

Supporting information

From Rags to Riches: Converting Cellulose containing waste to 5-(Chloromethyl)furfural (CMF)

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Characterization Methods

Ion Exchange Chromatography. Ion exchange chromatography (IC) was used for the quantification of soluble monosaccharides, namely: arabinose, rhamnose, galactose, glucose, xylose, mannose and fructose in HCl using anion exchange chromatography coupled with a pulsed amperometric detector (PAD). The analysis was performed on a Dionex ICS-5000 system, equipped with an auto sampler, dual pump, a detection compartment with a heated column compartment and an electrochemical detector with disposable gold electrode. The separation was achieved with a CarboPac PA1 Analytical Anion Exchange Column (2 x 250 mm). 10 μL sample, containing 1 $\text{mg} \cdot \text{mL}^{-1}$ mg/mL melibiose as internal standard, was injected and separated using a gradient. The mobile phase (flow rate: 0.4 $\text{mL} \cdot \text{min}^{-1}$, 30 $^{\circ}\text{C}$) consisted of a mixture of MilliQ water (solvent A) and 0.1 M sodium hydroxide in MilliQ water (solvent B). The initial percentage of solvent B was 0% held for 15 minutes and then increased linearly to 5% at 30 minutes after which it was increased to 100% in 0.1 minute and held for 4.9 minutes. The initial solvent B concentration was restored to the initial conditions in 0.1 minutes and maintained for 5.9. Between runs, the system was flushed with MilliQ for 8 minutes given a total run time of 50 minutes.

High Performance Liquid Chromatography. High Performance Liquid Chromatography (HPLC) was used to determine the concentration of sugar degradation products. HPLC was performed on an Agilent 1260 Infinity II system with 1260 series refractive index (RID) and diode-array (DAD WR) detectors. The column was an Aminex HPX-87H (300 \times 7.8 mm; dp 9 μm). 7 μL sample was injected and separated using 5 mM H_2SO_4 in MilliQ water (flow rate: 0.6 $\text{mL} \cdot \text{min}^{-1}$, 60 $^{\circ}\text{C}$) as the mobile phase. CMF, HMF and furfural were detected at 230 nm whereas RID was used to analyse acetic acid, formic acid, and levulinic acid.

Gas Chromatography. The final product yield of CMF was identified using gas an Agilent 5975C gas chromatograph (GC) with triple axis mass selective detector (MSD). The system was equipped

with two splitless injectors, an autosampler, and a headspace-autosampler. 0.5 μL of a 1 $\text{mg} \cdot \text{mL}^{-1}$ sample solution in methanol was injected on a Agilent J&W DB624 column (20 m x 0.18 mm x 1 μm) using Helium as the carrier gas (1.2 $\text{mL} \cdot \text{min}^{-1}$, 1:25 split ratio, 250 $^{\circ}\text{C}$ inlet temperature). Separation was achieved using a temperature gradient starting at 50 $^{\circ}\text{C}$ for 2 minutes after which the temperature increased to 170 $^{\circ}\text{C}$ with a 15 $^{\circ}\text{C} \cdot \text{min}^{-1}$ ramp immediately followed by a second ramp of 5 $^{\circ}\text{C} \cdot \text{min}^{-1}$ to 250 $^{\circ}\text{C}$ after which the temperature was held constant for 10 minutes having a total runtime of 36 minutes. Mass spectra were obtained at full scan mode. Compounds were ionized using electron ionization at an electron energy of 70 eV, source temperature of 230 $^{\circ}\text{C}$ and quadrupole temperature of 150 $^{\circ}\text{C}$. Agilent Mass Hunter program with NIST library 11 and a reference standard were used for identification.

CMF and degradation products were quantified with a Thermo Scientific Trace 1310 GC equipped with a TriPlus RSH autosampler for liquid injection, two SSL injectors and two FID detectors. In this project the front SSL injector and the front FID channel are used. 0.5 μL of a 1 $\text{mg} \cdot \text{mL}^{-1}$ sample solution in chlorobenzene were injected on a Agilent J&W DB-624 UI (30 m \times 0.25 mm \times 1.4 μm) using Helium as the carrier gas (2.5 $\text{mL} \cdot \text{min}^{-1}$, 1:100 split ratio, 250 $^{\circ}\text{C}$ inlet temperature). 1 $\text{mg} \cdot \text{mL}^{-1}$ 1,4-dioxane was used as an internal standard. The temperature gradient started with an initial temperature of 70 $^{\circ}\text{C}$ that was held constant for 8 minutes after which the temperature increased to 130 $^{\circ}\text{C}$ with a 15 $^{\circ}\text{C} \cdot \text{min}^{-1}$ ramp and a second ramp of 40 $^{\circ}\text{C} \cdot \text{min}^{-1}$ to 250 $^{\circ}\text{C}$ that was held constant for 5 minutes resulting in a total run time of 20 minutes.

¹H-NMR Spectroscopy. ¹H-NMR analysis was done on a Bruker Avance III HD 600 including a Cryo Probe Inverse Triple Resonance 5 mm with Z-gradient; 3 independent channels and lock channel; 1H, 2H, 13C and 15N; Cryo Cooling Unit 3m. The system was operated using Topspin

3.6 and data was processed with MestReNova. 15 mg sample was dissolved in 0.7 mL deuterated chloroform (CDCl₃).

Saccharide analysis of the starting material:

Analysis by Celignis Limited. In a typical procedure, the cellulosic waste sample was first hydrolyzed using 72% H₂SO₄, ensuring thorough mixing and maintenance at 30°C for 1 h and continuous monitoring every 10 minutes to ensure complete hydrolysis. The resulting hydrolysate underwent a five-fold dilution with a fucose-in-water solution before storage or direct chromatographic analysis. Sugar recovery solution pressure tubes were prepared to monitor sugar loss during hydrolysis. Subsequently, all tubes underwent autoclaving at 121°C for 60 minutes, followed by cooling to room temperature. Filtration of the hydrolysates through known-weight filter crucibles yielded the filtrate, while residual solids were washed with deionized water until all acid-insoluble residue remained on the filter. Before chromatographic analysis, the hydrolysate was diluted with a fucose-in-water solution.

The cleaning wipes provided by Reckitt laboratories were certified by them with a composition of 80% polyester and 20% viscose. The rest of the materials used in this study were sent to Celignis Limited for saccharide analysis and the results are summarized in Table S1.

Table S1. Saccharide composition of waste cellulosic materials

Sample	Tot. Sugars	Glucan	Xylan	Arabinan	Galactan	Mannan
Cigarette butts	51.4	48.8	0.8	0.1	0.1	1.7
PPL coffee cups	60.5	51.7	6.8	0.2	0.4	1.4
Cotton Jeans	95.3	94.9	0.1	0.1	0.2	

Corrugated cardboard	88.3	86.2	0.7	0.1	0.3	1.0
Pizza box	74.2	71.9	0.9	0.2	0.4	0.8
Montvale Cleaning Wipes	66.8	56.2	3.5	0.4	0.3	6.4
