

Microwave Heating for Rapid Conversion of Sugars and Polysaccharides to 5-chloromethyl furfural

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Supplementary Information

Typical Experimental Procedure

250 mg of fructose was charged into a 35 ml CEM microwave reactor vessel with a magnetic stirrer bar. To this 10 ml of 1,2-dichloroethane and 5 ml concentrated HCl were added. The reaction vessel was sealed with a rubber lid (CEM) and placed in A CEM Discover SP Microwave Synthesiser. A fixed temperature method protocol with 15 minute hold time at 80 °C and high stirring speed was used, with a 200 W max power setting and a typical ramp time of 2 minutes. After microwave heating the reaction mixture was passed into a separating funnel and the lower organic layer collected, filtered and the DCE removed *in vacuo* yielding a light brown oil (143 mg, 71% yield, 98% purity by GC). ¹H NMR (CDCl₃, 400 MHz): 4.59 (s, 2 H, CH₂), 6.55 (d, J = 3.6 Hz, 1 H, Ar-H), 7.16 (d, J = 3.6 Hz, 1 H, Ar-H), 9.58 (s, 1 H, CHO) ppm. ¹³C NMR (CDCl₃, 100 MHz): 36.6 (CH₂), 112.1, 121.9 (Ar), 152.9 (Ar), 156.1 (Ar), 177.8 (CHO) ppm. Spectroscopic data are in agreement with the literature.¹

Ball Milling Experimental Procedures

Ball-milling cellulose pre-treatment was performed in a Retsch PM400 planetary ball mill. Four 250 ml tungsten carbide vials were each charged with 10 g of microcrystalline cellulose and 5 20 mm titanium carbide balls (16.2 g each). This loading represents a ball to substrate ratio of 8:1. The mill was rotated at 100 rpm for the desired duration, up to a maximum of 110 minutes. The only pauses in the method were for collection of samples after 20 and 50 minutes.

Conventional Heating Experimental Procedure

Conventional heating experiments were performed as follows. A 35 ml CEM microwave tubes was charged with 10 ml solvent (either DCE or cyclohexane), 5 ml conc. HCl and 500 mg fructose and a magnetic stirrer bar. The microwave tube was then placed within a pre-heated water bath (70 °C) for 12 minutes. 12 minutes was selected for the duration of the conventional heating methodology as the typical ramp time for comparative microwave experiments was 2 minutes followed by a 10 minute hold a 70 °C. After microwave heating the reaction mixture was passed into a separating funnel and the lower organic layer collected, filtered and the DCE removed *in vacuo* yielding a light brown oil.

GC and GC-MS Analysis

Isolated 5-chloromethyl furfural (CMF) sample purity and selectivity of the reaction were determined by GC-FID. 10 mg of sample was dissolved in 1 ml of dichloromethane, with tetradecane as a standard. Samples were ran on an Agilent Technologies 6890N Network GC System fitted with Phenomenx Zebron ZB5-HT Inferno column of the dimensions 30 m x 0.25 mm x 0.25 µm. GC-FID peak retention times were compared against standard of levulinic acid, 5-hydroxymethyl furfural (HMF) and CMF, and also by peak assignment from GC-MS. Sample purity an reaction selectivity were calculated based on the ratio of peak areas of the present components. GC-MS samples were prepared as for GC-FID. GC-MS analysis was performed on a Perkin-Elmer 560 GC, using a Phenomenx Zebron ZB5-HT Inferno column of the dimensions 30 m x 0.25 mm x 0.25 µm, with a Perkin-Elmer 600 EI-MS (positive ion mode) attached

NMR Analysis

¹H and proton-decoupled ¹³C NMR spectra were obtained on a Jeol 400 spectrometer, in CDCl₃. Chemical shifts were calibrated using the internal solvent resonance and referenced to TMS.

References

- 1 K. Sanda, L. Rigal, M. Delmas, A. Gaset, *Synthesis*, 1992, **34**, 541.