

## Mechanocatalytic depolymerization of hemicellulose to low molecular weight oligosaccharides over Aquivion ionomer

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### 1. Chemicals

Pulp-HEM and Pine-HEM were kindly synthesized and provided by FCBA. Ethanol 96%, diethyl ether, KCl, NaOH, HCl 37%, H<sub>2</sub>SO<sub>4</sub> 96%, D<sub>2</sub>O and DMSO-*d*<sub>6</sub> were purchased to Sigma-Aldrich-Merck and were used without further purification. Aquivion PW98 (0.96 mmol SO<sub>3</sub>H/g) was kindly provided by Solvay. Standards of xylose, xylobiose, xylotriose, xylotetraose and xylopentaose were acquired from Carbosynth to calibrate the SEC-HPLC.

### 2. Analysis

#### 2.1. Analysis of wetness content on hemicellulose by thermogravimetric analysis

The water content of hemicellulose was determined by thermogravimetric analyses using a TGA analyzer (PerkinElmer TGA 4000). The analyses were done from 40 °C to 500 °C with a ramp of 10 °C/min under a flow of air (60 mL/min). The water content was calculated from TGA as the sum of mass losses from room temperature to 120°C.

#### 2.2. High Performance Liquid Size-Exclusion Chromatography (HPLC-SEC)

The solubilized fractions of Pine/Pulp-HEM were analyzed by size-exclusion chromatography in a Prominence UFLC system (Shimadzu) equipped with a refractive index detector (RID-10A Shimadzu), a guard column KS-G 6B (Shodex) and a KS-802 column (8.0 mm d.i. × 300 mm, Shodex) maintained at 40°C in an oven (Shimadzu CTO-40C). Analyses were performed using ultrapure water as an eluent at a flow rate of 0.8 mL/min. The volume of the injected sample was 20 µL. The calibration of the SEC HPLC was done with commercially available standards of xylose, xylobiose, xylotriose, xylotetraose and xylopentaose. A representative SEC profile is provided below (Fig. S5). These SEC profiles were deconvoluted using Origin 21 software. This analytical procedure allowed us to determine the yields in oligosaccharides for each DP range. Yields were calculated as follow: (mass of oligosaccharides/initial mass of hemicellulose) x 100.

#### 2.3 <sup>1</sup>H Nuclear Magnetic Resonance analysis (<sup>1</sup>H NMR)

25-100 mg of XOS was put on a 2 mL vial flask and dissolved with 0.7-1.0 mL of deuterated solvents (D<sub>2</sub>O or DMSO-*d*<sub>6</sub>). The solution was stirred and then filtered over a 0.2 µm PTFE membrane. The filtered solution was introduced in the NMR tube and analyzed on a Bruker Avance NEO ® 500 MHz NMR.

#### 2.4. Determination of the proton exchange capacity of Aquivion PW98

100 mg of (used or fresh) Aquivion PW98 was suspended in 10 mL of a solution of KCl at 0.1 N. The mixture was then stirred at 400 rpm for 2 h. Next, the Aquivion PW98 was removed by filtration and the solution was titrated with a solution of NaOH at 0.1 M to determine the amount of exchanged protons.

### 3. Experimental procedure

#### 3.1. Mechanocatalytic depolymerization

➤ Reactions with H<sub>2</sub>SO<sub>4</sub>: 1.5 g of Pine-HEM were suspended in 100 mL of diethylether. The desired amount (2-10 wt% relative to Pine-HEM) of H<sub>2</sub>SO<sub>4</sub> 96 wt% was added to the suspension and then diethylether was removed under vacuum in a rotary evaporator. The acid-impregnated Pine-HEM was introduced into a 125 mL ZrO<sub>2</sub> grinding jar together with twenty φ 12 mm ZrO<sub>2</sub> balls. The ball-milling of acidulated Pine-HEM was performed at 400 rpm in a planetary ball mill (Retsch PM 100), for the desired time. A sequence five minutes of milling and five minutes of pause was selected to avoid overheating. The reaction time provided in the article text corresponds to the time of ball-milling (*i.e.* pauses were not counted into the reaction time). At the end of the ball-milling time, the powder was recovered and analyzed by SEC-HPLC (see section below)

➤ Reactions with Aquivion PW98: Pine/Pulp-HEM (1.5g) and the desired amount of Aquivion PW98 were directly added into the a 125 mL ZrO<sub>2</sub> grinding jar together with twenty φ 12 mm ZrO<sub>2</sub> balls. The mix-milling of Pine/Pulp-HEM with Aquivion PW98 was performed at 400 rpm in a planetary ball mill (Retsch PM 100), for the desired time. As described above, a sequence five minutes of ball-milling and five minutes of pause was selected to avoid overheating.

#### 3.2. Solubility tests

➤ Case of Pine-HEM: after the mechanocatalytic process, the powder was stirred (600 rpm) at 25°C in 10 mL of an ethanol/mixture (9:1). The suspension was then filtered off and the solid residue was dried overnight in an oven at 60°C. The solubility was determined as the difference between the mass of Pine-HEM initially introduced into the planetary ball-mill and the mass of the recovered residue after extraction with the ethanol/mixture (9:1).

➤ Case of Pulp-HEM: a similar procedure as above was employed except that in this case water was directly used as an extraction solvent.

Note: in all cases, the mass of Aquivion PW98 was of course deduced

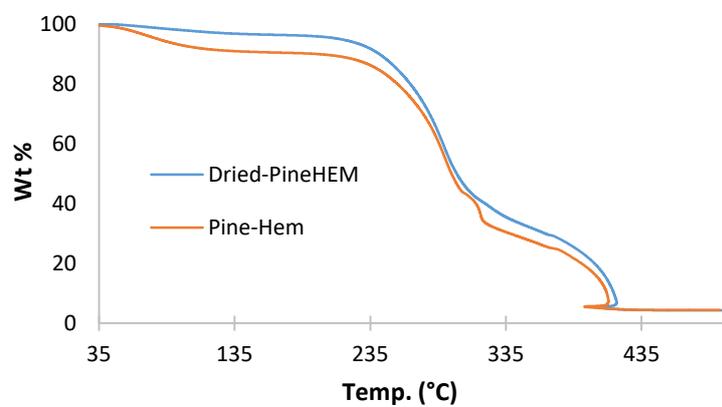
#### 3.3 Washing of Pulp-HEM with HCl 0.12 M

Pulp-HEM (2g) was introduced in a glass frit and washed with 50 mL of a solution of HCl at 0.12 M. Then, Pulp-HEM was thoroughly washed with water until neutral pH. Next, the recovered Pulp-HEM was lyophilized for 72 h

#### 3.4. Catalytic reductive amination

XOS (1.1255 g) was mixed with 3 mL of *n*-butylamine (50 eq.) in a high pressure reactor (Multiple reactor system Series 500, Paar Instruments). The mixture was stirred for 5 min at 25°C (*i.e.* to initiate the formation of the imine). Then 5% Pt/C (10 wt% relative to the mass of XOS) was added and the reactor was pressurized with 50 bar of hydrogen. The resulting mixture was heated at 50°C for 24 h. After this period of time, the reactor was cooled down to room temperature and the solution was filtrated on a filter paper to remove the solid Pt/C catalyst. The excess of *n*-butylamine was removed under vacuum in rotary evaporator and the as-obtained solid was thoroughly washed with ethanol to remove potential traces of *n*-butylamine. The solid was separated by centrifugation at 8000 rpm by 20 min and then re-dissolved in water, passed through a plug of celite in order to remove possible trace of insoluble matter and then lyophilized affording a white-yellowish powder.

From *n*-dodecylamine: In a high-pressure reactor, XOS (0.7206 g) were mixed with 1.0035 g of *n*-dodecylamine (3.7 eq.) for 15 h and 15 mL of 2-propanol was added to homogeneously dissolve both reactants. After stirring for 5 min at 25°C, the Pt/C (10 wt%) catalyst was added and the reactor was pressurized with 50 bar of H<sub>2</sub> and heated at 50°C for 48 h. After this period of time, the reactor was cooled down, the solution was diluted with 50 mL of boiling methanol and then filtered over celite to remove the Pt/C catalyst. After filtration, the solution was further diluted with 50 mL of dichloromethane and 50 ml of water was added yielding a biphasic system. The aqueous phase, containing most of the aminated XOS, was recovered and water (+ methanol) were removed under vacuum in a rotary evaporator. The as-obtained solid was lyophilized and then thoroughly washed with dichloromethane and methanol to remove traces of *n*-dodecylamine. At the end of this protocol, a white solid was recovered.



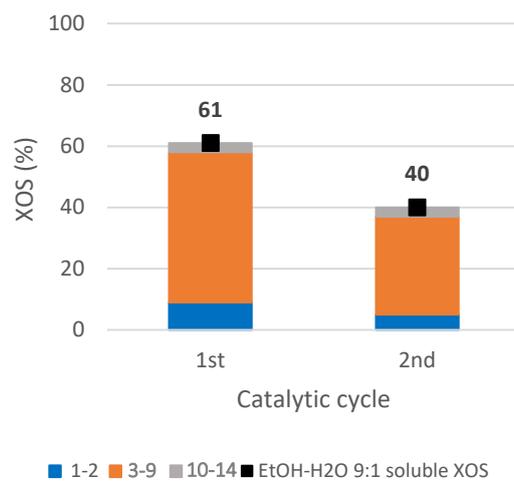
**Figure S1** Thermogravimetric analyses (TGA) of the Pine-HEM sample under air flow.



**Figure S2** Picture of oligosaccharides recovered after the mechanocatalytic depolymerization of Pine-HEM **A.** impregnated with 6.6 wt% of  $\text{H}_2\text{SO}_4$ , **B.** impregnated with 10 wt% of  $\text{H}_2\text{SO}_4$ , **C.** mixed with Aquivion PW98.

**Table S1** Proton exchange capacity of fresh and spent Aquivion PW98 (ball-milling time: 12 h, Pine-HEM (1.5 g), 1.5 g Aquivion PW98, 400 rpm).

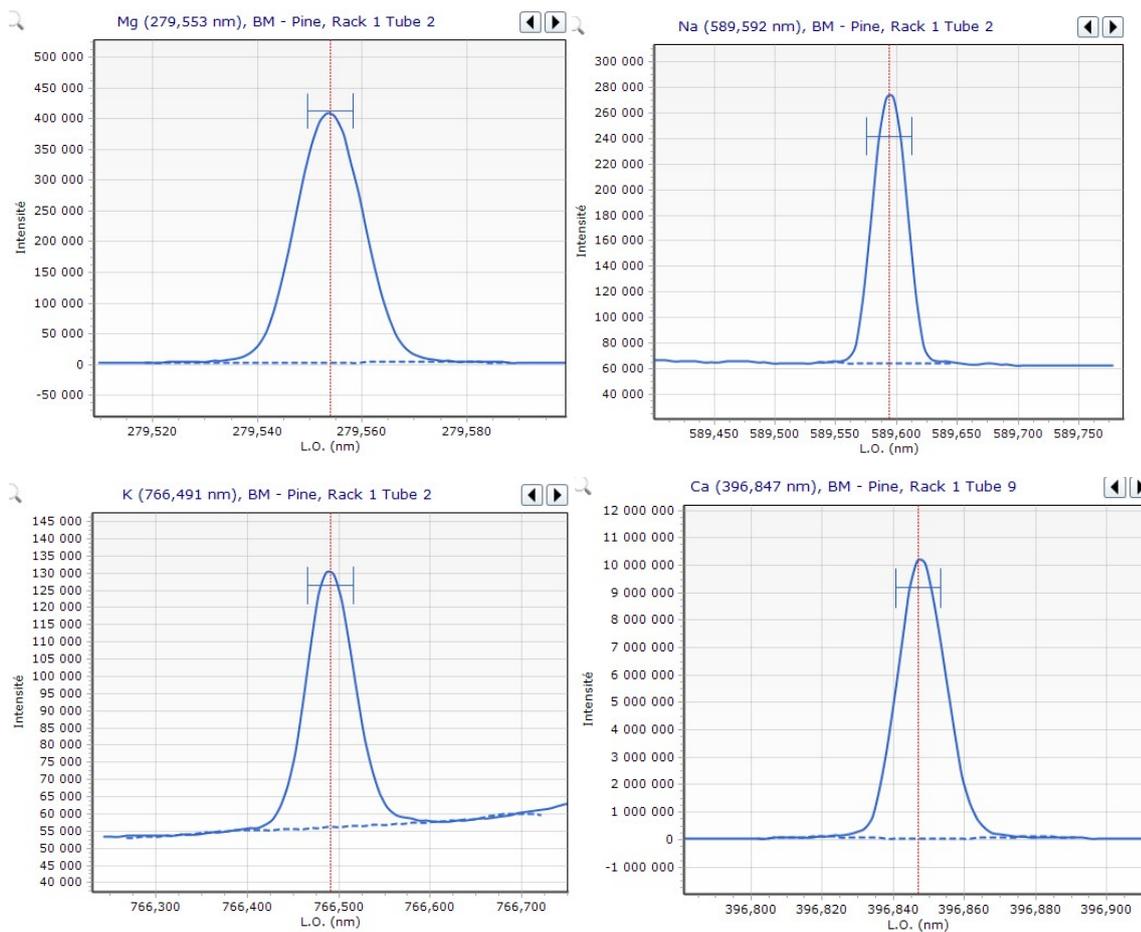
	<b>Fresh</b>	<b>After 1<sup>st</sup> cycle</b>	<b>After 2<sup>nd</sup> cycle</b>
<b>H<sup>+</sup> Sites (mmol/g)</b>	0,96	0,40	0,09



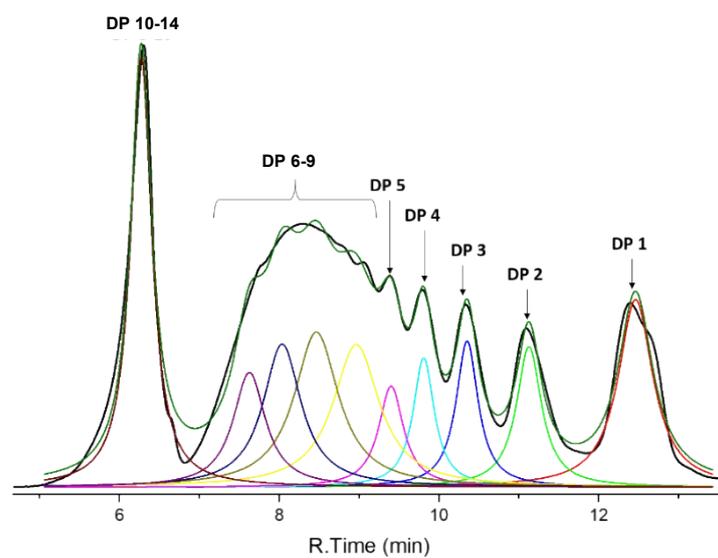
**Figure S3.** Recycling of Aquivion PW 98 using pine-HEM (Ball-miling time: 12 h, Pine-HEM (1.5 g), 1.5 g Aquivion PW98, 400 rpm).

**Table S2** ICP analysis of the total amount of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$  on Pine-HEM.

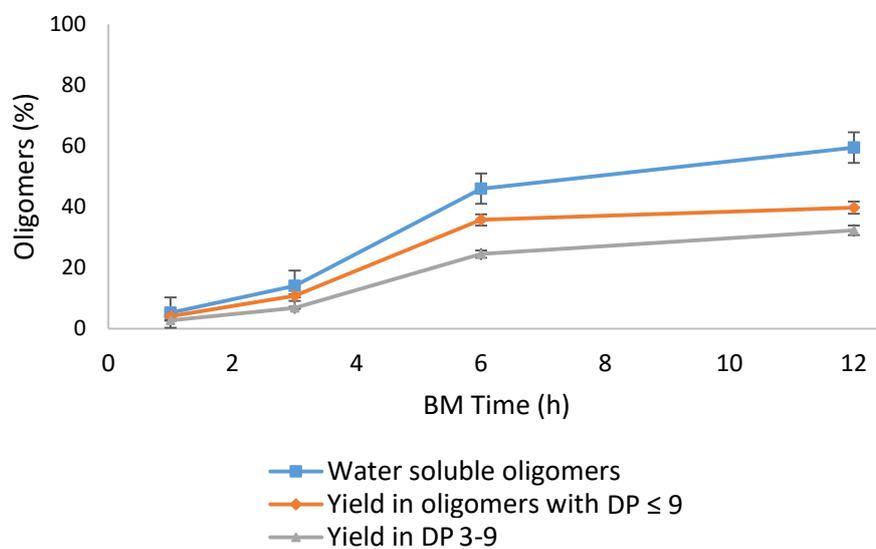
<b>Element</b>	<b>mg/kg</b>
<b><math>\text{Ca}^{2+}</math></b>	8419
<b><math>\text{Mg}^{2+}</math></b>	705
<b><math>\text{K}^+</math></b>	2065
<b><math>\text{Na}^+</math></b>	126



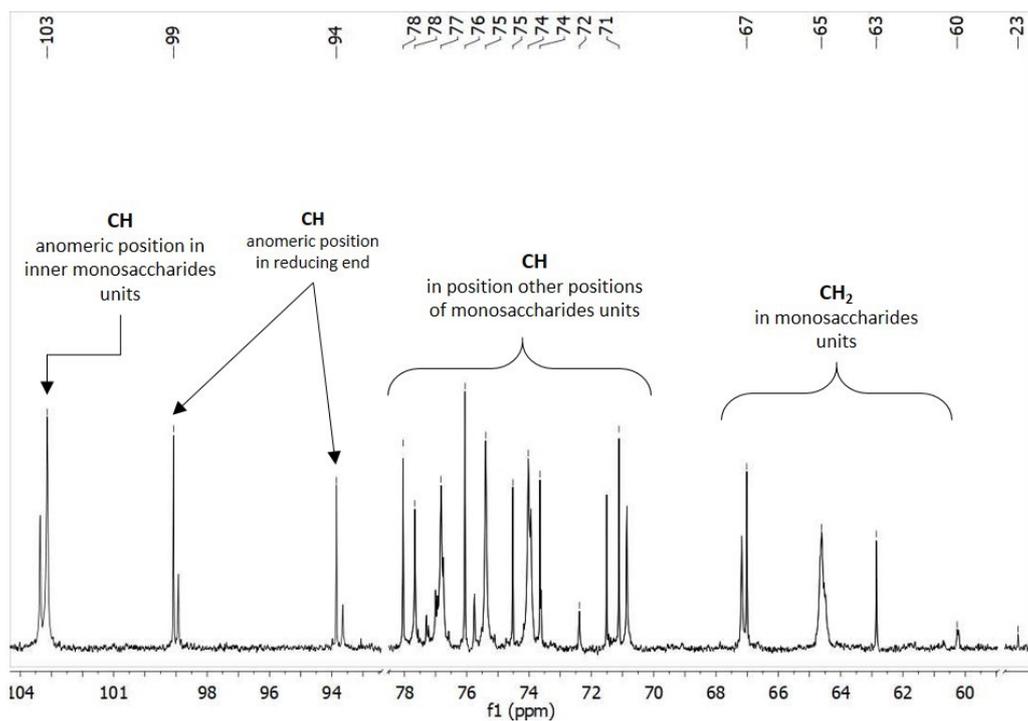
**Figure S4.** Qualitative detection by ICP of residual amounts of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$  and  $K^+$  present on Aquivion PW98 after the mechanocatalytic depolymerization of Pine-HEM



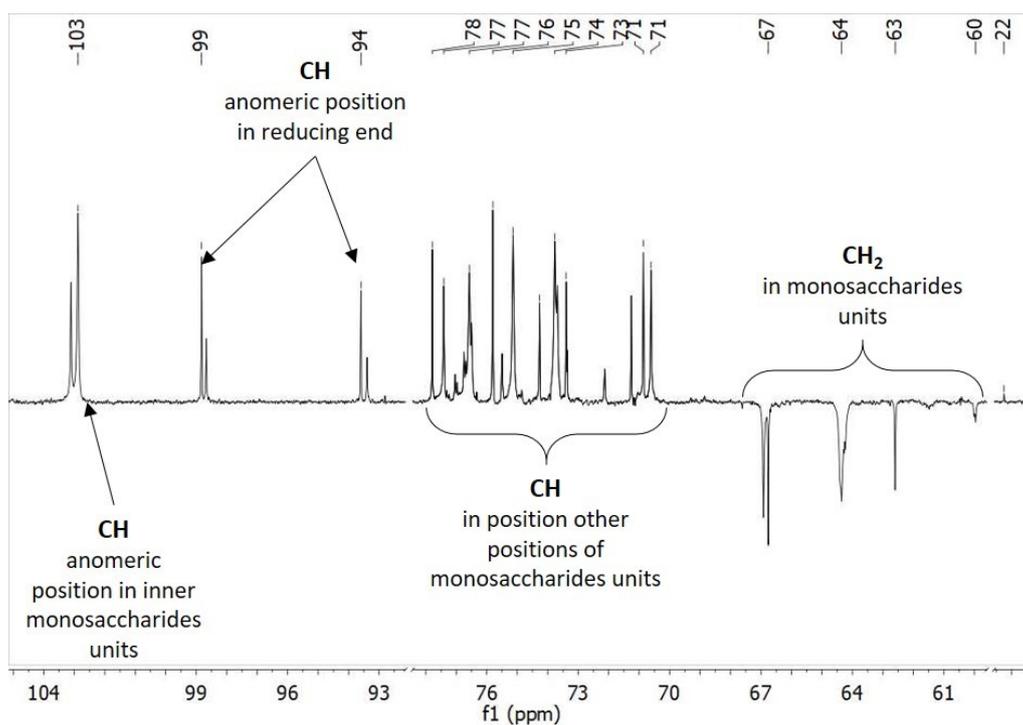
**Figure S5** SEC profile of water soluble oligosaccharides (DP < 14) obtained by mechanocatalytic depolymerization of Pulp-HEM using Aquivion PW98 as catalyst (ball-milling time: 12 h, Pulp-HEM (1.5 g) water content: 3.5 %, 1.5 g Aquivion PW98, 400 rpm).



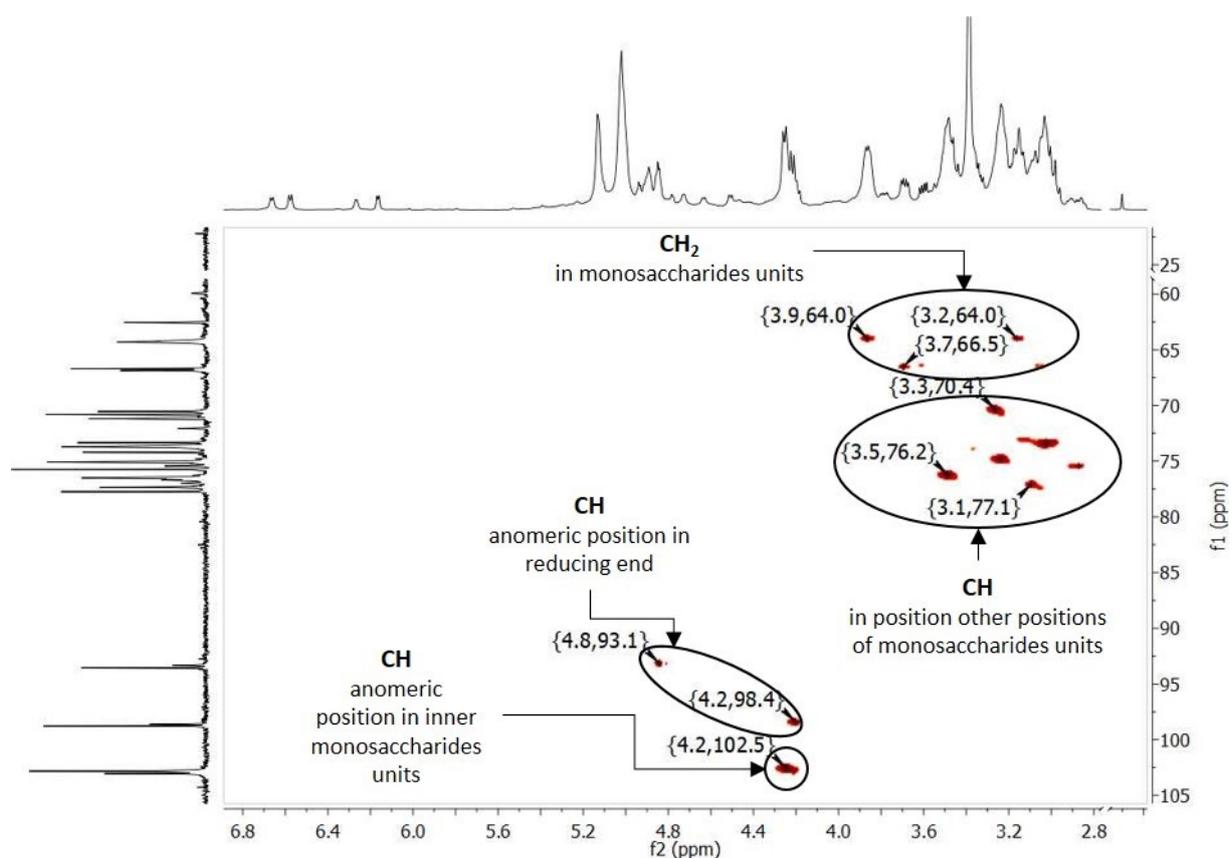
**Figure S6** Kinetic profile of the mechanocatalytic depolymerization of Pine-HEM using Aquivion PW 98 as acid catalyst (Pine-HEM (1.5 g) water content: 5 %, 1.5 g Aquivion PW98, 400 rpm)



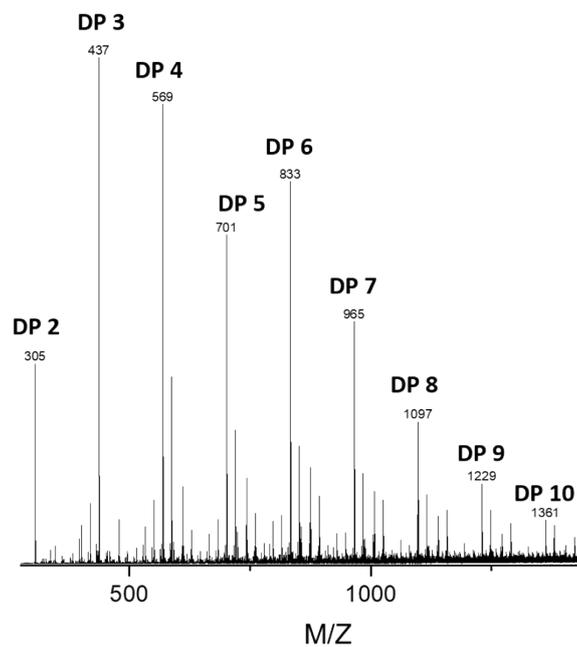
**Figure S7**  $^{13}\text{C}$  NMR spectrum in  $\text{DMSO-}d_6$  for XOS ( $\text{DP} \leq 9$ ) obtained from Pulp-HEM by mechanocatalytic depolymerization. (ball-milling time: 12 h, Pulp-HEM (1.5 g) water content: 3 %, 1.5 g Aquivion PW98, 400 rpm)



**Figure S8** DEPT  $^{13}\text{C}$  NMR spectrum in  $\text{DMSO-}d_6$  for XOS ( $\text{DP} \leq 9$ ) obtained from Pulp-HEM by mechanocatalytic depolymerization (ball-milling time: 12 h, Pulp-HEM (1.5 g) water content: 3 %, 1.5 g Aquivion PW98, 400 rpm).



**Figure S9** HSQC 2D NMR spectrum in DMSO-*d*<sub>6</sub> for XOS (DP ≤ 9) obtained from Pulp-HEM by mechanocatalytic depolymerization (ball-milling time: 12 h, Pulp-HEM (1.5 g) water content: 3 %, 1.5 g Aquivion PW98, 400 rpm).

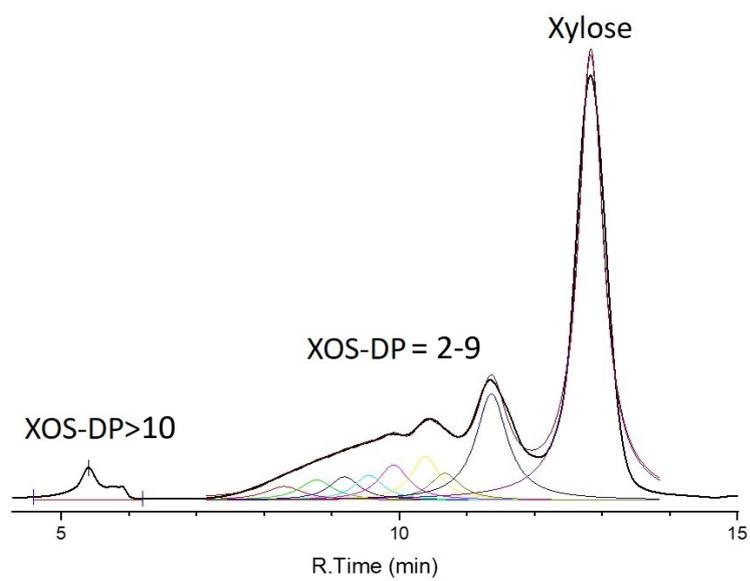


**Figure S10.** MS spectrum of XOS ( $DP \leq 14$ ) obtained from Pulp-HEM by mechanocatalytic depolymerization (ball-milling time: 12 h, Pulp-HEM (1.5 g) water content: 3 %, 1.5 g Aquivion PW98, 400 rpm).

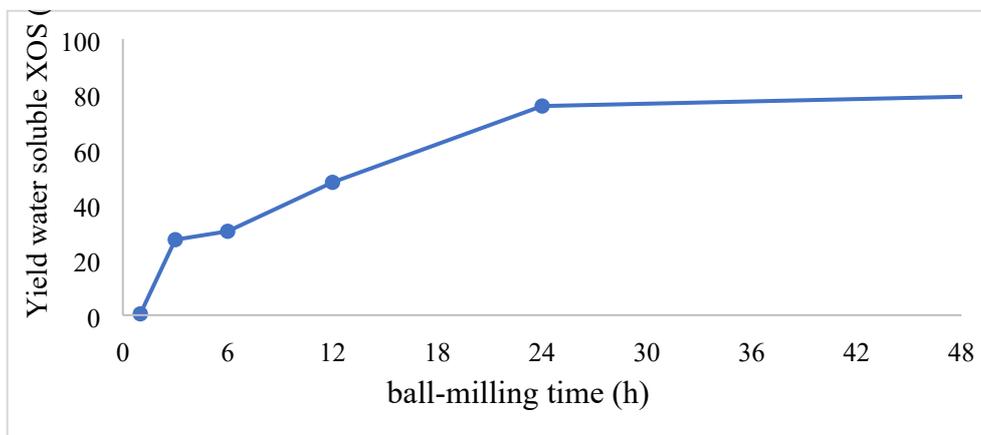
**Table S3** ICP titration of Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup> on Pulp-HEM before and after HCl washing

<b>Element</b>	<b>Quantification</b>	
	mg/kg	mg/kg <sup>a</sup>
<b>Ca<sup>2+</sup></b>	106	10
<b>Mg<sup>2+</sup></b>	142	104
<b>K<sup>+</sup></b>	< 0,1	< 0,1
<b>Na<sup>+</sup></b>	2721	< 0,1

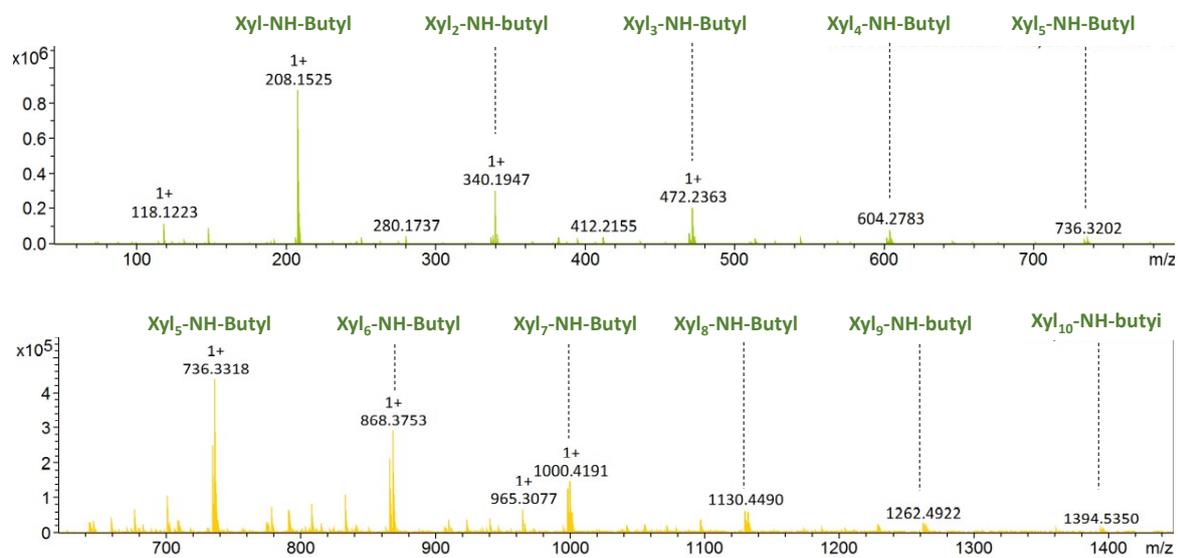
<sup>a</sup> after washing with HCl



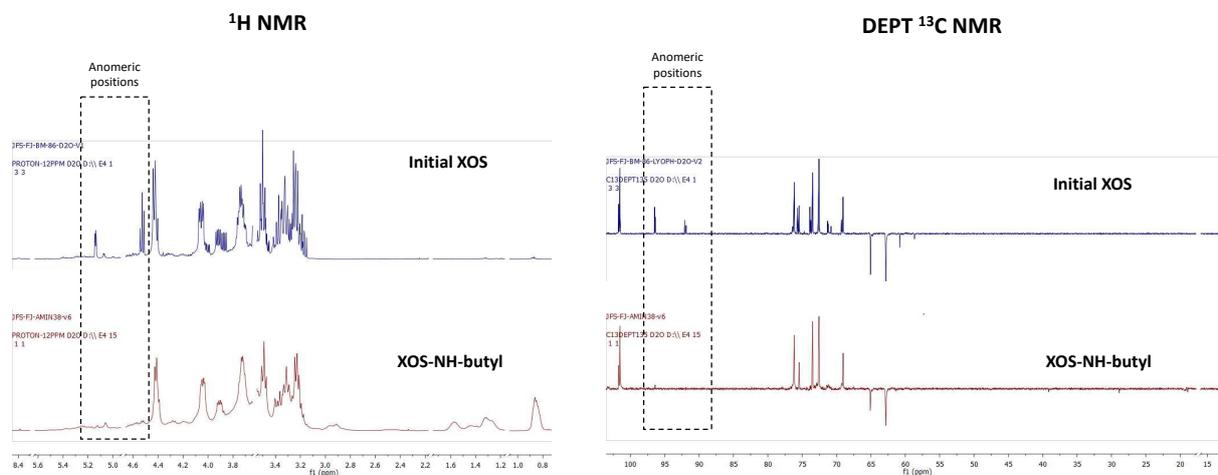
**Figure S11** Ball milling of xylose in presence of Aquivion® as acid catalyst (ball-milling time: 12 h, Xylose (1.5 g), 1.5 g Aquivion PW98, 400 rpm)



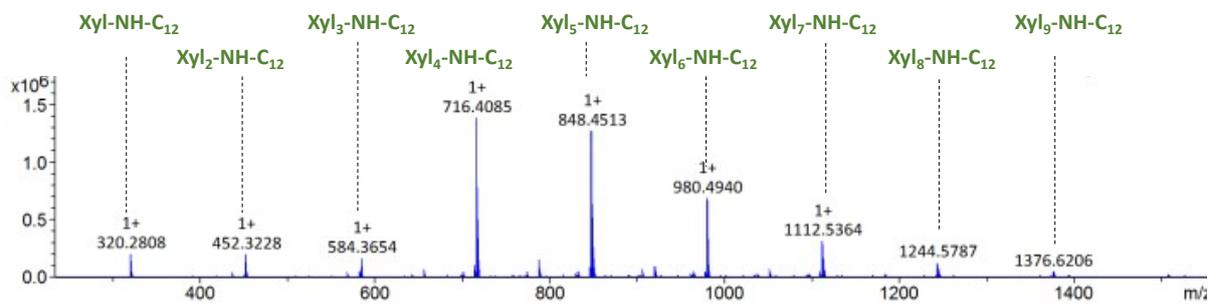
**Figure S3** Kinetic profile of the mechano-catalytic depolymerization of Pine-HEM using Aquivion at 50 %wt. of catalyst loading (Pulp-HEM (2.0 g) water content: 3 %, 1.0 g Aquivion PW98, 400 rpm)



**Figure S13** Catalytic reductive amination of XOS with *n*-butylamine (Pt/C, 50 bar, 50°C, 24 h). Positive mode.



**Figure S14** Monitoring of the anomeric positions of XOS by  $^1\text{H}$  and DEPT  $^{13}\text{C}$  NMR during their catalytic reductive amination over Pt/C (50 bar,  $50^\circ\text{C}$ )



**Figure S15** Catalytic reductive amination of XOS with *n*-dodecylamine in isopropanol (Pt/C, 50 bar, 50°C, 24 h). C12 = dodecyl chain. Positive mode.