Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

# Supporting Information

## Benign catalytic oxidation of potato starch using a homogeneous binuclear manganese catalyst and hydrogen peroxide

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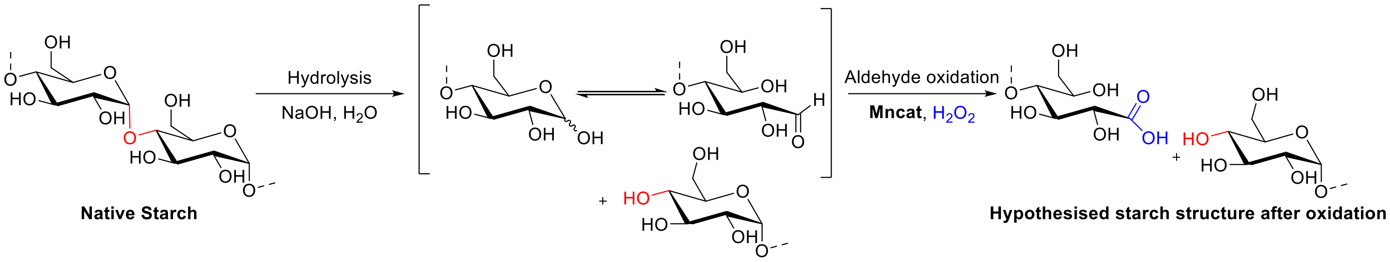

**Scheme S1.** Proposed reaction scheme for the oxidation of native starch by **Mncat** and $H_2O_2$ as supported by molecular weight data. First, oxidative cleavage breaks down the starch forming reactive groups such as aldehydes which are subsequently oxidised further to the observed carboxylic acid groups which are determined by titration.

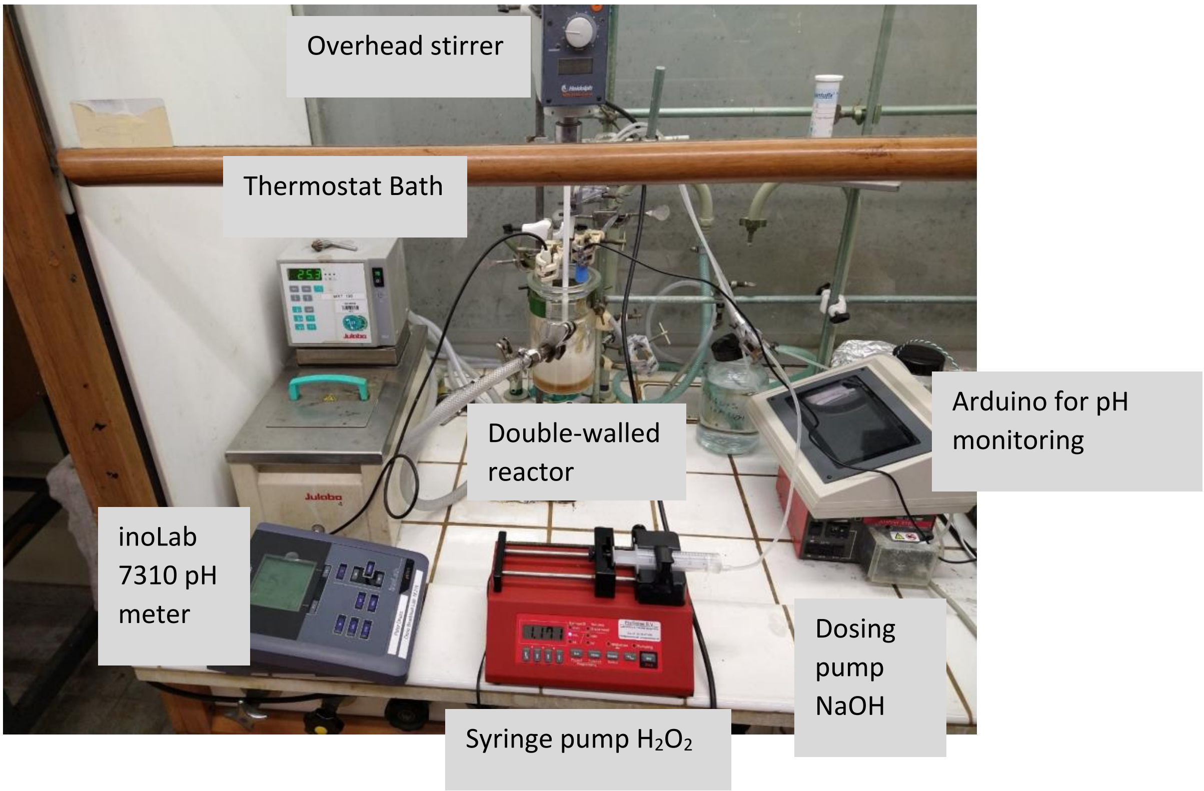

**Figure S1.** Reactor setup used for semi-batch oxidation of starch. For batch addition, the setup was the same but without the syringe pump. For details on the used equipment see experimental (section 2.1/2.2).

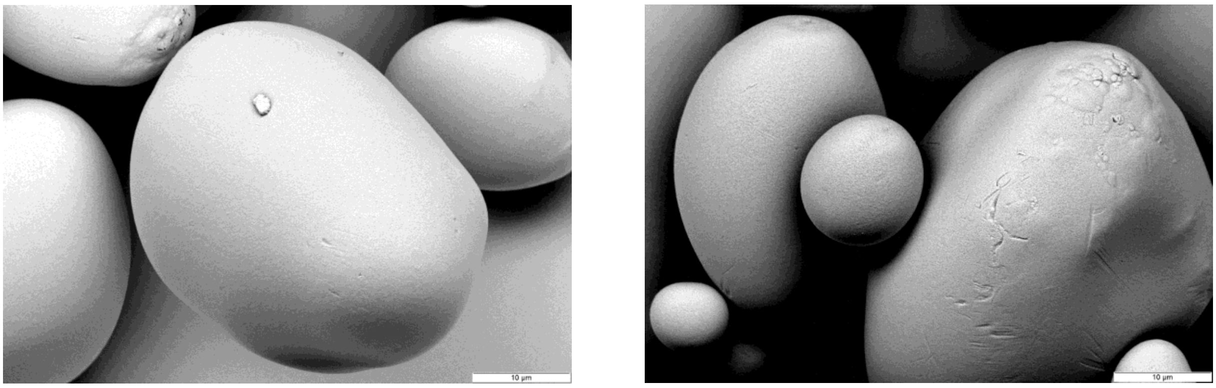

**Figure S2.** Scanning electron microscope (SEM) images of native potato starch.

**Table S1.** Overview of known systems using homogeneous iron-based catalysts and $H_2O_2$ as oxidant for the oxidation of starch. Although other systems have been used for the catalytic oxidation of starch with $H_2O_2$, only systems are shown which can be directly compared to our system (entry 8), i.e. using a homogeneous catalyst and granular, native potato starch oxidised below the gelatinisation temperature at alkaline pH.

| Entry | Catalyst | Cat. Amount (mol%)[a] | Oxidant (wt%)[b] | pH / T | Time (min)[c] | $DS_{COOH}$ (mol/ mol) | $DS_{CO}$ (mol/ mol) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| **1** | $FeSO_4$ | 0.29 | $H_2O_2$ (2.8, SB) | 10/ 40°C | 60 | 0.008 | 0.015 | 91 | [1] |
| **2** | FePcS | 0.0081 | $H_2O_2$ (10, SB) | 8.4/ 58°C | 420 | 0.0090 | 0.0519 | 83 | [2] |
| **3** | FePcS | 0.0083 | $H_2O_2$ (20, SB) | 10/ 55°C | 420 | 0.0161 | 0.0324 | 67 | [3] |
| **4** | FePcS | 0.0083 | $H_2O_2$ (20, SB) | 8.4/ 55°C | 420 | 0.0103 | 0.0528 | 89 | [3] |
| **5** | FePcS | 0.0083 | $H_2O_2$ (20, B) | 8.4/ 52°C | 1320 | 0.0079 | - | 88 | [4] |
| **6** | FePcS | 0.0166 | $H_2O_2$ (20, SB) | 8.4/ 52°C | 1400 | 0.0082 | - | 88 | [5] |
| **7** | FePcS | 0.0042 | $H_2O_2$ (5.6, 3B) | 10/ 50°C | 420 | 0.014 | 0.041 | 91 | [6] |
| **8** | **Mncat** | 0.0021 | $H_2O_2$ (1, SB) | 11/ 25°C | 34 | 0.025 | - | 96 | This work |

[a] Amount (mol%) with respect to amount of mol AGU of the starch

[b] Weight percentage based on dry starch weight, [SB]=semi-batch addition, [B]=batch addition with the number indicating the amount of additions to reach the total amount shown.

[c] From addition of first batch peroxide to quenching of the reaction

**Table S2.** Results of oxidation of potato starch using the traditional process with NaOCl at pH 8.3. NaOCl was added dropwise using a syringe pump. After the reaction the mixture was cooled to 30 °C and brought to pH 10.5 for 1h prior to neutralisation by acid.

| Entry | NaOCl (wt%)[a] | T (°C) | Time (min)[b] | $DS_{COOH}$ (mol/ mol) | Yield (%) | Average molecular weight (kDa) |
|---|---|---|---|---|---|---|
| **1** | 3.7 [SB] | 35 | 220 | 0.029 | 97 | 237 |

[a] Amount of active Cl with respect to dry starch weight. Semi-batch [SB] addition of NaOCl. The NaOCl was added over 10 min.

[b] Total reaction time from the start of NaOCl addition until no more active Cl was detected (test strips)

**Table S3.** Pasting properties of potato starch oxidised using the traditional process with NaOCl at pH 8.3. After the reaction the mixture was cooled to 30 °C and brought to pH 10.5 for 1h prior to neutralisation by acid.

| Entry | NaOCl (wt%)[a] | T (°C) | Time (min)[b] | Peak viscosity (mPa·s) | Hold viscosity (mPa·s) | Breakdown (mPa·s) | Final viscosity (mPa·s) | Setback (mPa·s) |
|---|---|---|---|---|---|---|---|---|
| **1** | 3.7 [SB] | 35 | 220 | 5595 | 158 | 5437 | 539 | 381 |

[a] Amount of active Cl with respect to dry starch weight. Semi-batch [SB] addition of NaOCl. The NaOCl was added over 10 min.

[b] Total reaction time from the start of NaOCl addition until no more active Cl was detected (test strips)

**Table S4.** Results of catalytic oxidation of potato starches by **Mncat** at pH 11

| **Entry** | **Cat. Amount (mol%)**[a] | **H2O2 (wt%)**[b] | **T (°C)** | **Time (min)**[c] | **$DS_{COOH}$ (mol/ mol)** | **Yield (%)** | **Average molecular weight (kDa)** |
|---|---|---|---|---|---|---|---|
| **1** | 0.0021 | 1 [B] | 10 | 360[e] | 0.013 | 98 | 260 |
| **2** | 0.0021 | 1 [B] | 25 | 32 ± 1.2 | 0.018 ± 0.0002 | 98 ± 1.0 | 96.2 ± 7.5 |
| **3** | 0.0021 | 1 [B] | 35 | 30 | 0.017 | 96 | 76.6 |
| **4** | 0.0021 | 1 [B] | 40 | 30 | 0.016 | 95 | 80.8 |
| **5** | 0.0021 | 1.65 [B] | 25 | 520[e,g] | 0.017 | 97 | 120 |
| **6** | 0.0021 | 2 [B] | 25 | 73[g] | 0.033 | 94 | 42.4 |
| **7** | 0.0042 | 2 [B] | 25 | 75 ± 10 | 0.029 ± 0.001 | 95 ± 0.1 | 38 ± 6.6 |
| **8** | 2 x 0.0021 | 2 x 1 [B] | 25 | 115 ± 5 | 0.029 ± 0.0004 | 98 ± 0.3 | 33.2 ± 0.8 |
| **9** | 0.0021 | 2 [B][k] | 25 | 420 | 0.014 | 99 | 200 |
| **10** | 0 | 1 [SB] | 25 | 480[e] | 0.004 | 99 | -[i] |
| **11** | 0.0005 | 1 [SB] | 25 | 221 | 0.011 | 99 | 267 |
| **12** | 0.0005 | 1 [SB][h] | 25 | 240 | 0.021 | 95 | 79.9 |
| **13** | 0.0010 | 1 [SB] | 25 | 48 | 0.023 | 96 | 115 |
| **14** | 0.0021 | 1 [SB] | 25 | 34 | 0.025 | 96 | 55.8 |
| **15** | 0.0021 | 1.5 [SB] | 25 | 64 | 0.030 | 86 | 32.4 |
| **16** | 0.0021 | 2 [SB] | 25 | 65 ± 3.7 | 0.033 ± 0.001 | 87 ± 1.7 | 28.8 ± 0.7 |
| **17** | 0.0021 | 4 [SB] | 25 | 230 | 0.034 | 69[f] | 23.9 |
| **18**[d] | 0.0021 | 1 [SB] | 25 | 125 | 0.010 | 99 | 244 |
| **19** | 0.0042 | 2 [SB] | 25 | 80 | 0.030 | 86 | 20.1 |
| **20** | 0.0042 | 2 [SB] | 40 | 80 | 0.015 | 63[f] | 12.4 |
| **21** | 0.0042 | 4 [SB] | 25 | 200 | 0.033 | 66[f] | 26.3 |
| **22** | 0.0021 [SB] | 1 [Direct] | 25 | 66 | 0.009 | 99 | 267 |
| **23** | 0.0021[j] | 2 [SB] | 25 | 200 | 0.036 | 87 | 26.1 |

[a] Amount (mol%) with respect to amount of mol of AGU of the starch

[b] Batch [B] or semi-batch [SB] addition of $H_2O_2$. For batch addition: 3, 4, and 6 batches for 1, 1.3, and 2 wt% $H_2O_2$, respectively. The wt% is with respect to dry starch weight. For semi-batch addition: 1 wt% of $H_2O_2$ was added in 30 min, the rate of all other semi-batch reactions was equivalent i.e. 2 wt% was added in 60 min.

[c] Total reaction time from the start of $H_2O_2$ addition until no more peroxide was detected (test strips)

[d] Reaction performed at pH 10

[e] (Traces of) $H_2O_2$ still present: these were quenched using $Na_2S_2O_3$

[f] Starch isolated by centrifugation as filtration was made difficult by solubilised starch. This could have impacted the yield

[g] Time between $H_2O_2$ batches different, see fig 4a

[h] Addition of peroxide over 2h instead of the 30 min per 1 wt% of $H_2O_2$ used in the other experiments. Furthermore, a magnetic stirring egg instead of an overhead stirrer was used during the experiment

[I] Viscosity too high for GPC measurement to be done

[j] Catalyst equilibrated at pH 11 for 2h prior to addition of peroxide

[k] Added in 3 batches

**Table S5.** Pasting properties of starches oxidised by **Mncat** at pH 11

| Entry | Cat. Amount (mol%)[a] | H2O2 (wt%)[b] | T (°C) | Peak viscosity (mPa·s) | Hold viscosity (mPa·s) | Breakdown (mPa·s) | Final viscosity (mPa·s) | Setback (mPa·s) |
|---|---|---|---|---|---|---|---|---|
| **1** | 0.0021 | 1 [B] | 10 | 8231 | 923 | 7308 | 9200 | 8277 |
| **2** | 0.0021 | 1 [B] | 25 | 5344 ± 2495 | 200 ± 51 | 5145 ± 2445 | 868 ± 252 | 669 ± 201 |
| **3** | 0.0021 | 1 [B] | 35 | 282 | 56 | 226 | 209 | 153 |
| **4** | 0.0021 | 1 [B] | 40 | 275 | 61 | 214 | 293 | 232 |
| **5** | 0.0021 | 1.65 [B] | 25 | 714 | 113 | 601 | 2102 | 1989 |
| **6** | 0.0021 | 2 [B] | 25 | 156 | 48 | 108 | 94 | 46 |
| **7** | 0.0042 | 2 [B] | 25 | 134 ± 5 | 48 ± 1 | 86 ± 4 | 95 ± 2 | 48 ± 2 |
| **8** | 2 x 0.0021 | 2 x 1 [B] | 25 | 129 ± 21 | 44 ± 2 | 85 ± 19 | 82 ± 2 | 38 ± 0 |
| **9** | 0.0021 | 2 [B][f] | 25 | 1043 | 158 | 885 | 3980 | 3822 |
| **10** | 0 | 1 [SB] | 25 | -[d] | -[d] | -[d] | -[d] | -[d] |
| **11** | 0.0005 | 1 [SB] | 25 | 3741 | 649 | 3092 | 9393 | 8744 |
| **12** | 0.0005 | 1 [SB][e] | 25 | 276 | 72 | 204 | 396 | 324 |
| **13** | 0.0010 | 1 [SB] | 25 | 624 | 127 | 497 | 448 | 321 |
| **14** | 0.0021 | 1 [SB] | 25 | 674 | 105 | 569 | 347 | 242 |
| **15** | 0.0021 | 1.5 [SB] | 25 | 82 | 47 | 35 | 78 | 31 |
| **16** | 0.0021 | 2 [SB] | 25 | 72 ± 2.1 | 40 ± 0.9 | 31 ± 2.9 | 68 ± 1.4 | 29 ± 0.5 |
| **17** | 0.0021 | 4 [SB] | 25 | 66 | 39 | 27 | 64 | 25 |
| **18**[c] | 0.0021 | 1 [SB] | 25 | 13227 | 1483 | 11744 | 11805 | 10322 |
| **19** | 0.0042 | 2 [SB] | 25 | 76 | 35 | 41 | 62 | 27 |
| **20** | 0.0042 | 2 [SB] | 40 | 556 | 58 | 498 | 245 | 187 |
| **21** | 0.0042 | 4 [SB] | 25 | 73 | 34 | 39 | 60 | 26 |
| **22** | 0.0021 [SB] | 1 [Direct] | 25 | 13650 | 1320 | 12330 | 13549 | 12229 |
| **23** | 0.0021[g] | 2 [SB] | 25 | 70 | 34 | 36 | 58 | 24 |

[a] Amount (mol%) with respect to amount of mol of AGU of the starch

[b] Batch [B] or semi-batch [SB] addition of $H_2O_2$. For batch addition: 3, 4, and 6 batches for 1, 1.3, and 2 wt% $H_2O_2$, respectively. For semi-batch addition: 1 wt% of $H_2O_2$ was added in 30 min, the rate of all other semi-batch reactions was equivalent i.e. 2 wt% was added in 60 min.

[c] Reaction performed at pH 10

[d] Viscosity too high for GPC or RVA measurements to be completed at a concentration of 30 wt% (a thick gel is formed during the RVA measurement within 3 min).

[e] Addition of peroxide over 2h instead of the 30 min per 1 wt% of $H_2O_2$ used in the other experiments. Furthermore, a magnetic stirring egg instead of an overhead stirrer was used during the experiment

[f] Added in 3 batches

[g] Catalyst equilibrated at pH 11 for 2h prior to addition of peroxide

## Glucose oxidation with Mncat/$H_2O_2$

alpha-D-Glucose (105.3 mg, 0.58 mmol) together with sulfolane (60.7 mg, 0.51 mmol) as internal standard was added to demineralized water (90 ml), which was brought to pH 11 by addition of 1.1 M NaOH and 25 °C using a Julabo 4 thermostat bath, followed by addition of a 1000 ppm stock solution of **Mncat** (685 µl, 0.2 mol%). During the reaction, the pH was kept constant at the desired pH by an Arduino Uno with an Atlas Scientific EZO circuit and Atlas Scientific pH electrode which controlled a Watson Marlow 101 dosing pump supplying 1.1 M NaOH. To the reaction mixture was added $H_2O_2$ (3 eq., 1.7 mmol, 10.2 mL, 0.5 wt% in water) using a New Era NE-1000 syringe pump over

16 h. After addition and consumption of all peroxide (test strips) the reaction mixture was acidified to pH 5. The oxidation products were analysed by an Agilent Technologies 1260 Infinity HPLC (5 mM $H_2SO_4$ eluent) with a RID and UV detector. Calibration curves of alpha-D-glucose and D-gluconic Acid with sulfolane as internal standard were used to quantify the amount of starting material and product in the samples. The HPLC samples were prepared by directly filtering an aliquot of the reaction mixture without dilution. HPLC samples were taken at the following times: 0 min, 15 min, 30 min, 80 min, 2 h, 4 h, 5 h 40 min, 8 h, 24 h.

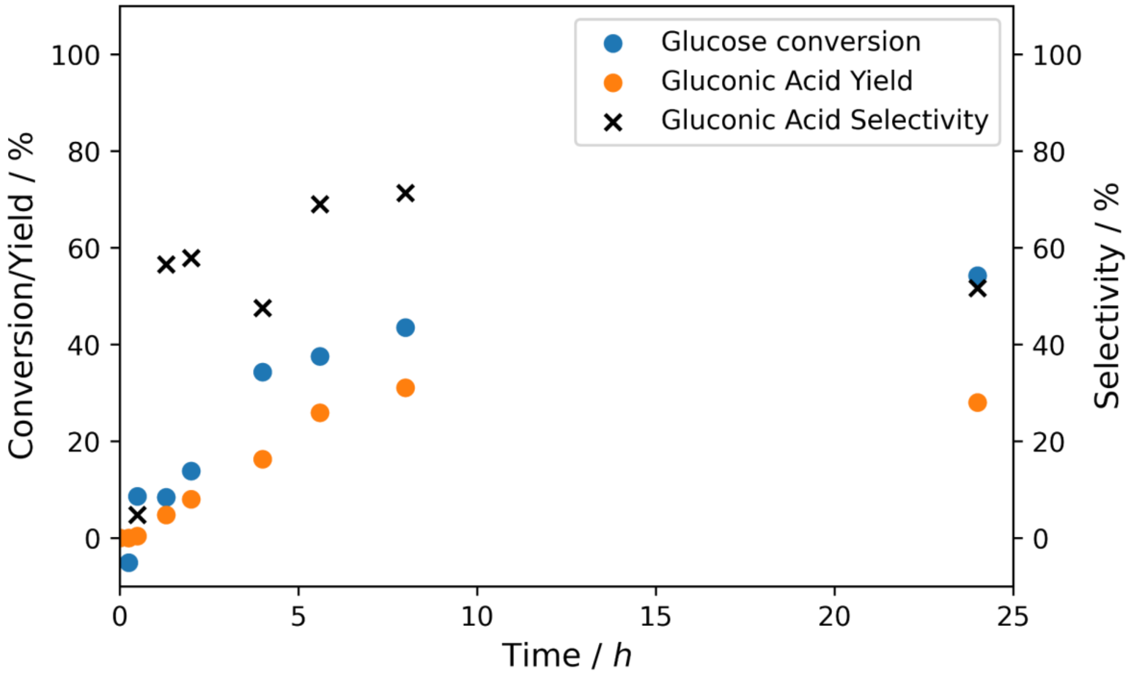

**Figure S3.** Results of the oxidation of glucose to gluconic acid by 0.2 mol% **Mncat**, 3 eq $H_2O_2$ (added over 16 h), at 25 °C and pH 11. A drop in the catalytic activity over the reaction time can be observed. The low selectivity is due to partial overlap of the peaks in the HPLC and formation of fructose due to (expected) isomerisation under the reaction conditions.

## Bibliography

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