Supporting Information

Highly Efficient Formic Acid-Mediated Oxidation of Renewable Furfural to Maleic Acid with H₂O₂

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General Information

Materials: all starting materials are commercially available and were used as received, unless otherwise indicated. Furfural (> 98%), formic acid (> 98%), and acetic acid (glacial) were purchased from Merck. Amberlyst 15, hydrogen peroxide (31%), propionic acid, and butyric acid were purchased from Sigma-Aldrich. The other chemicals not stated here were either purchased from Sigma-Aldrich, Merck, or Fisher Scientific.

Product analysis: analysis of the reactant and product in the oxidation of furfural to maleic acid was performed using HPLC (Agilent Technologies, 1200 series) with UV (254 nm and 280 nm) and refractive index (RI) detectors. The reactant and product were separated on an Agilent Hi-Plex H column (7.7 × 300 mm, 8 µm) that was operated at 25 °C. The eluent was a solution of H₂SO₄ (0.0001 M), flow rate 0.7 ml min⁻¹, 25 °C. The retention times were respectively 8.5 min and 58.0 min for maleic acid and furfural on the UV detectors. The wavelength of 280 nm was chosen for the UV detector because furfural is more responsive at 280 nm than at 254 nm. The retention time was 12.9 min for formic acid on the refractive index (RI) detector. ¹H and ¹³C NMR spectra were obtained using a Bruker AV-400 (400 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) with reference to tetramethylsilane with the solvent resonance as the internal standard.

Experimental Procedure

Furfural oxidation to MA: Furfural (96 mg, 1 mmol), formic acid (4 ml), and 31% H₂O₂ (1 ml) were charged into an around 8 ml thick wall glass tube. The glass tube was sealed and heated at 100 °C for 40 min. The glass tube was cooled to room temperature and an aliquot of the reaction mixture was analysed by HPLC to determine the MA yield (93%). The solvent of the reaction mixture was removed under reduce pressure to give a white solid product of MA (105 mg, 90% yield).

Solvent	Conv. (%)	Yield (%)
Acetic Acid	100	65
Water	99	15
1,4-Dioxane	74	0
MIBK	100	0
Toluene	100	0
DMSO	17	0
DMF	87	0
Acetonitrile	40	0
Ethanol	37	0
Ethyl Acetate	21	0

Table S1. The conversion of furfural to maleic acid in different solvents.

Extended Optimization Tables

Reaction conditions: furfural (1 mmol), solvent (4 ml), 31% H₂O₂ (1 ml), 100 °C, 4 h.

Table S2. The oxidation of furfural in formic acid (FA) with different water content.

Entry	$H_2O: FA(v/v)$	Conv. [%]	Yield [%]
1	1:1 ^[a]	100	28
2	1:1 ^[b]	100	27
3	3:1 ^[a]	100	13
4	3:1 ^[b]	100	13

[a] Reaction conditions: furfural (1 mmol), solvent (4 ml), 31% H₂O₂ (1 ml), 100 °C, 1 h.

[b] Reaction conditions: furfural (1 mmol), solvent (4 ml), 31% H₂O₂ (1 ml), 100 °C, 4 h.

T / °C	t / h	Vial	Conv. (%)	Yield (%)	
100	1	Sealed	100	91	
	1	Open	100	88	
60	Λ	Sealed	100	95	
	4	Open	100	84	

Table S3. Furfural oxidation to MA in sealed and open systems.

Reaction conditions: furfural (1 mmol), formic acid (4 ml), 31% H₂O₂ (1 ml). A condenser was used for the reactions operated in the open system.

Identification of Reaction Intermediates



Figure S1. ¹H NMR (400 MHz, DMSO- d_6) spectrum of the reaction mixture from furfural oxidation in acetic acid media with H₂O₂. Reaction conditions: furfural (1 mmol), acetic acid (4 ml), 31% H₂O₂ (1 ml), 100 °C, 4 h. After reaction some of the reaction mixture (0.1 ml) was dissolved in DMSO- d_6 (0.7 ml) for NMR analysis. Formic acid, $\delta = 8.126$ ppm; maleic acid, $\delta = 6.276$ ppm; acetic acid, $\delta = 1.933$ ppm.



Figure S2. The HPLC chromatogram of the reaction mixture from furfural oxidation in formic acid media with H_2O_2 . Reaction conditions: furfural (1 mmol), formic acid (4 ml), 31% H_2O_2 (1 ml), 100 °C, 40 min. After reaction some of the reaction mixture (30 mg) was dissolved in H_2O (1 ml) for HPLC analysis. Retention time: maleic acid, 8.5 min; furfural, 58.4 min. Acetic acid was not observed by the UV detector ($\lambda = 280$ nm).





¹³C NMR (400 MHz, DMSO-*d*₆), δ 130.50, 167.31



Figure S3. ¹H and ¹³C NMR (400 MHz, DMSO- d_6) spectra of the crude product from furfural oxidation in formic acid media with H₂O₂. Reaction conditions: furfural (1 mmol), formic acid (4 ml), 31% H₂O₂ (1 ml), 100 °C, 40 min. The solvent was removed by evaporation under reduced pressure and the obtained white solid was dissolved in DMSO- d_6 for NMR spectroscopic analysis.



Figure S4. ¹H NMR (400 MHz, DMSO-*d*₆) spectrum of the isolated furan-2(5H)-one. δ (ppm) = 4.96 (dd, *J* = 2.2, 1.7 Hz, 2H), 6.24 (dt, *J* = 5.8, 2.2 Hz, 1H), 7.91 (dt, *J* = 5.8, 1.7 Hz, 1H). Experimental procedure: furfural (1 mmol), formic acid (4 ml) and 31% H₂O₂ (1 ml) was stirred at room temperature (25 °C) for 1 h. The reaction mixture was diluted with 5 ml of water, and then extracted with 10 ml of dichloromethane (DCM). The DCM phase was separated and the solvent was removed under reduced pressure. The liquid product as obtained was subjected to ¹H NMR spectroscopic analysis and furan-2(5H)-one was detected as the major component.

Reaction Pathways for H₂O₂ Oxidation of Furfural to Maleic Acid



Scheme S1. The oxidation of furfural to maleic acid via the 2-furoic acid route (N. Alonso-Fagundez, I. Agirrezabal-Telleria, P. L. Arias, J. L. G. Fierro, R. Mariscal and M. Lopez Granados, *RSC Adv.* 2014, 4, 54960-54972).



Scheme S2. The oxidation of furfural to maleic acid via the Baeyer-Villiger oxidation of furfural to furanol formate ester (N. Alonso-Fagundez, I. Agirrezabal-Telleria, P. L. Arias, J. L. G. Fierro, R. Mariscal and M. Lopez Granados, *RSC Adv.* **2014**, 4, 54960-54972).