Supplementary Information (SI) for Green Chemistry.

Electronic supplementary Information

Continuous Flow tube-in-tube Oxidation of HMF to FDCA Using Heterogeneous Manganese Catalyst Under Mild Conditions.

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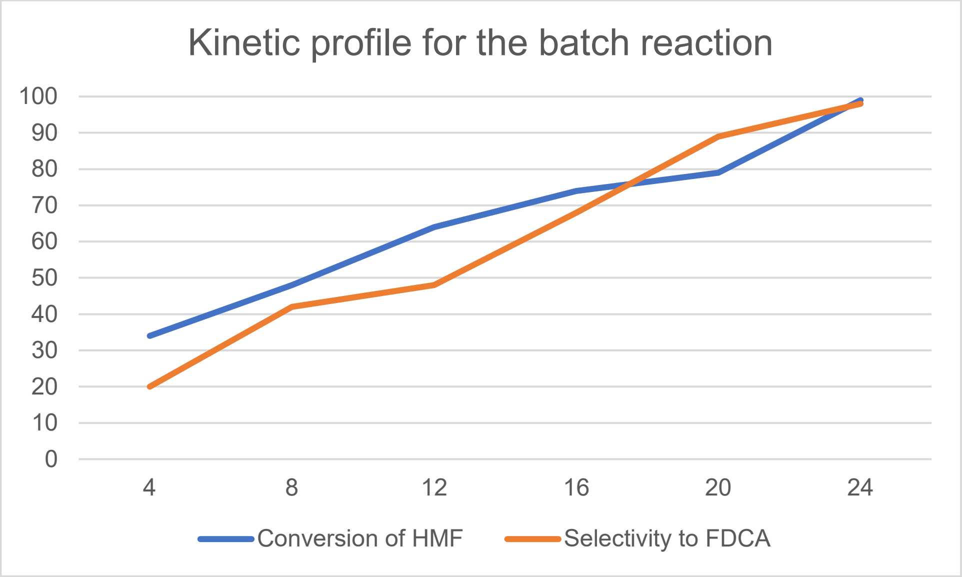
1. General Remarks

General Remarks: Unless otherwise stated, all chemicals were purchased and used without any further purification. HPLC analyses were performed by using Agilent 1200 series equipped with a Diod Array Detector (DAD) and a pre-packed column Bio-Rad Aminex HPX-87H (300 mm × 7.8 mm) using as eluent isocratic 0.005 M H_2SO_4 at 45°C with flow rate 0.4 mL/min. The experimental apparatus used for the optimization of reaction conditions consists of a stainless steel 40 mL autoclave reactor installed onto a common laboratory plate used for magnetic stirring and a thermostat oil bath. Air generator for compressed air was a Claind Air-Comp with a Swagelok pressure gauge and valve installed. Flow reactors were described in the dedicated section of the ESI.

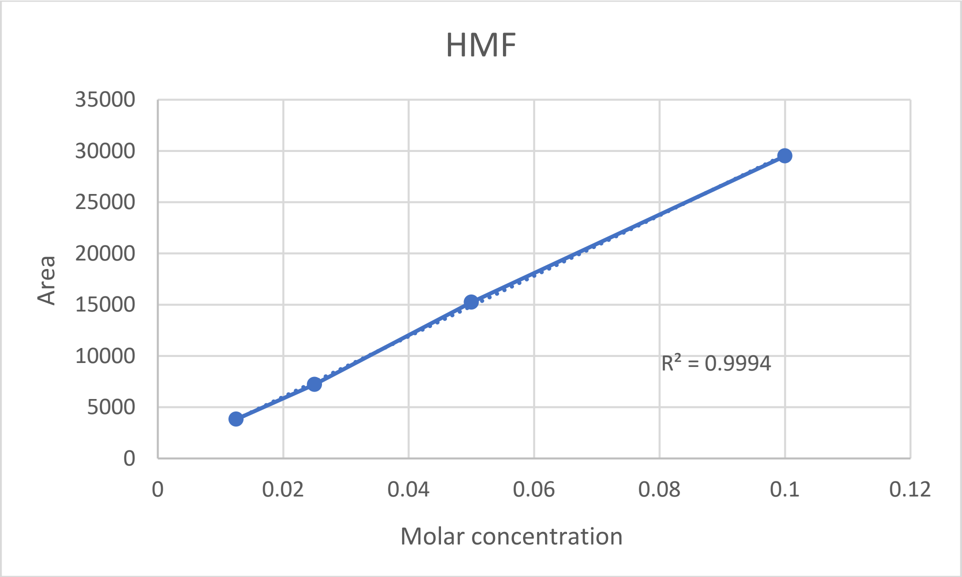
2. General Procedures

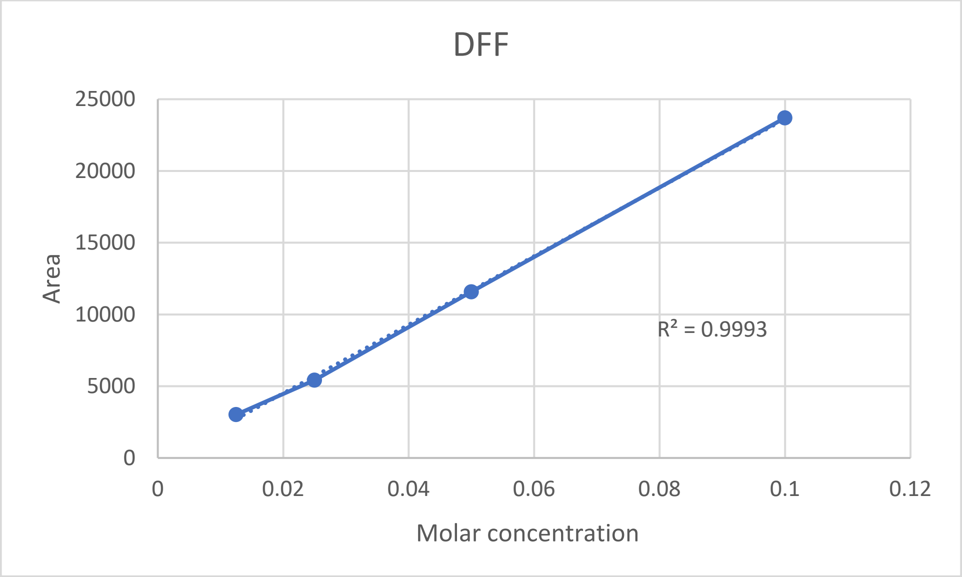
General procedure for optimization of reaction conditions in batch: In a 40 mL autoclave reactor equipped with a magnetic stirrer, HMF **1** (1 mmol), and 20 mL of a 0.1 M solution of selected base were consecutively added followed by the desired amount of catalyst (K-OMS-2 or H-OMS-2). The autoclave was properly closed, and the desired pressure of the oxidant (oxygen or air) was charged inside the reactor. The reactor was installed onto an oil bath at the desired temperature and the whole reaction was stirred for the desired time. After reaction completion the mixture was left cool to room temperature, the pressure inside the autoclave reactor was purged out and the reactor was safely opened. The whole mixture was filtrated over 4-8 μm porosity sintered glass funnel to remove the catalyst and the liquid phase was directly subjected to the HPLC analysis [method]

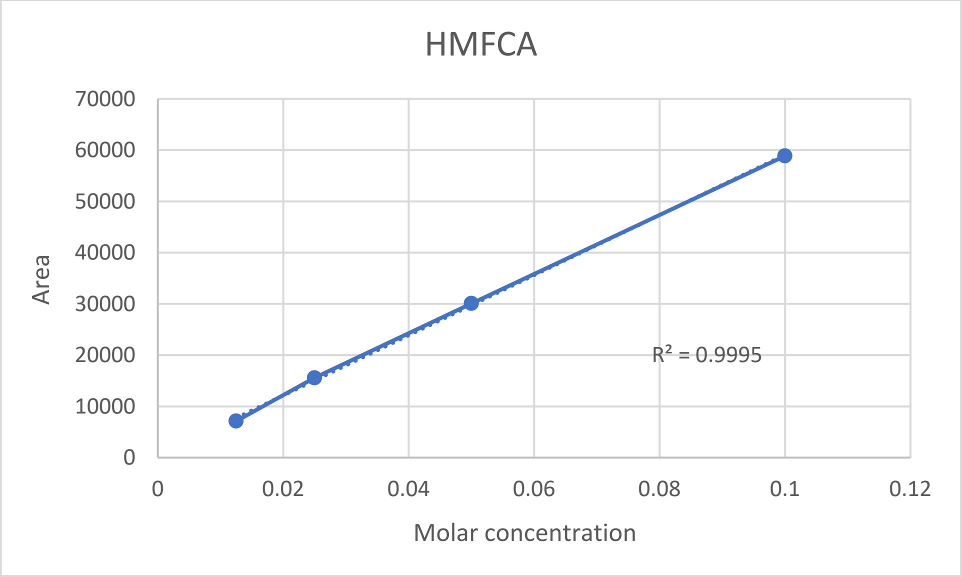
General procedure for isolation of FDCA in optimized batch conditions: In a 40 mL autoclave reactor equipped with a magnetic stirrer, HMF **1** (1 mmol), and 20 mL of a 0.1 M solution of $NaHCO_3$ were consecutively added followed by 18 mg of H-OMS-2 catalyst (20 mol % of Mn respect to HMF, being Mn amount 62 % w/w in the catalyst). The autoclave was properly closed, and 10 bar of oxygen or air were charged inside the reactor. The reactor was installed onto an oil bath at 120 °C and the whole reaction was stirred for 24 h. After reaction completion the mixture was left cool to room temperature, the pressure inside the autoclave reactor was purged out and the reactor was safely opened. The whole mixture was filtrated over 4-8 μm porosity sintered glass funnel to remove the catalyst and 30 mg of concentrated HCl were added. The mixture was left maturate at room temperature (25 °C) for 6-8 h and the white precipitate FDCA was collected in 91 % yield.

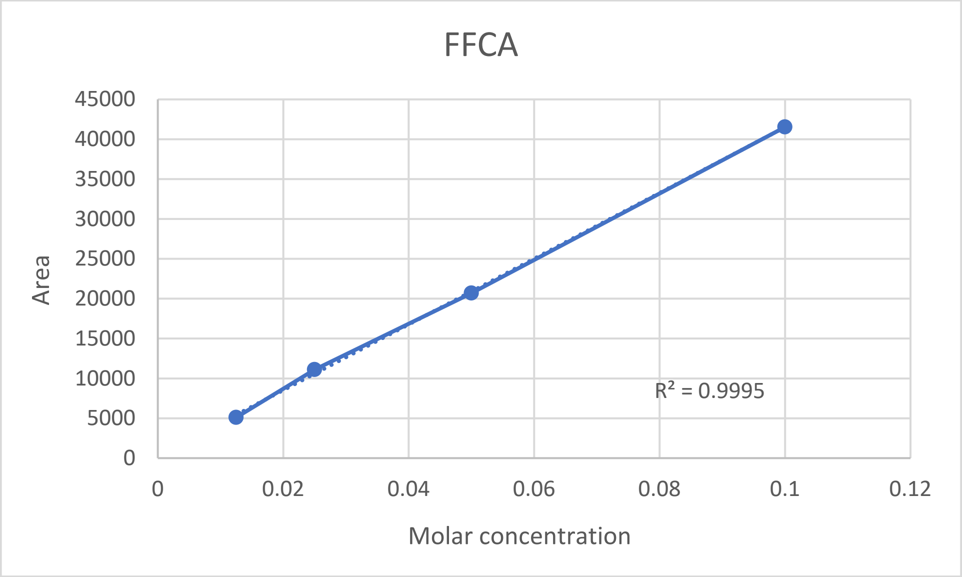


3. HPLC calibration curves






HMFCA
Area
70000
60000
50000
40000
30000
20000
10000
0
0
0.02
0.04
0.06
0.08
0.1
0.12
Molar concentration
R² = 0.9995


FFCA
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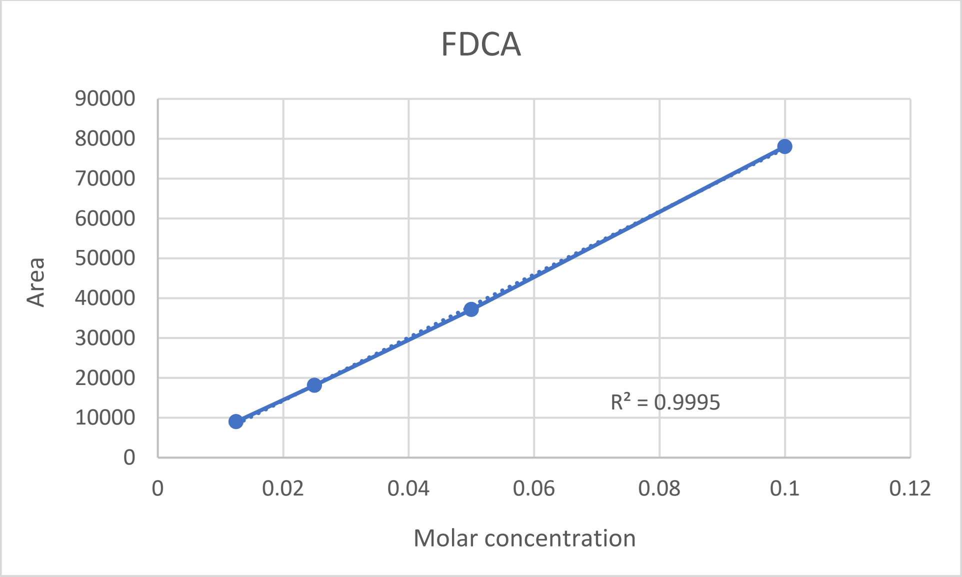
40000
35000
30000
25000
20000
15000
10000
5000
0
0
0.02
0.04
0.06
0.08
0.1
0.12
Molar concentration
R² = 0.9995


FDCA
Area
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
0
0.02
0.04
0.06
0.08
0.1
0.12
Molar concentration
R² = 0.9995

4. Flow reactors assembly details

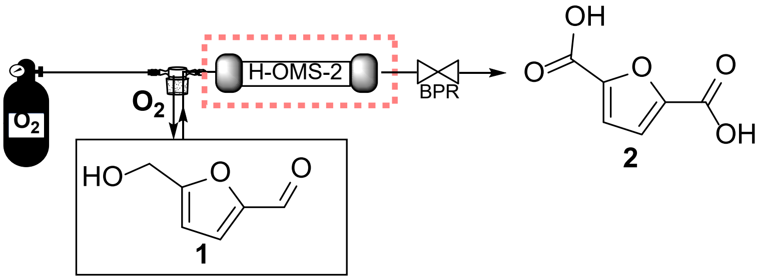


Figure S1: general set-up of Flow 1

Measures and materials of the packed bed reactor:

Length = 20 cm of PTFE tube

internal diameter = 0.4 cm

external diameter = 0.6 cm

catalyst loaded = 90 mg (100 mol % respect to 1 mmol of HMF) dispersed with 2.2 g of quartz powder

BPR: Zaiput, variable values (as of gas pressure, between 2-12 bar)

Assembly: both end caps of the packed bed reactor were realized with 316 stainless steel Swagelock nut/back ferrule/front ferrule and connected at the inlet with an ACE pressure tube modified as of Figure S2, and the outlet was directly connected with the Zaiput BPR followed by the collector reservoir.

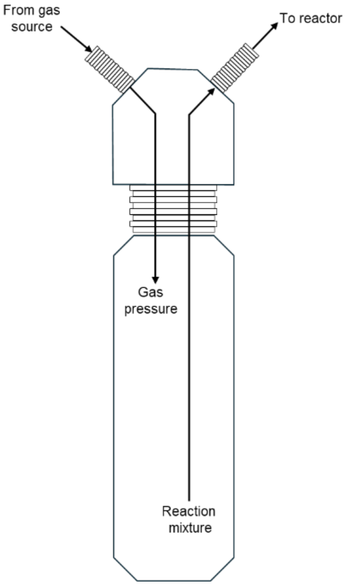
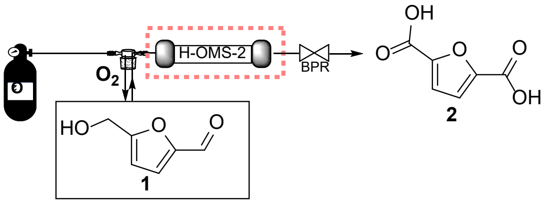


Figure S2: modified ACE pressure tube used as HMF reservoir and pressure chamber

Table S1. Oxidation of HMF to FDCA using ‘‘pump-free’’ flow system (Setting 1).[a]



Entry	O_2 (bar)	T (°C)	Residence time (h)	HMF C (%)[b]	FDCA SEL (%)[b]
1	10	120	3	13	2
2	10	100	3	9	2
3	10	100	2	0	-
4	5	120	3	0	-
5	5	100	3	0	-
6	5	100	2	0	-
7	2	120	3	0	-
8	1	120	3	0	-
9	1	120	5	0	-

[a] Reaction conditions: **1** (1 mmol), in 20 mL of 0.1 M $NaHCO_3$ water solution. Flow Reactor Parameters: Length of the packed bed reactor = 20 cm; internal diameter = 0.4 cm; catalyst loaded = 90 mg (100 mol %) [b] Conversion and selectivity, were determined by HPLC analysis, the remaining material, unless otherwise stated, is a mixture of DFF, HMFCA, FFCA and unreacted HMF **1**.

The Mean Residece Time (τ) for conditions at entry 1, with an outlet flow rate as 0.04 mL min^{-1} and a reactor volume of 2.5 mL is:

$$\tau = 2.5 / 0.04 = 62.5 \text{ min}$$

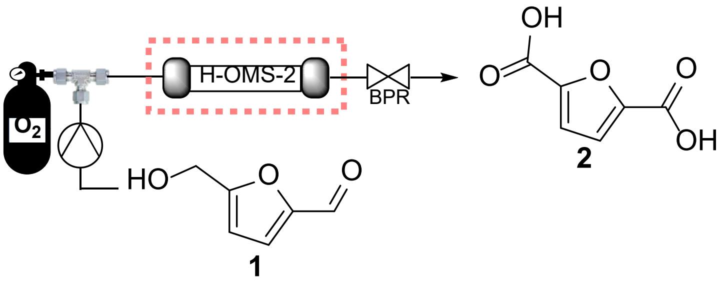


Figure S3: general set-up of Flow 2

Measures and materials of the packed bed reactor:

Length = 20 cm of PTFE tube

internal diameter = 0.4 cm

external diameter = 0.6 cm

catalyst loaded = 90 mg (100 mol % respect to 1 mmol of HMF) dispersed with 2.2 g of quartz powder

BPR: Zaiput, variable values (as of gas pressure, between 2-12 bar)

Assembly: both end caps of the packed bed reactor were realized with 316 stainless steel Swagelock nut/back ferrule/front ferrule and connected at the inlet with a 316 stainless steel Swagelock T piece configurated as of Figure S4, and at the outlet was directly connected with the Zaiput BPR followed by the collector reservoir.

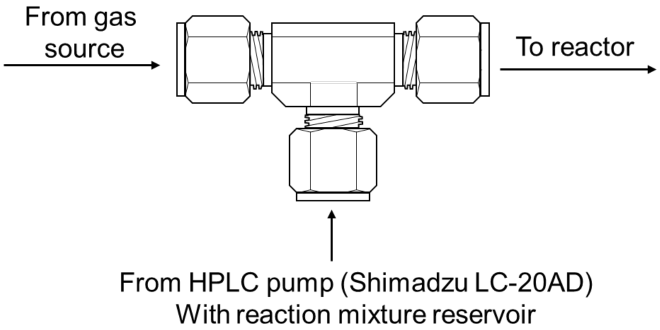


Figure S4: T piece configuration for Flow 2

The Mean Residece Time (τ) for conditions at entry 1, with an outlet flow rate as 0.05 mL min^{-1} and a reactor volume of 2.5 mL is:

$$\tau = 2.5/\ 0.05 = 50.0 \text{ min}$$

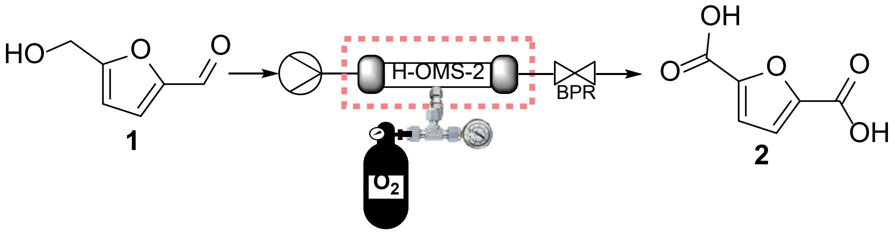


Figure S5: general set-up of Flow 3

Measures and materials of the packed bed reactor:

Total Length = 20 cm of PTFE tube (two packed bed reactor of 10 cm each)

internal diameter = 0.4 cm

external diameter = 0.6 cm

Total catalyst loaded = 90 mg (100 mol % respect to 1 mmol of HMF, 45 mg each packed bed reactor) dispersed with 2.2 gg of quartz powder

BPR: Zaiput, variable values (as of gas pressure, between 2-12 bar)

Assembly: Two PTFE reactor were connected by a 316 stainless steel Swagelock T piece configurated as of Figure S6. The beginning of the first reactor and the ending of the second reactor were capped with 316 stainless steel Swagelock nut/back ferrule/front ferrule and connected at the inlet with an HPLC pump (Shimadzu LC-20AD) with reaction mixture reservoir and at the outlet was directly connected with the Zaiput BPR followed by the collector reservoir.

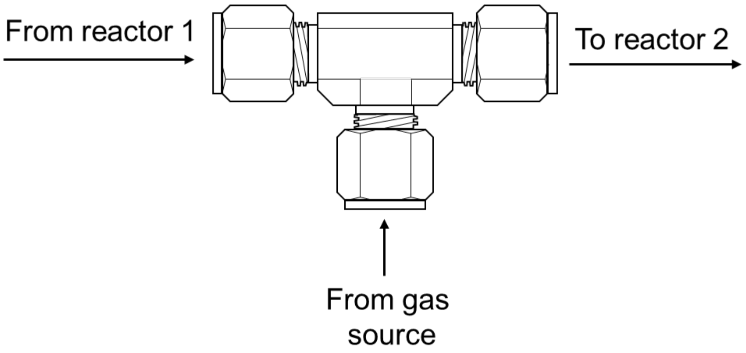


Figure S6: T piece configuration for Flow 3

The Mean Residece Time (τ) for conditions at entry 1, with an outlet flow rate as 0.03 mL min^{-1} and a reactor volume of 2.5 mL is:

$$\tau = 2.5/0.03 = 83.33 \text{ min}$$

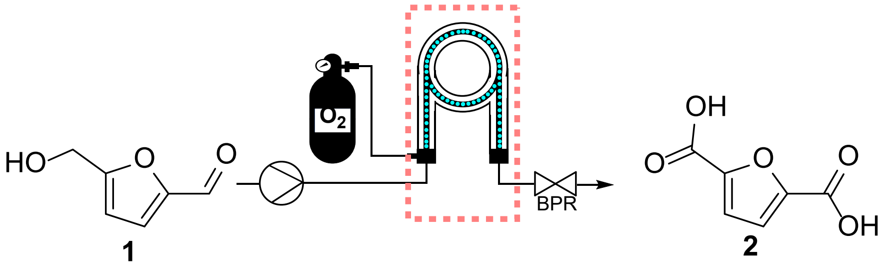


Figure S7: general set-up of Flow 4

Measures and materials of the packed bed reactor:

Length of the outside reactor = 20 cm of PTFE tube

internal diameter = 0.4 cm

external diameter = 0.6 cm

Length of the inside reactor = 20 cm of Teflon AF2400 tube

Internal diameter = 0.10 cm

External diameter = 0.16 cm

Total catalyst loaded = 36 mg (40 mol % respect to 1 mmol of HMF) dispersed with 50 mg of quartz powder

BPR: Zaiput, variable values (as of gas pressure, between 2-12 bar)

Assembly: The gas-liquid-solid reactor assembly was implemented with a section of Teflon AF2400 tube placed inside PTFE tube (0.6 cm external diameter). Each end of the resulting concentric reactor assembly was fastened to the 316 stainless steel Swagelock nut/back ferrule/ front ferrule. The liquid inlet section was connected to a stainless-steel T-piece in which the gas was supplied. The outlet section was mounted with a T-piece stainless steel connector in which a pressure gauge and a pressure release valve were connected (Figure S8). The catalyst was packed inside the Teflon AF2400 tube by placing in the tube outlet a piece of silica wool, then the catalyst was sucked into the inner tube by a vacuum pump. The inlet of the system was connected either with an HPLC pump (Shimadzu LC-20AD) or a syringe pump (NE-1010 High pressure) with reaction mixture reservoir and the outlet was directly connected with the Zaiput BPR followed by the collector reservoir.

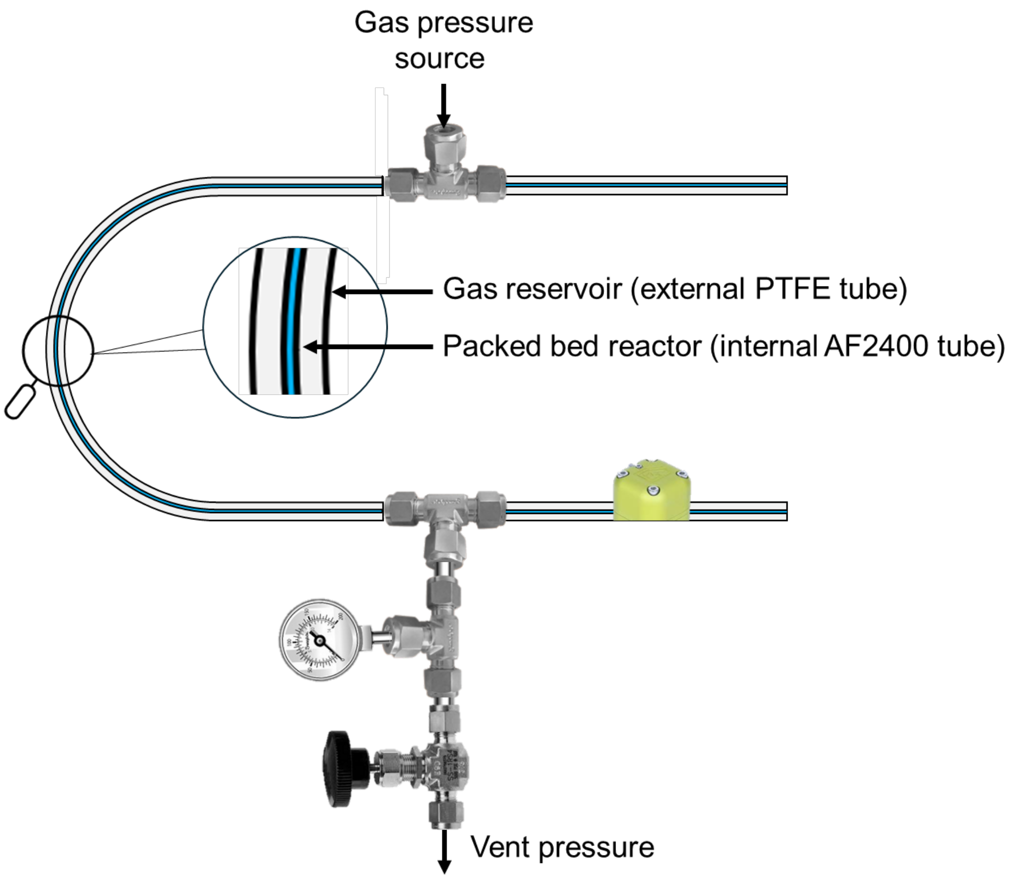
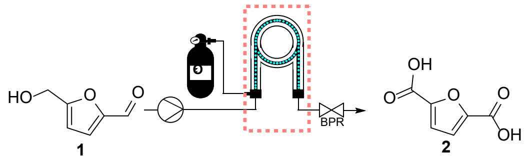


Figure S8: configuration of Flow 4

Table S2. Additional Flow parameters for Flow setting 4.[a]



Entry	O_2 (bar)	T (°C)	Residence time (h)	Set Flow Rate (mL min^{-1})	Outlet flow rate (mL min^{-1})	Outlet Gas Flow rate (mL min^{-1})	HMF C (%)[b]	FDCA SEL (%)[b]
1	10	120	3	0.12	0.005	57	84	69
2	10	100	3	0.15	0.007	54	76	72
3	10	100	2	0.17	0.008	54	65	70
4	5	120	3	0.15	0.007	28	60	68
5	5	100	3	0.15	0.007	26	54	75
6	5	100	2	0.20	0.010	26	48	70
7	2	120	3	0.17	0.007	13	34	66
8	1	120	3	0.15	0.007	6	30	61
9	1	100	3	0.15	0.006	5	24	64
10	1	120	5	0.05	0.002	6	38	62

[a] Reaction conditions: 1 (1 mmol), in 20 mL of 0.1 M NaHCO3 water solution. Flow Reactor Parameters: Length of the outer tube (gas reservoir tube) = 20 cm; internal diameter = 0.4 cm; Length of the inner tube (AF2400, packed bed) = 20 cm; internal diameter = 0.1 cm; catalyst loaded = 36 mg (40 mol %) [b] Conversion and selectivity, were determined by HPLC analysis, the remaining material, unless otherwise stated, is a mixture of DFF, HMFCA, FFCA and unreacted HMF 1..

The Mean Residece Time (τ) for conditions at entry 1, with an outlet flow rate as 0.005 mL min^{-1} and a reactor volume of 0.157 mL is:

$$\tau = 0.157/0.005 = 31.4 \text{ min}$$

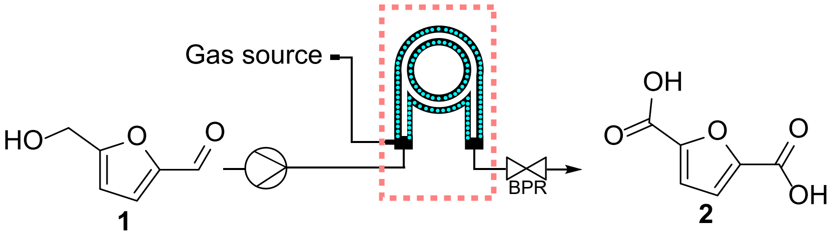


Figure S9: General set-up of Flow 5

Measures and materials of the packed bed reactor:

Length of the outside reactor = 20 cm of PTFE tube

internal diameter = 0.4 cm

external diameter = 0.6 cm

Length of the inside reactor = 20 cm of Teflon AF2400 tube

Internal diameter = 0.10 cm

External diameter = 0.16 cm

Total catalyst loaded = 36 mg (40 mol % respect to 1 mmol of HMF) dispersed with 1.8 g of quartz powder

BPR: Zaiput, variable values (as of gas pressure, between 2-12 bar)

Assembly: The gas-liquid-solid reactor assembly was implemented with a section of Teflon AF2400 tube placed inside PTFE tube (0.6 cm external diameter). Either an HPLC pump (Shimadzu LC-20AD) or a syringe pump (NE-1010 High pressure) serving as reaction mixture reservoir was connected through a 316 stainless steel Swagelock nut/back ferrule/front ferrule with the PTFE tube (external section). The inlet section (AF2400 gas reservoir), which pass through the inside whole length of the PTFE tube was fastened with a cross union 316 stainless steel Swagelock connector in which a pressure gauge a pressure release valve and the gas source were connected (Figure S10 and Figure S11). Before fastening the outline end of the reactor, the catalyst was packed inside the PTFE tube. The outlet of the resulting reactor assembly was directly connected with the Zaiput BPR followed by the collector reservoir.

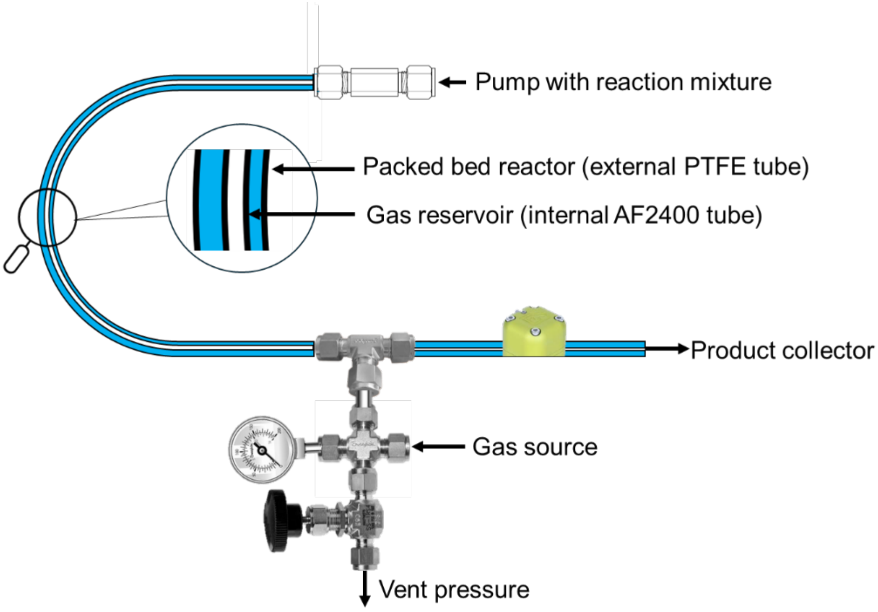
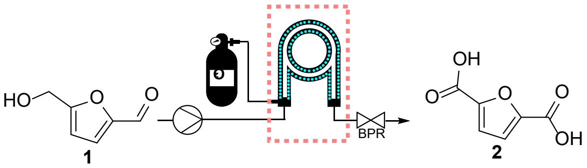


Figure S10: configuration of Flow 5

Table S3. Additional Flow parameters for Flow setting 5 using Air.[a]



Entry	Air (bar)	T (°c)	Residence time (h)	Set Flow Rate (mL min^{-1})	Outlet flow rate (mL min^{-1})	Outlet Gas Flow rate (mL min^{-1})	HMF C (%)[b]	FDCA SEL (%)[b]
1	10	120	3	0.25	0.10	3.95	> 99	100
2	10	100	3	0.30	0.10	4.10	> 99	100
3	10	100	2	0.45	0.17	4.10	> 99	100
4	5	120	3	0.35	0.12	1.80	> 99	100
5	5	100	3	0.30	0.10	2.00	> 99	100
6	5	100	2	0.50	0.18	2.00	95	100
7	2	120	3	0.45	0.15	1.10	83	85
8	1	120	3	0.35	0.12	0.48	60	43
9	1	120	5	0.30	0.10	0.48	67	59
10	2	80	5	0.15	0.08	1.25	35	56
11	5	80	5	0.15	0.08	2.30	41	62

[a] Reaction conditions: **1** (1 mmol), in 20 mL of 0.1 M $NaHCO_3$ water solution. Flow Reactor Parameters: Length of the outer tube (packed bed) = 20 cm; internal diameter = 0.4 cm; Length of the inner tube (AF2400, gas reservoir) = 20 cm; internal diameter = 0.1 cm; catalyst loaded (at the outer tube) = 36 mg (40 mol %) [b] Conversion and selectivity, were determined by HPLC analysis, the remaining material, unless otherwise stated, is a mixture of DFF, HMFCA, FFCA and unreacted HMF **1**.

The Mean Residece Time (τ) for conditions at entry 5, with an outlet flow rate as 0.1 mL min^{-1} and a reactor volume of 2.1 mL is:

$$\tau = 2.1/\ 0.1 = 21 \text{ min}$$

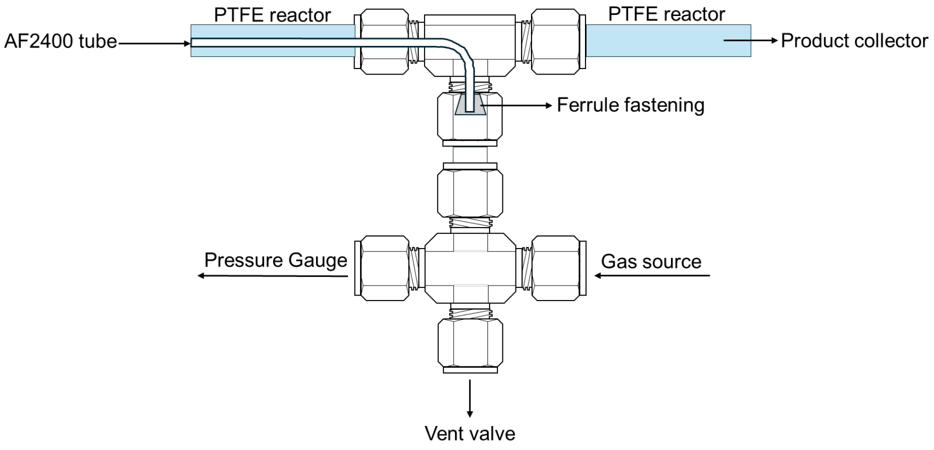


Figure S11: configuration of the cross-union connection

5. Metrics calculations

RTHI & RPHI

Reference	T (°C)	T (°K)	P (bar)	P (atm)	RTHI	RPHI
ChemSusChem 2017, 10, 654 – 658 (small scale)	100	373	10	9.871	0.777	0.00014
ChemSusChem 2017, 10, 654 – 658 (large scale)	100	373	10	9.871	0.777	0.00014
ACS Omega 2023, 8, 47846 – 47855 (K)	200	473	6	5.923	0.555	0.00727
ACS Omega 2023, 8, 47846 – 47855 (Ca)	200	473	6	5.923	0.555	0.00727
J. Chem. Sci. 2014, 126, 403–413.(Ru-OMS)	120	393	20	19.743	0.727	7.24223E-09
This work	100	373	5	4.935	0.777	0.0195

RTHI and RPHI were calculated using the following equations:

RTHI = $\exp\left[-\frac{Trxn-Tamb}{Tamb}\right]$

Where Trxn is the temperature of the reaction in °K and Tamb is 298 °K

RPHI = $\exp\left[-\frac{Prxn-Pamb}{Pamb}\right]$

Where Prxn is the pressure of the reaction in atm and Pamb is 1 atm

E-factor

Reference	Procedure	E-factor
ChemSusChem 2017, 10, 654 – 658 (small scale)	A typical procedure for the catalytic oxidation of HMF was as follows. HMF (0.2 mmol), activated MnO_2 (0.1 g), $NaHCO_3$ (0.6 mmol), water (5 mL), and O_2 (1 MPa) were charged into the autoclave reactor. The reaction solution was heated at 100 °C for 24 h. After the reaction was completed, the catalyst was separated by filtration and the filtrate was diluted 10 times with water. The recovered catalyst was washed with water (25 mL), dried at 80 °C, and reused	E-factor = [25.2 mg (HMF) + 100 mg (MnO_2) + 50.4 mg ($NaHCO_3$) + 5000 mg (water) + 45000 mg (water) – 28.4 (FDCA)]/28.4 (FDCA) = 1765 Note: E-factor became 1762 (if 100 mg of the catalyst are not accounted as recyclable, while as declared by the authors, the recycling need 25 mL of water leading to an E-factor value of 2642.5)
ChemSusChem 2017, 10, 654 – 658 (large scale)	A procedure for the larger-scale catalytic oxidation of HMF was as follows. HMF (2.23, g, 17.65 mmol), activated MnO_2 (10 g), $NaHCO_3$ (3.02 g, 36.00 mmol), water (90 mL), and O_2 (1 MPa) were charged into the autoclave reactor. The reaction solution was heated at 100 °C for 24 h. After the reaction was completed, the catalyst was separated by filtration. The filtrate was evaporated to dryness to give the yellow powders. Addition of 12 M HCl (30 mL) into the aqueous solution (40 mL) containing the resulting yellow powders leads to the formation of crude products. The crude products were dissolved in ethanol (350 mL) followed by addition of activated carbon (2.0 g) into the solution to remove unidentified by-products. The activated carbon was separated by filtration, and the resulting filtrate was evaporated to dryness to give the analytically pure FDCA (2.36 g, 86% yield)	E-factor = [2.23 g (HMF) + 10 g (MnO_2) + 3.02 g ($NaHCO_3$) + 90 g (water) + 35.4 g (HCl 12 M, d: 1.18) + 40 g (water) + 2 g (carbon) + 276.15 g (EtOH, d: 0.789) – 2.36 (FDCA)]/2.36 (FDCA) = 193.4 Note: E-factor would become 189.16 (if 10 g of the catalyst are not accounted as recyclable, while authors do not report the recyclability procedure for this larger scale reaction)
ACS Omega 2023, 8, 47846 – 47855 (K)	HMF (0.25 mmol, 32 mg) was dissolved in H_2O (5 cm^3) and then 1 mol/dm^3 of $NaHCO_3$ (3 equiv). The catalysts were used by calculating the same amount of manganese oxide at 100 mg based on mass % in each element from MP-AES analysis. After that the catalysts of activated commercial MnO_2 (100 mg), K−MnO_2 (125 mg), or Ca−MnO_2 (125 mg) was directly added into the reactor and pressurized with O_2. After completion of the reaction, the internal solution was quenched by 1 mol/dm3 of HCl and the solid catalyst separated out by centrifugation at 7500 rpm for 10 min. The crude products were collected and washed by methanol and DI water several times. (Yield FDCA: 49%, 19.1 mg)	E-factor = 31.5 mg (HMF) + 5000 mg (water) + 63 mg (NaHCO3) + 3960 mg (MeOH, d:0.792) + 5000 mg (water) – 19.12 mg (FDCA)/19.12 mg (FDCA) = 734.1 Note: 1) 5 mL of MeOH and 5 mL of water were accounted for the final washing 2) catalyst is not accounted because is recycled
ACS Omega 2023, 8, 47846 – 47855 (Ca)	HMF (0.25 mmol, 32 mg) was dissolved in H_2O (5 cm^3) and then 1 mol/dm^3 of $NaHCO_3$ (3 equiv). The catalysts were used by calculating the same amount of manganese oxide at 100 mg based on mass % in each element from MP-	E-factor = 31.5 mg (HMF) + 5000 mg (water) + 63 mg (NaHCO3) + 3960 mg (MeOH d:0.792) + 5000

	AES analysis. After that the catalysts of activated commercial MnO_2 (100 mg), $K-MnO_2$ (125 mg), or $Ca-MnO_2$ (125 mg) was directly added into the reactor and pressurized with O_2. After completion of the reaction, the internal solution was quenched by 1 mol/dm3 of HCl and the solid catalyst separated out by centrifugation at 7500 rpm for 10 min. The crude products were collected and washed by methanol and DI water several times. (Yield FDCA: 85%, 33.2 mg)	mg (water) – 33.16 mg (FDCA) /33.16 mg (FDCA) = 422.8 Note 1) 5 mL of MeOH and 5 mL of water were accounted for the final washing 2) catalyst is not accounted because is recycled
J. Chem. Sci. 2014, 126, 403–413.(Ru-OMS)	The procedure for the isolation is not described	-
This work	**1 mmol Flow experiment:** A solution of 126 mg (1 mmol) of HMF, 168 mg (2 mmol) of $NaHCO_3$, in 20 mL of water was charged in a 60 mL syringe and installed in a high-pressure syringe pump (NE-1010). The syringe pump was connected to the preheated flow system assembly (Flow 5) and the flow was started at 0.1 mL min^{-1}. After the whole reaction mixture is collected at the outlet of the flow system, 30 mg of HCl (12 M) were dropped into the product reservoir and the mixture was left maturate for 6 h at 25°C. Filtration of the precipitate furnished 145 mg of FDCA (93% yield) **72 h Flow experiment (24 mmol)** A solution of 3.0 g (24 mmol) of HMF, 4.0 g (2 equiv.) of $NaHCO_3$, in 480 mL of water was prepared in a Duran bottle and installed to a Shimadzu HPLC pump (LC-20AD). The pump was connected to the preheated flow system assembly (Flow 5) and the flow started at 0.1 mL min^{-1}. After the whole reaction mixture is collected at the outlet of the flow system, 720 mg of HCl (12 M) were dropped into the product reservoir and the mixture was left maturate for 8 h at 25°C. Filtration of the precipitate furnished 3.48 g of FDCA (93% yield)	E-factor (1 mmol) = [126 mg (HMF) + 168 mg ($NaHCO_3$) + 20000 mg (water) + 30 mg (HCl, 12M) – 145.17 mg (FDCA)]/145.17 (FDCA) = 139.0 E-factor (24 mmol) = [3.0 g (HMF) + 4.0 g ($NaHCO_3$) + 480 g (water) + 0.72 g (HCl, 12M) – 3.48 g (FDCA)]/3.48 g (FDCA) = 139.0

STY

Reference	Product (g)	Volume of reactor (L)	Time (h)	STY ($g\ L^{-1}\ h^{-1}$)
ChemSusChem 2017, 10, 654 – 658 (small scale)	0.028	0.013	24	0.08974359
ChemSusChem 2017, 10, 654 – 658 (large scale)	2.55	0.3	24	0.354166667
ACS Omega 2023, 8, 47846 – 47855 (K)	0.019	0.02	24	0.039583333
ACS Omega 2023, 8, 47846 – 47855 (Ca)	0.033	0.02	24	0.06875

J. Chem. Sci. 2014, 126, 403–413. (Ru-OMS)	0.145	0.05	6	0.483333333
This work	0.145	0.0025	3	19.12

STY is calculated using the following equation: $\frac{\boldsymbol{Product\ (g)}}{\boldsymbol{Volume\ (L)\times Time\ (h)}}$

Oxygen Efficiency

Reference	Vreactor (mL)	Vreaction (mL)	V tot (mL)	P(bar)	mmol O_2	mmol product	Oxygen efficiency
ChemSusChem 2017, 10, 654 – 658 (small scale)	13	5	8	10	3.23	0.18	8.4 %
ChemSusChem 2017, 10, 654 – 658 (large scale)	300	90	210	10	85.00	15.14	26.7 %
ACS Omega 2023, 8, 47846 – 47855 (K)	20[a]	5	15	5.2	3.15	0.12	5.7 %
ACS Omega 2023, 8, 47846 – 47855 (Ca)	20[a]	5	15	5.2	3.15	0.21	10.0 %
J. Chem. Sci. 2014, 126, 403–413.(Ru-OMS)	50	20	30	20	24.21	0.93	5.8 %
This work	The Air flow that exits the reactor is measured as 2 mL min^{-1} that is 120 mL h^{-1}. In 3 h of continuous flow (at the steady state) the total volume of Air is 360 mL. Which furnish 14.53[b] mmol of Air and therefore 3.05 mmol of Oxygen (21%).				3.05	0.93	45.7 %

[a] The volume of 20 mL is approximated as in the publication there is no mention of the reactor volume

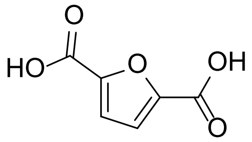
[b] Calculated as n = P (1 bar, as measured at ambient pressure) * V (0.36 L) / R * T (298, measured at room temperature)

Oxygen efficiency is calculated using the following equation: $\frac{O_2\text{-}equiv}{\frac{mol\ oxygen}{mol\ product}}\ \text{x}\ 100$

With O_2-equiv is the stoichiometric coefficient of molecular oxygen in the reaction (that for the process in exam, is 1.5 based on the balanced equation below) and the moles of Oxygen used were calculated using PV = nRT using R = 0.08314 L bar K^{-1} mol^{-1}. The total volume used (Vtot) is calculated by Vreactor – Vreaction. The temperature used in the equation is always 298 °K because the pressure is charged at room temperature in all the literature experiments analyzed and for our protocol the oxygen flow at the outlet has been experimentally measured at the temperature of 298 °K.

$$\begin{array}{lcl}
C_6H_6O_3 + 1/2\ O_2 & \longrightarrow & C_6H_4O_3 + H_2O \\
C_6H_4O_3 + 1/2\ O_2 & \longrightarrow & C_6H_4O_4 \\
C_6H_4O_4 + 1/2\ O_2 & \longrightarrow & C_6H_4O_5 \\
\hline
C_6H_6O_3 + 3/2\ O_2 & \longrightarrow & C_6H_4O_5 + H_2O \\
\textit{(HMF)} & & \textit{(FDCA)}
\end{array}$$

6. NMR spectra and data of isolated FDCA



^{1}H NMR (400 MHz, d_6-DMSO) δ 7.29 (s, 2H), 13.61 (broad s, 2H). **^{13}C NMR** (101 MHz, d_6-DMSO) δ 158.9, 147.0, 142.2, 118.4.