Pulcherrimin: a bio-derived iron chelate catalyst for base-free oxidation of 5-hydroxymethylfurfural to furandicarboxylic acid

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Table S1. BET surface area, pore volume, pore size, surface and bulk elemental percentage (C, H, N, Fe) of pulcherrimin

Material	Pulcherrimin	Fe_2O_3/C
BET Surface area (m^2g^{-1})	29.05± 3	768±12
Average Pore Size (nm)[a]	15.2± 0.2	3.8±0.3
Pore Volume (cm^3g^{-1})	0.153	0.523±0.007
Bulk elemental analysis[b]		
C	47.80± 0.12	68.21±0.18
H	6.75± 0.26	-
N	8.95± 0.64	-
Fe[c]	11.6 ± 0.2	11.6±0.4

[a] Pore volume calculated at P/Po = 0.99, [b] Measured by CHNS elemental analysis, [c] Measured by ICP-OES.

Table S2. Results of pulcherrimin stability test at 120 °C in water

	Initial mass (mg)	Final mass after stability test (mg)	Mass loss during stability test (%)	Residue in solvent (mg)	Residue in solvent (%)	Total recovery (%)
Pulcherrimin	50	49.8	0.4	0.0	0	99.6

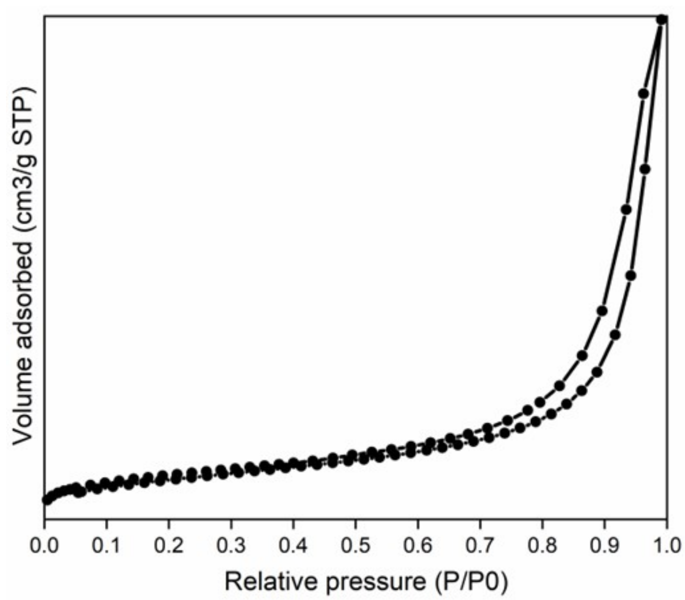

Fig. S1 N_2 adsorption-desorption isotherm of pulcherrimin

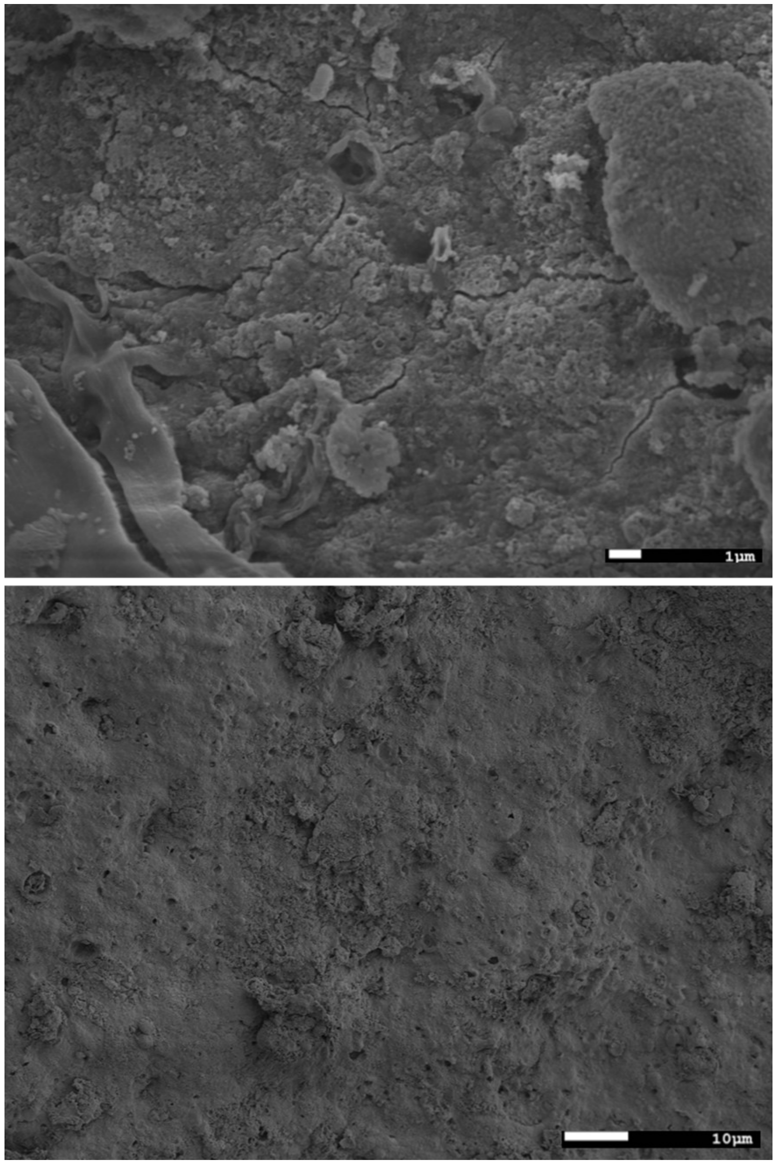

Fig. S2 FE-SEM image of pulcherrimin

Techno-economic analysis:

Catalyst costs and reaction energy requirements for FDCA production over pulcherrimin were estimated using a previously published techno-economic analysis for FDCA production over a 5% Pt/C system.[1] Neither system requires the addition of a base catalyst, and 5-HMF to FDCA yields are comparable overall. First, we used the reference to calculate the specific catalyst and energy cost for the baseline 5% Pt/C catalyst before estimating corresponding costs for our novel pulcherrimin catalyst system.

Baseline system (5% Pt/C):

Data given in the reference:

Yield (FDCA/5-HMF), $Y_{FDCA/HMF}$ = 93% (n/n)

Yield (5-HMF/fructose), $Y_{HMF/fruc}$ = 70.3% (n/n)

Catalyst loading ratio (5-HMF/Pt), $R_{HMF/Pt}$ = 30 (n/n)

Pt loading on catalyst: $X_{Pt/C}$ = 5% (w/w)

Catalyst cost, $Cost_{cat}$= 194.0 \$ kg^{-1}

Catalyst deactivation, D_{cat} = 20% year^{-1}

Catalyst refurbishment factor, F_{ref} = 20% of catalyst cost

Reaction time, t_{react} = 16 h run^{-1}

Heating duty, Q_{Heat} = 6.9 MW

Cooling duty, Q_{Cool} = 22.0 MW

Electric duty, Q_{elec} = 0.3 MW

Fructose feed rate, W_{fruc} = 500 t day^{-1}

Additional data:

Molecular weight of platinum, MW_{Pt} = 195.08 g mol^{-1}

Molecular weight of 5-HMF, MW_{HMF} = 126.11 g mol^{-1}

Molecular weight of FDCA, MW_{FDCA} = 156.09 g mol^{-1}

Molecular weight of fructose, MW_{fruc} = 180.16 g mol^{-1}

Assumptions:

Annual days of operation, t_{op} = 330 days year^{-1}

Heating price, P_{Heat} = 0.05 $ kWh^{-1}

Cooling price, P_{Cool} = 0.03 $ kWh^{-1}

Electricity price, P_{Elec} = 0.07 $ kWh^{-1}

(i) Calculate catalyst to product mass ratio, $\grave{R}_{Cat/F}$:

FDCA mass yield, $\grave{Y}_{FDCA/HMF} = Y_{FDCA/HMF} \times \frac{MW_{FDCA}}{MW_{HMF}} = 0.93 \times \frac{156.09}{126.11} = 1.151$ (w/w)

Catalyst to 5-HMF mass ratio,

$$\grave{R}_{Cat/H} = \frac{1}{R_{HMF/Pt}} \times \frac{MW_{Pt}}{MW_{HMF}} \times \frac{1}{X_{Pt/C}} = \frac{1}{30} \times \frac{195.08}{126.11} \times \frac{1}{0.05} = 1.031 \text{ (w/w)}$$

Catalyst to FDCA mass ratio, $\grave{R}_{Cat/FDCA} = \frac{\grave{R}_{Cat/HMF}}{\grave{Y}_{FDCA/HMF}} = \frac{1.031}{1.151} = 0.896$ (w/w)

(ii) Calculate catalyst regeneration cost per kg of product, $Cost_{reg}$:

Number of runs per year, $N_{runs} = \frac{t_{op}}{t_{react}} = \frac{330 \times 24}{16} = 495$ runs year^{-1}

Catalyst consumption, $\grave{X}_{Cat/FDCA} = D_{cat} \times \frac{\grave{R}_{Cat/HMF}}{N_{runs}} = 0.2 \times \frac{0.896}{495} = 0.000362$ kg kg^{-1} year^{-1}

Catalyst regeneration cost,

$$Cost_{reg} = F_{reg} \times \dot{X}_{Cat/FDCA} \times Cost_{cat} = 0.2 \times 0.000362 \times 194 = 0.0140 \text{ \$ kg}^{-1}$$

(iii) Calculate energy requirements per kg of product

The baseline study includes the conversion of fructose to 5-HMF prior to FDCA production. As the system has been fully heat integrated, it is difficult to isolate energy associated with 5-HMF production from other stages, and energy costs will be determined for the whole system. The same approach will be taken for calculating energy costs with the pulcherrimin catalyst to provide a like-for-like comparison between the two systems.

Fructose to 5-HMF mass yield,

$$\dot{Y}_{HMF/fruc} = Y_{HMF/fruc} \times \frac{MW_{HMF}}{MW_{fruc}} = 0.703 \times \frac{126.11}{180.16} = 0.492 \text{ (w/w)}$$

Daily FDCA production,

$$W_{FDCA} = W_{fruc} \times Y_{HMF/fruc} \times Y_{FDCA/HMF} = 500 \times 0.492 \times 1.151 = 283.2 \text{ t day}^{-1}$$

Specific heat duty, $\dot{Q}_{Heat} = \frac{Q_{Heat} \times time}{W_{FDCA}} = \frac{6.9 \times 24}{283.2} = 0.5847$ MWh t^{-1} = 0.5847 kWh t^{-1}

Specific cooling duty, $\dot{Q}_{Cool} = \frac{Q_{Cool} \times time}{W_{FDCA}} = \frac{22.0 \times 24}{283.2} = 1.8643$ MWh t^{-1} = 1.8643 kWh t^{-1}

Specific electric duty, $\dot{Q}_{elec} = \frac{Q_{Cool} \times time}{W_{FDCA}} = \frac{0.3 \times 24}{283.2} = 0.0254$ MWh t^{-1} = 0.0254 kWh t^{-1}

(iv) Calculate energy cost per kg of product

Heating cost, $Cost_{heat} = \dot{Q}_{Heat} \times P_{Heat} = 0.5847 \times 0.05 = 0.0292$ \$ kg^{-1}

Cooling cost, $Cost_{cool} = \dot{Q}_{cool} \times P_{Heat} = 1.8643 \times 0.03 = 0.0559$ \$ kg^{-1}

Heating cost, $Cost_{elec} = \dot{Q}_{elec} \times P_{Heat} = 0.0254 \times 0.07 = 0.00178$ \$ kg^{-1}

Pulcherrimin system:

Data from our study:

Pulcherrimin Yield (pulcherrimin/biomass), $Y_{Pul/BM}$ = 0.26 (w/w)

Initial FDCA yield, $Y1_{FDCA/HMF}$ = 65.2% (w/w)

FDCA yield after 6 cycles, $Y6_{FDCA/HMF}$ = 23.5% (w/w)

Pulcherrimin Fe content, $X_{Fe/Pul}$ = 11.2% (w/w)

Catalyst loading (Pul/5-HMF), $R_{Pul/HMF}$ = 0.1 (w/w)

Additional data and assumptions

Sugar cost, P_{sug} = 70 \$ t^{-1}, ref[2]

Fermentation efficiency, $Y_{BM/sug}$ = 0.70 (w/w)[3]

Cost of $FeCl_3$, P_{FeCl_3} = 1.50 \$ kg^{-1}, (industrial grade costing from Alibaba.com)

$FeCl_3$ Fe content, $X_{Fe/FeCl_3}$ = 34.4% (w/w)

Cost of fermentation process, $Cost_{ferm}$ = 0.50 \$ kg^{-1}, based on U.S. Department of Agriculture (USDA) report[4]

Cost for pulcherrimin precipitation and drying, $Cost_{proc}$ = 0.20 \$ kg^{-1}, based on data from microbial pigment production studies, such as melanin and astaxanthin[5]

(v) Calculate pulcherrimin production cost:

Sugar cost, $$Cost_{sug} = \frac{P_{sug}}{Y_{Pul/BM} \times Y_{BM/sug}} = \frac{70 \times 10^{-3}}{0.26 \times 0.70} = 0.385 \text{ \$ kg}^{-1}$$

Iron cost, $$Cost_{FeCl_3} = \frac{X_{Fe/Pul}}{X_{Fe/FeCl_3}} \times P_{FeCl_3} = \frac{0.112}{0.344} \times 1.5 = 0.4880 \text{ \$ kg}^{-1}$$

Total catalyst cost, $$Cost_{Pul} = Cost_{sug} + Cost_{FeCl_3} + Cost_{ferm} + Cost_{proc}$$

$$= 0.385 + 0.4880 + 0.50 + 0.20 = 1.573 \text{ \$ kg}^{-1}$$

(vi) Calculate catalyst replacement cost

Excel goal seek function was used to estimate the catalyst deactivation per run, D_{pul}, as 18.4% from the overall reduction in FDCA yield after 6 cycles (65.2% to 23.5% (w/w)).

Therefore, the catalyst replacement cost to retain initial FDCA yield can be calculated:

$$Cost_{repl} = Cost_{Pul} \times D_{pul} \times \frac{R_{Pul/HMF}}{Y1_{FDCA/HMF}} = 1.573 \times 0.184 \times \frac{0.1}{0.652} = 0.0445 \text{ \$ kg}^{-1}$$

(vii) Calculate energy requirements

To estimate energy requirements for production of FDCA over pulcherrimin, it is assumed that heating and cooling costs are directly proportional to the FDCA yield produced from 5-HMF. *I.e.*, reducing conversion/selectivity will increase the energy costs of the reaction and subsequent separation processes.

Therefore:

Heating cost, $$Cost_{heat} = Cost_{heat,\,Pt} \times \frac{\dot{Y}_{\frac{FDCA}{HMF},Pt}}{Y1_{FDCA/HMF}} = 0.0292 \times \frac{1.151}{0.652} = 0.05161 \text{ \$ kg}^{-1}$$

Cooling cost, $$Cost_{cool} = Cost_{cool,\,Pt} \times \frac{\dot{Y}_{\frac{FDCA}{HMF},Pt}}{Y1_{FDCA/HMF}} = 0.0559 \times \frac{1.151}{0.652} = 0.09874 \text{ \$ kg}^{-1}$$

Electricity cost, $$Cost_{elec} = Cost_{elec,\,Pt} \times \frac{\dot{Y}_{\frac{FDCA}{HMF},Pt}}{Y1_{FDCA/HMF}} = 0.00178 \times \frac{1.151}{0.652} = 0.00314 \text{ \$ kg}^{-1}$$

E-Factor calculation for catalysts:

The E-factor is calculated using the formula:

E-factor= Total mass of waste generated by the process (g)/ Total mass of product formed (g)

For Pt/C system (reaction conditions as provided in reference):

5-HMF Solution: 7.0 mL aqueous solution

Mass of 5-HMF: 0.13 g

Solvent used: Water (7.0 mL ≈ 7.0 g)

Catalyst: Pt/C (0.045 g)

Base used: NaOH (0.084 g)

Catalyst consumption factor (0.04 %): 0.2/495 * 0.045 g

FDCA Yield= 79 %

Total FDCA (product) produced= 0.103 g

Total input mass=substrate mass+ solvent+ catalyst+ base

Total input mass= 0.13+7.0+0.045+0.084=7.259 g

Total input mass per kg of FDCA=7.259/0.103= 70.68 kg

Mass raw waste = Total input mass - Mass of target product= 70.68 kg- 1 kg= 69.68 kg

Solvent recovery (water, 90% of 7 kg) = 0.63 kg/0.103= 61.34 kg

Catalyst recovery (Pt/C, 99.96% of 0.045 kg) = 1-0.2/495* 0.045= 0.44 kg

Mass of recovered materials= recovered solvent+ recovered catalyst= 61.78 g

Mass adjusted waste = Mass raw waste - Mass recovered materials= 69.68- 61.78= 7.90

E-factor= Total mass of waste generated by the process (g)/

Total mass of product formed (g)= 7.90/1= 7.90

For Pd/C system (reaction conditions as provided in reference):

5-HMF Solution: 7.0 mL aqueous solution

Mass of 5-HMF: 0.13 g

Solvent used: Water (7.0 mL ≈ 7.0 g)

Catalyst: Pt/C (0.047 g)

Base used: NaOH (0.084 g)

FDCA Yield= 71 %

Total FDCA (product) produced= 0.0923 g

Total input mass=substrate mass+ solvent+ catalyst+ base

Total input mass= 0.13+7.0+0.047+0.084=7.259 g

Total input mass per kg of FDCA=7.259/0.0923= 78.67 kg

Mass raw waste = Total input mass - Mass of target product= 78.67 kg- 1 kg= 77.67 kg

Solvent recovery (water, 90% of 7 kg) = 6.3 kg/0.0923= 68.26 kg

Catalyst recovery (Pd/C, 99% of 0.047 kg) = 0.465/0.0923 kg= 0.504 kg

Mass of recovered materials= recovered solvent+ recovered catalyst= 68.76 g

Mass adjusted waste = Mass raw waste - Mass recovered materials= 77.67- 68.76= 8.91

E-factor= Total mass of waste generated by the process (g)/

Total mass of product formed (g)= 8.91/1= 8.91

For pulcherrimin system (current study):

Reaction conditions:

5-HMF Solution: 40 mL aqueous solution

Mass of 5-HMF: 0.52 g (4.15 mmol)

Solvent used: Water (40 mL ≈ 40 g)

Catalyst: Pulcherrimin (0.05 g)

Base used: none

FDCA Yield: 65.2 %

Total FDCA (product) produced= 0.34 g

Total input mass=substrate mass+ solvent+ catalyst

Total input mass= 0.52 g+ 40 g+ 0.05 g= 40.57 g

Total input mass per kg of FDCA=40.57/0.339= 119.66 kg

Mass raw waste = Total input mass - Mass of target product= 119.66-1= 118.66 kg

Solvent recovery (water, 90% of 40 g) = 36/0.339= 106.18 kg

Catalyst recovery (Pulcherrimin, 80 % of 0.05 g) = 0.04/0.339= 0.117 kg (considering 20 % loss)

Mass of recovered materials= recovered solvent+ recovered catalyst= 106.18+ 0.117 kg=

106.30 kg

Mass adjusted waste = Mass raw waste - Mass recovered materials= 118.66- 106.30 g= 12.36 kg

E-factor= Total mass of waste generated by the process (g)/

total mass of product formed (g) = 12.36/1= 12.36

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