained xylose and its derivation ([Xyl+Na]⁺, [2Xyl+H+Na]²⁺, etc.), the intermediate species ([Xyl-H₂O+Na]⁺, [2Xyl-H₂O+H]⁺, [2Xyl-H₂O+Na]⁺) were also detected. The substances like [Xyl-FA+H]⁺, [Xyl-FA+Na]⁺, [2Xyl-H₂O-FA+2H]²⁺ were also detected, whose appearance confirmed that formic acid could be directly generated from xylose (Figure S3). Xylose was partly converted to these oligomers rather than directly dehydrated to furfural in the initial stage of the reaction, especially in NaCl-H₂O solvent system, which might demonstrate that the reaction route of xylose conversion to furfural in NaCl-H₂O might undergo the condensation firstly and then dehydration as well as degradation.

2.5 Inhibition of furfural degradation by THF

Williams studied the destruction of furfural in dilute acidic solution. It was found that the rate of furfural destruction was proportional to furfural concentration and to hydrogen ion concentration.³¹ Tang reported that tetrahydrofuran (THF) suppresses the polymerization of 5-hydroxymethylfufural (HMF) to byproducts in NaCl-H₂O/THF biphasic system.³⁵ The results obtained from adding THF as extraction agent in the reaction were shown in Table 5. In NaCl-H₂O-THF biphasic system, the rates of xylose conversion and furfural yield were greater than that in other two systems in the initial stage of the reaction. The optimal furfural yield was 76.7% at 2 hours, meanwhile xylose was converted completely. The selectivity of furfural could maintain about 75% without remarkably decline in 4 hours. Meanwhile, there's a good performance of carbon balance in the biphasic system especially with prolonged reaction time. Due to

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the extraction effect of THF, more product interacted with oxygen atom of THF by hydrogen bonding and got away from aqueous phase reducing the repolymerization or decomposition of furfural in the presence of NaCl and FA, resulting in higher stability of furfural yield and selectivity with longer time. THF is a kind of low boiling point organic solvent, which is beneficial to gain high purity product using distillation with low energy consumption. Theoretically, separated aqueous phase and organic phase could be recycled and reused.

 Table 5
 The conversion of xylose in NaCl-H₂O/THF biphasic system^a.

Entry	t ^b (min)	Con. (Xyl)	Y. (FF)	S. (FF)	Carbon balance
1	30	75.0%	55.4%	73.9%	85.7%
2	60	89.4%	68.0%	76.1%	82.3%
3	120	98.8%	76.7%	77.6%	80.0%
4	180	99.3%	77.1%	77.6%	79.6%
5	240	99.6%	75.0%	75.4%	77.3%

^{*a*} Reaction conditions: 0.5 g xylose, 25 mL H₂O, 25 mL THF, 9 g NaCl,463 K, ₁2 MPa (N₂), 400 r/min. ^{*b*} t refers to reaction time.

3. Conclusions

In summary, NaCl decreasing the pH of the solution providing the H^{+} for the acid catalytic dehydration of xylose. In the initial stage of the reaction, NaCl could accelerate the conversion of xylose and promote the formation of oligomers, especially at low reaction temperature. Generated formic acid in the reaction could further catalyze and accelerate the reaction. Organic solvents like THF could restrain the formation of humins, and further enhance the yield and selectivity of furfural. There was a synergistic effect between NaCl, THF and FA, which promoted the xylose conversion, furfural yield and selectivity.

4. Experimental

Materials. D-xylose (Xyl, 99%), furfural (FF, 98%) and formic acid (FA, 99%) were purchased from J&K Scientific Ltd (Beijing, emina). Sodium chloride (NaCl, analytically pure), tetrahydrofuran (THF, analytically pure) were obtained from Kelong Chemical Regent Factory (Chengdu, China). Ultrapure water (18.25 M Ω cm⁻¹, 298 K) was obtained from Aike Labpure water system. All materials were used without further purification.

Experimental procedure. Kinetic experiments were conducted in a 100 mL Parr reactor. In a typical run, 0.5 g xylose with 50 mL H₂O and a certain amount of NaCl was loaded in the reactor. Then the reactor was sealed and the inner air was replaced by pure nitrogen for three times. The initial pressure was added to 2.0 MPa with nitrogen. The sealed reactor was heated from room temperature to desired temperature within 25 minutes and then kept at the desired value for a certain period of time. The stirring rate was 400 r/min. The counting of reaction time was started when the temperature reached the desired value. After reaction, the reactor was moved from the heating furnace, and cooled down to room temperature with cold water. After releasing the gas off the reactor, the mixture of reaction system was collected, and the reactor was washed at least three times with high purity water. The total liquid was transferred with water to a 100 mL volumetric flask. When using NaCl-H₂O-THF biphasic system, the reaction liquid was transferred to a 500 mL volumetric flask with water to obtain a homogenous phase. The liquid was diluted and filtered prior to analysis.

Gaseous products analysis. Gaseous products were collected with a 2 L gas bag after reaction and cool down. A gas chromatograph with Plot-C2000 capillary column was used for the analysis of the gaseous products.

Liquid products analysis. Liquid products were quantitatively measured by High Performance Liquid Chromatography (HPLC, Waters-e2695) equipped with a pump, an aminex column (HPX-87H, 300 mm × 7.8 mm, Bio-rad), a Variable UV-vis Wavelength Detector (model 2998) and a refractive index detector (RI detector, model 2414). The temperature of the oven and detector were 50 $^\circ C$ and 35 $^\circ C$, respectively. The injection volume was 50 μ L, and the mobile phase was 0.005 mol/L H₂SO₄ aqueous solution at a flow rate of 0.6 mL/min. Xylose (Xyl) was detected by the RI detector. Furfural (FF), xylulose and formic acid (FA) were detected by the UV-vis detector at the wavelength of 284 nm and 210 nm, respectively. All the compounds were quantified by external standard method. The conversion of xylose, yield and selectivity of furfural, yield and selectivity of formic acid, as well as the carbon balance, are defined by the following equations:

Conversion of xylose, Con. (Xyl)

Con. (Xyl) = (moles of initial xylose - moles of final xylose)/(moles of initial xylose) × 100%

Yield of furfural, Y (FF)

Y (FF) = (moles of generated furfural)/(moles of initial xylose) × 100%

Selectivity of furfural, S (FF)

S (FF) = (moles of generated furfural)/(moles of initial xylose - moles of final xylose) \times 100%

Yield of formic acid, Y (FA)

Y (FA) = (moles of generated formic acid)/(moles of initial xylose \times 5) \times 100%

Selectivity of formic acid, S (FA)

S (FA) = (moles of generated formic acid)/(moles of initial xylose - moles of final xylose) \times 5) \times 100%

Yield of xylulose, Y (Xylulose)

Y (Xylulose) = (moles of generated xylulose)/(moles of initial xylose) × 100%

Selectivity of xylulose, S (xylulose)

S (Xylulose) = (moles of generated xylulose)/(moles of initial xylose - moles of final xylose) × 100%

Carbon balance

Carbon balance = (output of carbon)/(input of carbon) × 100%

Gel permeation chromatography (GPC). The oligomers formed in H_2O were analyzed by GPC (1260, Agilent) equipped with a column (PL aquagel-OH, Agilent) and a RI detector. Ultrapure water was used as the mobile phase at a flow rate of 1.0 mL/min and the column temperature was maintained at 303 K. Saccharide standards (90-20 000 Da) were used to obtain the calibration curve.

Electrospray ionization mass spectrometry (ESI-MS). ESI-MS (LCMS-IT-TOF, Shimadzu) was used to analyze the possible chemical structure of liquid products. The instrument was operated with the following parameters: ionization voltage, 4.5 Kv; interface temperature, 250 °C; nebulizer gas (N₂) flow, 90 L/h; detector voltage, 1.60 kV; continuum mode.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2019xxxxx.

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