UNIVERSITY *of York*

This is a repository copy of *Sodium Chloride-Assisted Depolymerisation of Xylo-oligomers to Xylose*.

Article:

White Rose
university consortium
Universities of Leeds, Sheffield & York

Sodium Chloride-Assisted Depolymerisation of Xylo-oligomers to Xylose

Zhicheng Jiang,[a,b] Vitaliy L. Budarin,[b] Jiajun Fan,*[b] Javier Remón,[b] Tianzong Li,[b] Changwei Hu,*[a] James H. Clark [b]

[a] Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan, 610064, China.

[b] Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, YO10 5DD, U.K.

*alice.fan@york.ac.uk (Jiajun Fan)

*changweihu@scu.edu.cn (Changwei Hu)

ABSTRACT

The depolymerisation of hemicellulose is essential in the downstream processing of biomass within a bio-refinery, with the search for energy efficient selective pathways for its conversion presenting a significant challenge. Herein, the process of NaCl promoted depolymerisation of xylo-oligomers to xylose through use of sea water and NaCl, under microwave hydrolytic conditions is investigated by systematic kinetic study assisted by deuterated agents. It was found that NaCl shortened the reaction time (10 min in NaCl-H_2O *vs* 60 min in H_2O) to obtain the maximum yield of xylose (about 90 wt.%) without significant secondary reaction products formed. NaCl was observed to generate acidic products from residual xylose structure, rate limiting the process, but providing acids that simultaneously catalysed the depolymerisation of xylose-oligomers. It was also found that Cl⁻ cleaved the hydrogen bonding in xylo-oligomers, releasing separated xylo-oligomers chain and enhancing the interaction of H⁺ with xylo-oligomers. The high concentration of Cl⁻ in seawater was observed to significantly enhance the depolymerisation process. This abundant solvent is a great prospect for the production of xylose from the depolymerisation of hemicellulosic-rich biomass.

INTRODUCTION

Lignocellulosic biomass has been widely regarded as renewable alternative for energy and chemical industry.[1] Hemicellulose is the second most abundant polysaccharides (15 to 35% of plant biomass) in nature after cellulose. [2-3] It is not a homogeneous polymer but contains different monomeric units mainly consisting of xylose, glucose, arabinose, galactose and mannose.[4] Unlike cellulose, they are branched polymers with a smaller molecular weight and a lower degree of polymerisation.[5] In the search for more efficient strategies to convert biomass to fuels and high-value chemicals, the transformation of hemicellulose, represents unique challenges and opportunities.[6-7] Depolymerisation of the polysaccharide components in biomass to their constituent monomeric sugars with high selectivity, increases flexibility in its further bio-refining for production of variable chemicals.[8] To meet this objective, solid-acid catalysts (e.g. zeolite and HT_5-HSO_3-mesoporous carbon nanoparticle) are used for catalytic-hydrolysis of (1-4)-β-D-xylan into xylose with high yield in aqueous reaction medium.[9-10] Furthermore, dilute acids are also widely employed to give high reaction rates and lower costs than enzyme catalysts.[11] However, the degradation process of xylan to xylose is always accompanied by its further conversion to furfural and other products.[12-14] Recently, acidic catalysts were adopted for the decomposition of xylose to furfural in the presence of NaCl.[15-17] This decomposition process reduces the yield of xylose, and the increased formation of byproducts inhibited its subsequent fermentation and enzymatic hydrolysis.[18] In our previous work, $NaCl$-H_2O was used for the solubilisation and depolymerisation of cellulose in the absence of any acids by conventional heating, where it was found that almost all cellulose could be degraded into low molecular weight oligomers without significant proportions of decomposed products (below 18 wt%).[19] In this paper, we present our results from a study of the effect of NaCl on the depolymerisation of xylo-oligomers, a xylose-based oligomer to yield xylose by microwave irradiation. Microwave heating is enhanced by the presence of salts, making it more energy efficient.[20-21] An autocatalytic hydrolysis of xylo-oligomers assisted by NaCl is proposed. We also used seawater (from Scarborough UK) with high concentration of NaCl for the depolymerisation process.

EXPERIMENTAL SECTION

Typical microwave reaction. 0.2 g xylo-oligomers (Sigma Aldrich, V900513) and designed amounts of salts (0.8 g, except where noted) were mixed directly with 4 mL deionised water in a microwave glass tube. The reaction tube was heated using a Mono Anton Parr microwave (Graz, Austria) with continuous stirring at 1000 rpm. A Ruby probe was used to measure the inner vessel temperature for the reaction system during the reaction process. Besides, the reaction pressure and the supplied microwave power were recorded automatically. Each reaction was heated from room temperature to a designated temperature (e.g. 140 ^{o}C, 200 ^{o}C) within 5 min, and held for varying periods. After treatment, the reaction system was cooled to below 70 ^{o}C using compressed air. The post-treated liquid fraction was poured out and the glass tube washed three times with deionised water. The collected liquid products were stored for further analysis. Because the xylo-oligomers are water-soluble and consisted of oligomers with various degrees of polymerisation, the conversion of xylo-oligomers was not calculated. Xylose and other liquid products were quantitatively analysed by High Performance Liquid Chromatography (HPLC), and yields are defined as follows:

Yield of xylose (wt%) = (weight of xylose at the end of reaction) / (weight of pure xylo-oligomers   before   reaction) (1)

Yield of other products (wt%) = (weight of specific products at the end of reaction) / (weight of xylo-oligomers before reaction)   (2)

Charaterisation of the liquid fraction. In order to quantitively analyse xylo-oligomers, sugars, acids and furans, HPLC was performed using an Agilent 1260 , fitted with an Infinity II RI Detector. For analysing the content of xylo-oligomers before and after reaction, a Hi Plex Na column (300 × 7.7 mm, 10 μm particle size) was used with 0.15 ml/min flow rate of water as the mobile phase. For sugars and acids, an Agilent Hi-Plex H column (7.7 × 300 mm, 8 μm (p/n

PL1170-6830)) was used. 0.005 M H_2SO_4 solution was adopted as the mobile phase. An ACE C18 column (250 × 4.6 mm, 5 µm particle size) was also used to analyse HMF and furfural, using acetonitrile/water (25/75, vol: vol) as the mobile phase, with a 0.8 ml/min flow rate (isocratic). The Heteronuclear Single-Quantum coherence (HSQC) 2D NMR spectra of the xylo-oligomers before and after the reaction in D_2O solvent, were analysed on a JEOL ecs400 NMR spectrometer (Tokyo, Japan). For ^1H-dimension, 1024 data points were used with an acquisition time of 64 ms, while 256 data points were used for the ^{13}C-dimension. The $^1J_{C-H}$ used was 145 Hz. The xylo-oligomers in the presence and absence of NaCl in water, at room temperature, were also analysed by Bruker "compact" time-of-flight MS (Bruker Daltonics, Bremen, Germany). The dry gas flow rate was 3 L/min, and the detector voltage was 3.5 kV. A 50% methanol solution was used as the eluent with a flow rate of 0.2 mL/min, and an injection volume of 1 µL was used. Data was collected in mass range 50 to 1200 m/z. Raman spectra were recorded on a Horiba R-XploRA Plus (Japan) with the excitation wavelength of 532 nm. The Raman spectrometer was equipped with an optical microscope (BX41, Olympus) for focusing. The Raman shift was calibrated with a silicon wafer. All Raman spectra of the liquid samples were collected at room temperature under ambient pressure.

Charaterisation of the solid samples. Elemental analysis, based on carbon, hydrogen and nitrogen content, was carried out using an Exeter Analytical CE440 Elemental Analyser (Warwick, UK), calibrated against acetanilide, with a S-benzyl-thiouronium chloride internal standard.

RESULTS AND DISCUSSION

NaCl-enhanced xylose production from xylo-oligomers. Xylo-oligomers purchased from Sigma Aldrich were analysed to determine, the differences between the water-soluble xylo-oligomers properties and commercial xylan.[22] From the results of elemental analysis (Table S1), GPC (Table S2) and HPLC, the purity of xylo-oligomers was calculated to be 74.46 wt%, with the degree of polymerisation

ranging from 2 to 5. 10.36 wt% gluco-oligomers were also present. The effect of NaCl on the hydrothermal depolymerisation of xylo-oligomers was systematically investigated over the temperature range of 140 to 200 $^\circ$C (Figure 1 and Figure S1), utilising different holding times in the Anton Paar microwave reactor. The addition of NaCl did not cause any significant effect on the depolymerisation of xylo-oligomers at temperature below 140 $^\circ$C, with the dominant compositions after reaction being xylotetraose, xylotriose and xylobiose, (with a distribution very close to the original xylo-oligomers). When the reaction temperature was greater than 160 $^\circ$C, the generation rate of xylose with NaCl added was much higher than the corresponding value in pure H_2O. For example, at 180 $^\circ$C, the maximum rate of xylose generation in a NaCl-H_2O system was as 4.58 times that of a pure H_2O system. (Figure 1B). The yield of xylose in NaCl-H_2O increased rapidly to 90.02 wt% at 180 $^\circ$C after 10 min of treatment, compared to 19.31 wt% yield of xylose in the absence of NaCl under the same reaction conditions. Higher yield of xylose was possible reaching 90 wt% in both H_2O and NaCl-H_2O systems at higher reaction temperature or through longer reaction time, for example, 60 min for H_2O giving about 90 wt% yield of xylose compared to 10 min with NaCl-H_2O at 180 $^\circ$C. This maximum yield of xylose is equivalent to that using solid catalyst in literature.[10] The Arrhenius activation energy was calculated based on the yield of xylose, with activation energies being very similar in H_2O and NaCl-H_2O systems (Figure 1C). The pre-exponential factor A in NaCl-H_2O system (2.85×10^{16}) was higher than that in a H_2O system (1.26×10^{16}), ascribing to higher concentrations of H^+ with the addition of NaCl.[19] All kinetic traces obtained in the temperature range of 150 to 180 $^\circ$C in the presence and absence of NaCl demonstrate S-shaped forms, which could be attributed to the new catalytic species generated during the conversion. Furthermore, the strong ionic solution can be expected to couple more efficiently with microwaves.[23] NaCl reduced the required microwave output, thus decreasing the total energy consumed by 17% compared to microwave hydrolysis without salt (Figure S2).
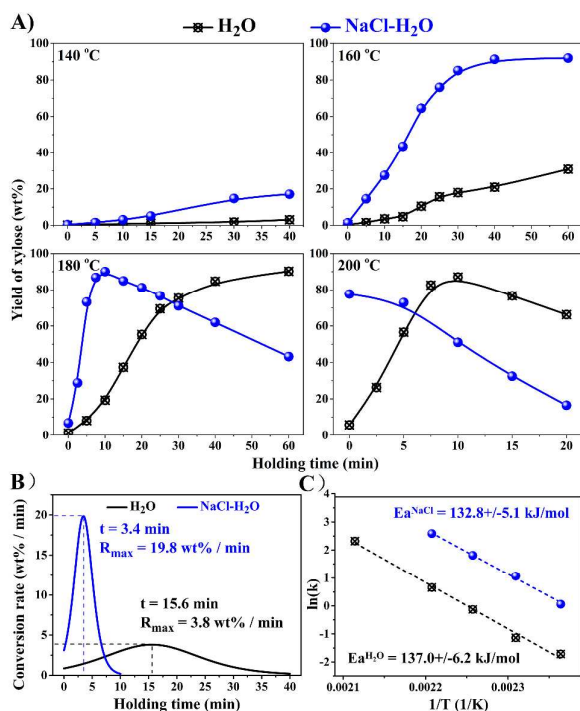
Figure 1. (A) Yield of xylose from the depolymerisation of xylo-oligomers in H_2O and NaCl-H_2O systems at different reaction temperatures; (B) Reaction rate for xylose production from depolymerisation of xylo-oligomers in H_2O and NaCl-H_2O systems at 180 $^{\circ}$C (calculated by the differential of the xylose yield trace); (C) Total activation energy based on xylose yield.

NaCl-promoted depolymerisasion and decomposition process. After the depolymerisation process, the remaining xylo-oligomers were measured by HPLC (Figure 2A). Higher reaction temperature resulted in increased selectivity to xylose, with only a very weak signal due to xylo-oligomers observed in NaCl-H_2O after 10 min at 180 $^{\circ}$C. The addition of NaCl was observed to produce a different distribution of the xylo-oligomers. For example, 28.56 wt% of xylotriose remained in H_2O system, followed by 18.06 wt% of xylobiose and 6.69 wt% of xylotetraose at 180 $^{\circ}$C for 10 min; whereas almost all xylo-oligomers were converted with an associated intensive peak for xylose after addition of NaCl under the same conditions. This is very promising for the development of a controllable depolymerisation process for xylose production with high yield and selectivity. From the results of 2D HSQC NMR analysis (Figure S3), both α and β anomeric structures could be identified for

xylo-oligomers.[24-26] The non-reducing end (X-NR), reducing end (X-R) and internal unit (X-I) peaks of xylo-oligomers were clearly observed before treatment with all signals not showing significant changes after treatment in pure H_2O. Nearly all X-I signals disappeared with the addition of NaCl, while X-R signals remained or strengthened, suggesting a high selectivity to xylose.[27]

Monosaccharides and small molecular products from further conversion of xylose were also detected at 180 ^oC (Figure 2B and Figure S4). Gluco-oligomers are easily degraded, and almost all gluco-oligomers could be converted to glucose in a NaCl-H_2O system within 20 min. This is consistent with our previous reports on NaCl-promoted conversion of glucose chains.[19] In addition to glucose, rhamnose is another monosaccharide product from xylo-oligomers, and these two hexoses gradually decomposed with longer time in NaCl-H_2O system. NaCl also accelerated the decomposition of xylose and as a result, the fast generation of furfural and acetic acid was seen. The generation rates of acetic acid and formic acid were substantially enhanced by NaCl, with a 5.07-fold and 2.24-fold increase, respectively in first 10 min of holding time. Associated with the fact that low yields of acids were obtained using pure xylose as starting material (Figure S5), acetic acid was predominantly released from the partial cleavage of the residual acetyl groups in xylo-oligomers, while the main backbone of xylose was maintained.[28-29] The decomposition of hexoses and xylose contributed to the formation of formic acid.[30-31] These acidic products mainly from leftover structures in xylo-oligomers would act as new catalysts for the autocatalytic depolymerisation of xylo-oligomers. However, higher reaction temperature (over 180 ^oC) and more acid trigger the generation of liquid products and biochars, complicating the constituents in the hydrolysate and creating a potential problem in the downstream purification of products.
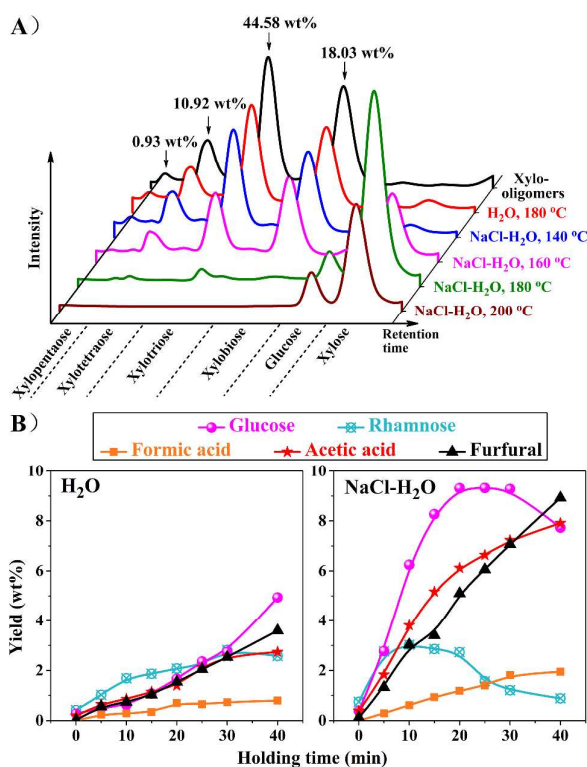
Figure 2. A) Distribution of polysaccharides and monosaccharides before and after depolymerisation of xylo-oligomers; B) Yield of small molecular products in H_2O and NaCl-H_2O systems at 180 $^{\circ}$C.

Acid effect on the autocatalytic hydrolysis. To investigate the effect of acidic products on autocatalytic hydrolysis, acetic acid (AA), one of the major carboxylic acids formed in biomass depolymerisation, was used (Figure 4 and Figure S6). It should be noted that the xylose yield no longer followed an S-shaped form when using of AA as an additive (Figure 4A, pink and blue lines). This can be ascribed to the weakened autocatalytic nature of xylo-oligomers depolymerisation due to the generated acidic products. Compared with the use of pure water, the rate of xylose generation in the early stage of reaction significantly increased when using AA-H_2O solvent, similar to that obtained in a NaCl-H_2O system. However, the yield of xylose in AA-H_2O became lower than that in NaCl-H_2O with prolonged holding time. This may be ascribed to the generated acidic products in a NaCl-H_2O system exerting a co-operative effect with NaCl on the depolymerisation process. Literature has reported that NaCl can also facilitate the ionisation of acids, decreasing their pH

values. [32-33] Thus, control experiments were carried out using two reaction solutions with the same initial pH value – a lower concentration of acetic acid in the presence of NaCl and a higher concentration of acetic acid in the absence of NaCl (Figure 4B). The yield of xylose in AA-NaCl-H_2O was higher than that of a AA-H_2O system (e.g. 47.41 wt% *vs.* 25.38wt% for 10 min), with the difference in yields increased with longer reaction holding time (28.17 wt% *vs.* 23.77 wt% of increased yields from 10 to 20 min), confirming the synergistic effect of NaCl with the gradually generated acids. The yield of xylose could be maintained at a very high level, even after 30 min of treatment at 160 ^{o}C (Figure 4A, pink line). When xylose was adopted as starting material in NaCl-H_2O system at 160 ^{o}C (Figure S5), the conversion of xylose was very low with unobvious decomposition process. This further demonstrates an efficient and controllable NaCl-H_2O reaction system for the high yield of xylose from xylo-oligomers without further decomposition.
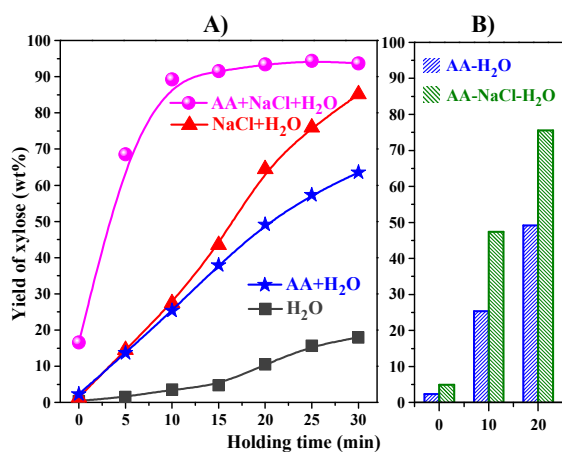
Figure 4. (A) Yield of xylose from the depolymerisation of xylo-oligomers in different systems (H_2O, 0.3 wt% AA-H_2O, NaCl-H_2O and 0.3 wt% AA-NaCl-H_2O) at 160 ^{o}C; (B) Comparison of 0.3 wt% AA-H_2O and 0.025 wt% AA-NaCl-H_2O solutions with the same initial pH value (2.58) on the yield of xylose from the depolymerisation of xylo-oligomers at 160 ^{o}C.

Deuterated agents were also used to study the acid effect for the depolymerisation process at 160 ^{o}C. The yield of xylose in H_2O was 7.76 wt% higher than that obtained

in D_2O solvent after 30 min of treatment (Figure 5A). This can be attributed to the K_w of H_2O being higher than that of D_2O (1.6×10^{-15}),[34] thereby, a higher concentration of H^+ from the ionisation of H_2O (comparing with D^+ in D_2O) benefits the catalytic depolymerisation process. The moderately higher concentration of H^+ in H_2O solvent can also promote the decomposition process to generate acidic products, whereby 1.24 wt% of carboxylic acids were obtained in H_2O within 30 min, (compared with only 0.21 wt% in D_2O). Thus, more H^+ from the generated acids in H_2O solvent is also responsible for the depolymerisation of xylo-oligomers to yield xylose. In the presence of NaCl, the difference in xylose yield from H_2O and D_2O increased, with approximately a 12 wt% difference after 20 min of reaction time (Figure 5B). This can be explained by greater amounts of xylose being produced in H_2O (as compared to D_2O) leading to the formation of greater numbers of H^+ ions, especially in the presence of NaCl. Nearly 10 times the acid yield could be achieved in a NaCl-H_2O, than a NaCl-D_2O system, with the further acceleration of the depolymerisation process to xylose. However, the addition of acid made yields of xylose in H_2O and D_2O close to each other, whether using acetic acid or deuterated acetic acid (DAA) (Figure 5C).

As the amount of added acetic acid we used is 30 times greater than that of the in-situ generated acetic acid, high concentrations of H^+ and D^+ in AA-H_2O and DAA-D_2O systems are sufficient for the depolymerisation of xylo-oligomers, with a resulting similar yield of xylose. Although the different yields of xylose were obtained using NaCl-H_2O and in NaCl-D_2O solvents (Figure 5B), the yield of xylose in AA-NaCl-H_2O and DAA-NaCl-D_2O was approximately the same (Figure 5D). It further demonstrated the critical role of acidic catalyst, with acid generation from xylose decomposition being the rate-limiting step for the autocatalytic depolymerisation process.
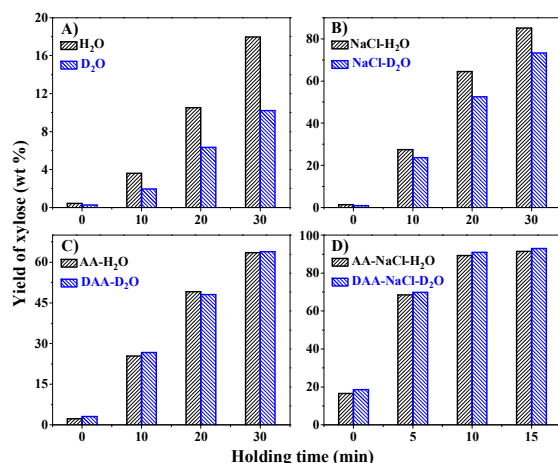
Figure 5. Comparison of xylose yield from the depolymerisation of xylo-oligomers in traditional and deuterated systems at 160 ^{o}C (the concentrations of AA and DAA are 0.3 wt%).

NaCl-promoted cleavage of the interactions between xylo-oligomers. As well as in cellulose, some hydrogen bonds also exist in xylo-oligomers.[35] The Electrospray Ionization−Mass Spectroscopy (ESI-MS) of an aqueous solution of xylo-oligomers in the absence or presence of NaCl were studied (Figure 6). Xylobiose and xylotriose were found to be the dominant positive ion peaks at *m/z* of 305 and 437, followed by xylotetraose and xylose, being in accordance with the results from HPLC. Besides, the xylo-oligomers complexes connecting by hydrogen bonds, instead of by glycosidic bonds after dehydration was observed. For example, xylobiose···xylobiose, xylobiose···xylotriose, xylotriose···xylotriose and xylotriose···xylotetraose were presented at *m/z* of 587, 719, 851 and 983. These four peaks decreased and even disappeared after the addition of NaCl. On the contrary, at the same time the peaks for separated xylo-oligomers showed a significant increase. In the negative-ion spectra of ESI-MS (Figure S7), signals of xylo-oligomers combining with Cl$^-$ were also strengthened with the use of NaCl. It was shown that Cl$^-$ can break the original hydrogen bonding in xylo-oligomers by generating new hydrogen bonds with the hydroxyl groups of xylo-oligomers, dismantling the xylo-oligomers complex and exposing more active centres. The effect of Cl$^-$ is similar to that of the cleavage of hydrogen bonding in cellulose.[36-37] The signals at m/z of 479 and 611 were ascribed to

the dehydration between cellobiosan and xylose/xylobiose, revealing the connection of the residual cellulosic groups with xylo-oligomers.

Raman spectra of the xylo-oligomers samples before and after reactions in H_2O and NaCl-H_2O provided information on the structural variations of xylo-oligomers and xylose (Figure 7). The attribution of each peak is summarised in Table S3 according to the literature.[6, 38] The 485 cm^{-1} glycosidic ν(COC) of the oligomers decreased after treatment, especially in NaCl-H_2O solution. The declined strength of signals at 898, 987, 1376 and 1466 cm^{-1} also demonstrated the lower concentration of xylo-oligomers in NaCl-H_2O solution. It is worthy to note that the peak at 1246 cm^{-1}, attributed to a C-O stretch, δ(CH) and / or δ(COH) in xylo-oligomers,[39-40] showed a significant shift after treatment in a NaCl-H_2O system. This could be attributed to the breaking of the hydrogen bonding in xylo-oligomers and the formation of new interactions between xylo-oligomers and Cl$^-$. These altered interactions might also lead to the shift of peaks at 420 and 898 cm^{-1}, which involve the oxygen-based chemical bonds in xylo-oligomers.

According to these analyses, NaCl contributes to not only the decomposition of the residual groups on xylo-oligomers to new catalysts (acids), but also the cleavage of the hydrogen bonding of xylo-oligomers, leading to substantial depolymerisation (Scheme 1).As the structures of xylo-oligomers and real hemicellulose are similar except the different degree of polymerisation, this study also gave a possibility for the depolymerisation starting with real hemicellulose.
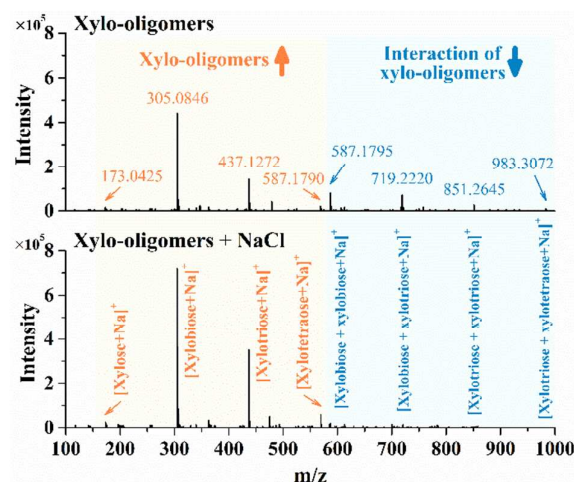
Figure 6. ESI-MS spectra (positive) of xylo-oligomers samples in the absence/presence of NaCl in water at room temperature.
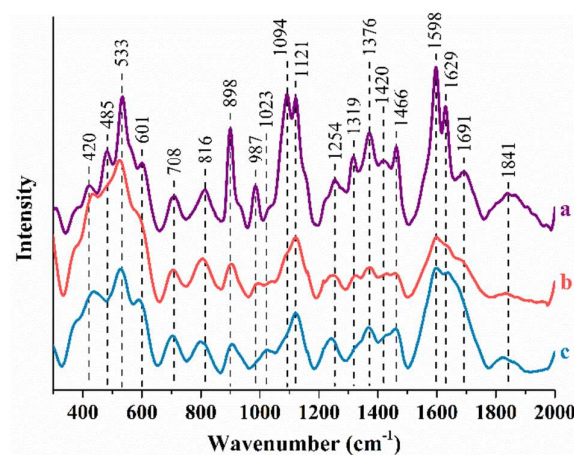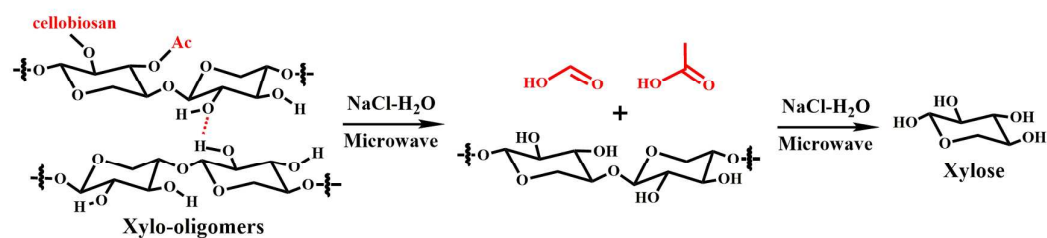

Figure 7. Raman spectra of the xylo-oligomers samples before and after reaction. a) xylo-oligomers in H_2O; b) xylo-oligomers in H_2O at 160 ^oC for 15 min; c) xylo-oligomers in NaCl-H_2O at 160 ^oC for 15 min.

Scheme 1. Promoting effect of NaCl on depolymerisation of xylo-oligomers to xylose.

Application of seawater as reaction solvent for xylose production. A comparison of the effects of different alkali halide salts at the same molar concentration for the depolymerisation of xylo-oligomers was also carried out (Figure 8A). LiCl, NaCl and KCl showed similar positive effects on the rate of xylose production, and the yield of xylose dramatically increased even at low salt concentration. At 1 mol/L+ of alkali chlorides, the yield of xylose reached its maximum. When comparing different sodium halides, NaCl exhibited the greatest positive effect on the yield of xylose. Only 48.75 wt% xylose could be obtained using

NaI, and NaBr had little effect on xylose production. This data demonstrates that it is indeed Cl^{-} rather than Na^{+} that plays the main role in the rate enhancement due to the disruption of the hydrogen bonding network of xylo-oligomers and in depolymerisation of xylo-oligomers.

Several articles dealing with the use of seawater in biomass conversion have been recently reported, where the concentration of total salts is as high as 30 g/L with approximately 0.5 mol/L of Cl^{-} ion in seawater.[41-43] Encouraged by this research, we used seawater for the depolymerisation of xylo-oligomers to xylose. The effect of seawater on xylose yield is presented in Figure 8B, where significant seawater-promotion effects were exerted at the data points on the right side. The effects of seawater were insignificant at 160 ^{o}C, but amplified at higher reaction temperatures. For example, after treatment at 180 ^{o}C for 10 min, 19.26 wt% xylose was obtained in distilled water compared with 34.45 wt% yield in seawater. The use of seawater to increase the rate of xylose production is slightly less beneficial than that of direct NaCl use, which might be due to the lower concentration of Cl^{-} in seawater.
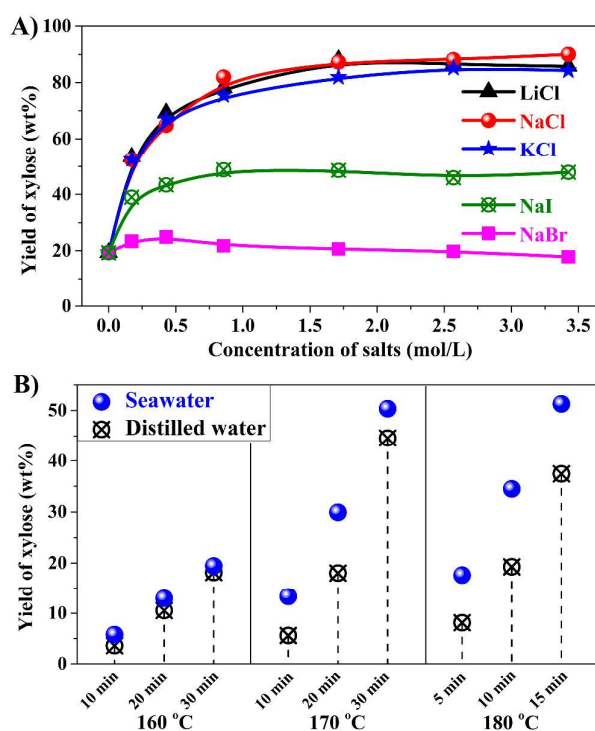

Figure 8. (A) Effect of different salts on the depolymerisation of xylo-oligomers to

xylose at 180 ^{o}C for 10 min; (B) Comparison of seawater and pure water on the yield of xylose from xylo-oligomers.

CONCLUSION

Greater than 90 wt% xylose could be obtained from xylo-oligomers using NaCl and with shorter microwave heating time. Almost all xylo-oligomers were degraded to xylose without significant further decomposition, resulting in high selectivity to xylose in the liquid hydrolysate. NaCl also enhances the formation of acidic products, especially acetic acid from residual acetyl groups, which is the rate-limiting step for xylose generation as indicated from isotopic experiments, and the generated H$^+$ further catalysed the depolymerisation process. NaCl breaks the hydrogen bonding between xylo-oligomers, leading to Raman shift of the signals involving oxygen-based chemical bonds in xylo-oligomers. The cleavage separates the unique xylo-oligomers chain, and xylo-oligomers are more easily attacked by H$^+$. NaCl addition reduces the required microwave output to only 17% as compared to conventional microwave hydrolysis when using pure water. Seawater with natural chloride was also successfully adopted as an alternative reaction medium to degrade xylo-oligomers. Thus, an abundant natural solvent can be used to enhance the conversion of a renewable material with benefits to the energy and chemical industries.

ASSOCIATED CONTENT

Supporting Information

Depolymerisation of xylo-oligomers to xylose at 150 and 170 ^{o}C, energy comparison in H$_2$O and NaCl-H$_2$O systems, yield of the other liquid products, xylose conversion in different systems, ESI-MS spectra and elemental analysis of xylo-oligomers, Raman assignments.

AUTHOR INFORMATION

Corresponding Author

*alice.fan@york.ac.uk

*changweihu@scu.edu.cn

Notes

The authors declare no competing financial interest.

REFERENCES

1.   Jiang, Z.; Zhang, H.; He, T.; Lv, X.; Yi, J.; Li, J.; Hu, C. Understanding the cleavage of inter- and intramolecular linkages in corncob residue for utilization of lignin to produce monophenols. *Green Chem.* **2016,** *18*, 4109-4115. DOI: 10.1039/C6GC00798H

2.   Kacurakova, M.; Wellner, N.; Ebringerova, A.; Hromadkova, Z.; Wilson, R. H.; Belton, P. S. Characterisation of xylan-type polysaccharides and associated cell wall components by FT-IR and FT-Raman spectroscopies. *Food Hydrocolloids* **1999,** *13*, 35-41. DOI: 10.1016/S0268-005X(98)00067-8

3.   Chaikumpollert, O. Structural elucidation of hemicelluloses from vetiver grass. *Carbohydr. Polym.* **2004,** *57*, 191-196. DOI: 10.1016/j.carbpol.2004.04.011

4.   Nie, X.; Liu, J.; She, D.; Sun, R.; Xu, F. Physicochemical and structural characterization of hemicelluloses isolated by different alcohols from rice straw. *Bioresources* **2013,** *8*, 3817-3832. DOI: 10.15376/biores.8.3.3817-3832

5.   Peng, P.; Peng, F.; Bian, J.; Xu, F.; Sun, R.; Kennedy, J. F. Isolation and structural characterization of hemicelluloses from the bamboo species phyllostachys incarnata wen. *Carbohydr. Polym.* **2011,** *86*, 883-890. DOI: 10.1016/j.carbpol.2011.05.038

6.   Zeng, Y.; Yarbrough, J. M.; Mittal, A.; Tucker, M. P.; Vinzant, T. B.; Decker, S. R.; Himmel, M. E. In situ label-free imaging of hemicellulose in plant cell walls using stimulated Raman scattering microscopy. *Biotechnol. Biofuels* **2016,** *9*, 256-271. DOI: 10.1186/s13068-016-0669-9

7.   Dietrich, K.; Hernandez-Mejia, C.; Verschuren, P.; Rothenberg, G.; Shiju, N. R. One-pot selective conversion of hemicellulose to xylitol. *Org. Process Res. Dev.* **2017,** *21*, 165-170. DOI: 10.1021/acs.oprd.6b00169

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

8. Binder, J. B.; Raines, R. T. Fermentable sugars by chemical hydrolysis of biomass. *Proc. Natl. Acad. Sci.* **2010,** *107*, 4516-4521. DOI: 10.1073/pnas.0912073107

9. Chung, P.; Charmot, A.; Olatunji-Ojo, O. A.; Durkin, K. A.; Katz, A. Hydrolysis catalysis of miscanthus xylan to xylose using weak-acid surface sites. *ACS Catal.* **2013,** *4*, 302-310. DOI: 10.1021/cs400939p

10. Carà, P. D.; Pagliaro, M.; Elmekawy, A.; Brown, D. R.; Verschuren, P.; Shiju, N. R.; Rothenberg, G. Hemicellulose hydrolysis catalysed by solid acids. *Catal. Sci. Technol.* **2013,** *3*, 2057-2061. DOI: 10.1039/C3CY20838A

11. Hosseini, S. A.; Lambert, R.; Kucherenko, S.; Shah, N. Multiscale modeling of hydrothermal pretreatment: From hemicellulose hydrolysis to biomass size optimization. *Energy Fuels* **2010,** *24*, 4673-4680. DOI: 10.1021/ef9012246

12. Gómez Bernal, H.; Bernazzani, L.; Raspolli Galletti, A. M. Furfural from corn stover hemicelluloses. A mineral acid-free approach. *Green Chem.* **2014,** *16*, 3734-3740. DOI: 10.1039/C4GC00450G

13. Morais, A. R. C.; Matuchaki, M. D. D. J.; Andreaus, J.; Bogel-Lukasik, R. A green and efficient approach to selective conversion of xylose and biomass hemicellulose into furfural in aqueous media using high-pressure CO_2 as a sustainable catalyst. *Green Chem.* **2016,** *18*, 2985-2994. DOI: 10.1039/c6gc00043f

14. He, T.; Jiang, Z.; Wu, P.; Yi, J.; Li, J.; Hu, C. Fractionation for further conversion: From raw corn stover to lactic acid. *Sci. Rep.* **2016,** *6*, 38623-38633. DOI: 10.1038/srep38623

15. Rong, C.; Ding, X.; Zhu, Y.; Li, Y.; Wang, L.; Qu, Y.; Ma, X.; Wang, Z. Production of furfural from xylose at atmospheric pressure by dilute sulfuric acid and inorganic salts. *Carbohydr. Res.* **2012,** *350*, 77-80. DOI: 10.1016/j.carres.2011.11.023

16. Hongsiri, W.; Danon, B.; de Jong, W. The effects of combined catalysis of oxalic acid and seawater on the kinetics of xylose and arabinose dehydration to furfural. *Int. J.Energy Environ. Eng.* **2014,** *6*, 21-30. DOI: 10.1007/s40095-014-0146-9

17. Le Guenic, S.; Gergela, D.; Ceballos, C.; Delbecq, F.; Len, C. Furfural production from D-xylose and xylan by using stable nafion NR50 and NaCl in a microwave-assisted biphasic reaction. *Molecules* **2016,** *21*, 1102-1112. DOI: 10.3390/molecules21081102

18. Zhang, T.; Kumar, R.; Tsai, Y.; Elander, R. T.; Wyman, C. E. Xylose yields and relationship to combined severity for dilute acid post-hydrolysis of xylooligomers from hydrothermal pretreatment of corn stover. *Green Chem*. **2015,** *17*, 394-403. DOI: 10.1039/c4gc01283f

19. Jiang, Z.; Yi, J.; Li, J.; He, T.; Hu, C. Promoting effect of sodium chloride on the solubilization and depolymerization of cellulose from raw biomass materials in water. *ChemSusChem* **2015,** *8*, 1901-1907. DOI: 10.1002/cssc.201500158

20. Li, K.; Xia, L.; Li, J.; Pang, J.; Cao, G.; Xi, Z. Salt-assisted acid hydrolysis of starch to D-glucose under microwave irradiation. *Carbohydr. Res.* **2001,** *331*, 9-12. DOI: 10.1016/S0008-6215(00)00311-6

21. Tsubaki, S.; Oono, K.; Onda, A.; Yanagisawa, K.; Azuma, J. Microwave-assisted hydrothermal hydrolysis of cellobiose and effects of additions of halide salts. *Bioresour. Technol.* **2012,** *123*, 703-706. DOI: 10.1016/j.biortech.2012.07.086

22. Li, T.; Remón, J.; Shuttleworth, P. S.; Jiang, Z.; Fan, J.; Clark, J. H.; Budarin, V. L. Controllable production of liquid and solid biofuels by doping-free, microwave-assisted, pressurised pyrolysis of hemicellulose. *Energy Convers. Manage.* **2017,** *144*, 104-113. DOI: 10.1016/j.enconman.2017.04.055

23. Xiouras, C.; Radacsi, N.; Sturm, G.; Stefanidis, G. D. Furfural synthesis from D-xylose in the presence of sodium chloride: Microwave versus conventional heating. *ChemSusChem* **2016,** *9*,

2159-2166. DOI: 10.1002/cssc.201600446

24.   Obel, N.; Erben, V.; Schwarz, T.; Kuhnel, S.; Fodor, A.; Pauly, M. Microanalysis of plant cell wall polysaccharides. *Mol. Plant* **2009,** *2*, 922-932. DOI: 10.1093/mp/ssp046

25.   Chylla, R. A.; Van Acker, R.; Kim, H.; Azapira, A.; Mukerjee, P.; Markley, J. L.; Storme, V.; Boerjan, W.; Ralph, J. Plant cell wall profiling by fast maximum likelihood reconstruction (FMLR) and region-of-interest (ROI) segmentation of solution-state 2D ^{1}H-^{13}C NMR spectra. *Biotechnol. Biofuels* **2013,** *6*, 45-58. DOI: 10.1186/1754-6834-6-45

26.   Zhao, X.; Tong, T.; Li, H.; Lu, H.; Ren, J.; Zhang, A.; Deng, X.; Chen, X.; Wu, A. M. Characterization of hemicelluloses from neolamarckia cadamba (rubiaceae) during xylogenesis. *Carbohydr. Polym.* **2017,** *156*, 333-339. DOI: 10.1016/j.carbpol.2016.09.041

27.   Kim, H.; Ralph, J. A gel-state 2D-NMR method for plant cell wall profiling and analysis: A model study with the amorphous cellulose and xylan from ball-milled cotton linters. *RSC Adv.* **2014,** *4*, 7549-7560. DOI: 10.1039/c3ra46338a

28.   Nabarlatz, D.; Ebringerová, A.; Montané, D. Autohydrolysis of agricultural by-products for the production of xylo-oligosaccharides. *Carbohydr. Polym.* **2007,** *69*, 20-28. DOI: 10.1016/j.carbpol.2006.08.020

29.   Hilpmann, G.; Becher, N.; Pahner, F. A.; Kusema, B.; Mäki-Arvela, P.; Lange, R.; Murzin, D. Y.; Salmi, T. Acid hydrolysis of xylan. *Catal. Today* **2016,** *259*, 376-380. DOI: 10.1016/j.cattod.2015.04.044

30.   Fu, X.; Dai, J.; Guo, X.; Tang, J.; Zhu, L.; Hu, C. Suppression of oligomer formation in glucose dehydration by CO_2 and tetrahydrofuran. *Green Chem.* **2017,** *19*, 3334-3343. DOI: 10.1039/C7GC01115F

31.   Ahmad, T.; Kenne, L.; Olsson, K.; Theander, O. The formation of 2-furaldehyde and formic acid from pentoses in slightly acidic D_2O studied by nmr spectroscopy. *Carbohydr. Res.* **1995,** *276* 309-320. DOI: 10.1016/0008-6215(95)00176-T

32.   Yu, Y.; Mohd Shafie, Z.; Wu, H. Effect of alkali and alkaline earth metal chlorides on cellobiose decomposition in hot-compressed water. *Ind. Eng. Chem. Res.* **2015,** *54*, 5450-5459. DOI: 10.1021/acs.iecr.5b01007

33.   Akiya, N.; Savage, P. E. Roles of water for chemical reactions in high-temperature water. *Chem. Rev.* **2002,** *102*, 2725–2750. DOI: 10.1002/chin.200243293

34.   Covington, A. K.; Robinson, R. A.; Bates, R. G. The ionization constant of deuterium oxide from 5 to 50[o]. *J. Phys. Chem.* **1966,** *72*, 3820-3824. DOI: 10.1021/j100884a011

35.   Sedlmeyer, F. B. Xylan as by-product of biorefineries: Characteristics and potential use for food applications. *Food Hydrocolloids* **2011,** *25*, 1891-1898. DOI: 10.1016/j.foodhyd.2011.04.005

36.   Rabideau, B. D.; Ismail, A. E. Mechanisms of hydrogen bond formation between ionic liquids and cellulose and the influence of water content. *Phys. Chem. Chem. Phys.* **2015,** *17*, 5767-5775. DOI: 10.1039/C4CP04060K

37.   Pinkert, A.; Marsh, K. N.; Pang, S.; Staiger, M. P. Ionic liquids and their interaction with cellulose. *Chem. Rev.* **2009,** *109*, 6712-6728. DOI: 10.1002/chin.201017232

38.   Shen, Q.; Rahiala, H.; Rosenholm, J. B. Raman evaluation of the structure and acid-base properties of bulk wood by FT-Raman spectroscopy. *J. Colloid Interface Sci.* **1998,** *206*, 558-568. DOI: 10.1006/jcis.1998.5960

39.   Agarwal, U. P.; Ralph, S. A. Ft-raman spectroscopy of wood: Identifying contributions of lignin and carbohydrate polymers in the spectrum of black spruce (picea mariana). *Appl. Spectrosc.* **1997,** *51*, 1648-1655. DOI: 10.1366/0003702971939316

40. Wetzel, D. L.; Eilert, A. J.; Pietrzak, L. N.; Miller, S. S.; Sweat, J. A. Ultraspatially-resolved synchrotron infrared microspectroscopy of plant tissue in situ. *Cell. Mol. Biol.* **1998,** *44*, 145-168.

41. Grande, P. M.; de Maria, P. D. Enzymatic hydrolysis of microcrystalline cellulose in concentrated seawater. *Bioresour. Technol.* **2012,** *104*, 799-802. DOI: 10.1016/j.biortech.2011.10.071

42. Lin, C. S. K.; Luque, R.; Clark, J. H.; Webb, C.; Du, C. A seawater-based biorefining strategy for fermentative production and chemical transformations of succinic acid. *Energy Environ. Sci.* **2011,** *4*, 1471-1479. DOI: 10.1002/bbb.328

43. Grande, P. M.; Bergs, C.; Dominguez de Maria, P. Chemo-enzymatic conversion of glucose into 5-hydroxymethylfurfural in seawater. *ChemSusChem* **2012,** *5*, 1203-1206. DOI: 10.1002/cssc.201200065

For Table of Contents Use Only
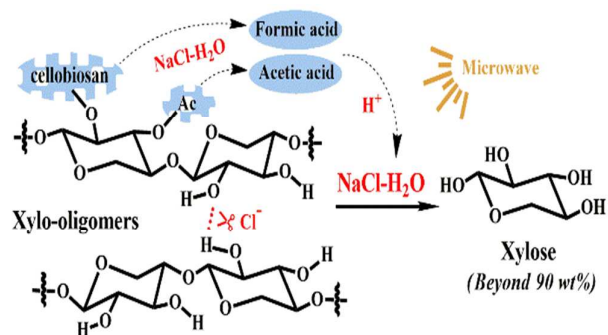
NaCl promotes the depolymerisation of xylo-oligomers to xylose (beyond 90 wt% yield) by enhancing the generation of acidic products from the residual structures and breaking the hydrogen bonding between xylo-oligomers.