Electronic Supplementary Material (ESI) for Green Chemistry.

Materials

Corn stover used in this study consisted only of leaves and stems and was collected from San Piero a Grado, Pisa (Italy). After being dried, this lignocellulosic material was ground using a high-speed rotary cutting mill and then screened to a particle size within 0.149-0.21 mm. All the samples were dried in a conventional oven at 105 °C to a constant weight before experiments. The composition of the dry corn stover was 24.4 wt% hemicellulose, 42.2 wt% cellulose and 12.5 wt% lignin, as evaluated by the Van Soest methodology [46]. Analyses were carried out in triplicate.

Xylose reagent grade (Carlo Erba), glucose (Sigma-Aldrich, 99.5%), acetic acid (J.T. Baker, 99-100%), formic acid (J.T. Baker, 98%) and furfural (Aldrich, >99%) were used as received for HPLC calibration and, in the case of xylose, also as model compound. Xylan from birchwood (Sigma-Aldrich) was used as reference compound for IR characterization.

Niobium phosphate ($NbOPO_4$, NbP) ADF25 (surface area 180 m^2/g) was supplied by CBMM (Companhia Brasileira de Metalurgia e Mineração). NbP was treated at 255°C for 6 h under high vacuum and its effective acidity resulted in 0.33 meq/g [47].

Experimental Procedures

Microwave assisted autohydrolysis of corn stover was performed using a commercially available mono-mode microwave unit (CEM Discover S-class system). In a typical procedure, 500 mg of dry corn stover and 10 mL of distilled water were loaded in a 35 mL reactor equipped with a magnetic Teflon stir bar. The reactor was capped and heated to the desired temperature under maximum stirring. A typical temperature profile for MW assisted autohydrolysis tests is displayed in figure S1. As observed, initial reaction time (t=0) was taken when the temperature set point was reached. After reaction time was finished, samples were quenched in an ice bath and filtered with a G4 Schott Gouch crucible. The liquid fraction was filtered with 0.2 μm PTFE syringe filter prior to HPLC analysis. The solid to liquid ratio fed into the reactor is the maximum allowed by the equipment still maintaining good stirring. Also, a comparative autohydrolysis test was performed in a conventionally heated and mechanically stirred Parr 4560 autoclave (300 ml) equipped with a P.I.D. controller 4843 (comprising a thermocouple inside the autoclave). This reaction was performed adding 2 g of dry corn stover to 40 mL of distilled water and pressurized with nitrogen to 30 bar. After reaction time was finished, the reactor was rapidly cooled to room temperature. Solid and liquid products were separated from each other just as in MW assisted autohydrolysis tests.

The solid fraction was washed with water and oven dried at 105°C to constant weight for further quantification and IR characterization.

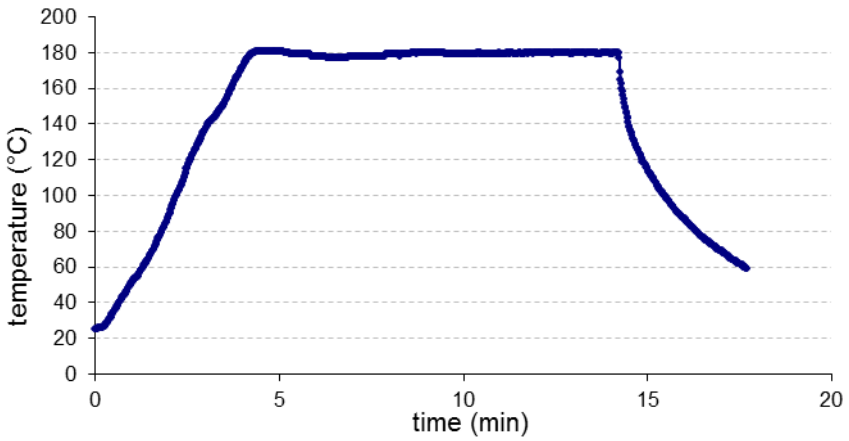

Figure S1. Typical temperature profile for MW assisted autohydrolysis of corn stover performed at T=180°C and t=10 min.

Microwave assisted dehydration reactions leading to furfural were performed in a 10 mL reactor. 5 mL of solutions of pure xylose (containing 250 mg) or of raw corn stover hydrolysates and 200 mg of NbP were fed into the reactor comprising a magnetic Teflon stir bar. The reaction mixture was heated to the desired temperature under maximum stirring and quenched in an ice bath when the reaction time was finished.

Before performing catalytic recycle tests, the spent catalyst was washed with water and acetone to remove residues of reactants or products and dried under vacuum at 100°C. Then, it was weighed and fed to the microwave vial along with fresh xylose solutions (5 wt.%). Efforts were made during catalyst washing not to lose any solids, but little changes in the catalyst to substrate weight ratio were observed (from 0.8 to 0.69).

Samples were filtered with 0.2 μm PTFE syringe filter and diluted when needed prior to HPLC analysis.

Reproducibility of repeated autohydrolysis and catalytic runs resulted within 5%.

Product analysis and characterization of solid fraction

Products present in the aqueous solutions were quantitatively analyzed by HPLC (Perkin Elmer Flexar) equipped with refractive index detector. Twenty microliter samples were loaded into a PolyporeCA column (4.6 mm × 220 mm × 10 μm) and eluted with 5 mM H_2SO_4 at a flow rate of 0.1 mL/min. The column was maintained at 60°C, and the calibration was carried out using commercial standards.

The percentage of biomass solubilization in the first autohydrolysis stage was calculated as:

$$\text{Solubilization (wt.\%)} = \frac{\text{Dry initial biomass (g)} - \text{dry biomass residue (g)}}{\text{Dry initial biomass (g)}} \times 100$$

Conversion of xylose, yield of furfural and Selectivity were defined as follows:

$$\text{Conversion: } X_{Xy}\ (\text{mol\%}) = \frac{\text{Moles of Xylose reacted}}{\text{Moles of initial Xylose}} \times 100$$

$$\text{Yield: } Y_{Fur}\ (\text{mol\%}) = \frac{\text{Moles of furfural produced}}{\text{Moles of initial Xylose}} \times 100$$

$$\text{Selectivity: } S_{Fur}\ (\text{mol\%}) = \frac{\text{Moles of furfural produced}}{\text{Moles of Xylose reacted}} \times 100$$

Yields of Xylose and Furfural from corn stover were calculated as follows:

$$\text{Xylose Yield: } Y_{Xy}\ (\text{mol\%}) = \frac{\text{Moles of xylose produced}}{\text{Moles of pentosan units in corn stover}} \times 100$$

$$\text{Furfural Yield: } Y_{Fur}\ (\text{mol\%}) = \frac{\text{Moles of furfural produced}}{\text{Moles of pentosan units in corn stover}} \times 100$$

The solid fraction obtained from the first autohydrolysis stage was characterized with Spectrum One FTIR system (Perkin Elmer, Wellesley, MA) comprised of a universal ATR (Attenuated Total Reflection) accessory. The sample was uniformly pressed against the ZnSe surface using a spring-loaded anvil. Mid-IR spectra were obtained by averaging 15 scans from 4,000 to 400 cm-1 at 2 cm-1 resolution. Baseline and ATR corrections for penetration depth and frequency variations were carried out using the Spectrum One software supplied with the equipment