Selective Aerobic Oxidation of *para*-Xylene in Sub- and Supercritical Water. Part 3: Effects of Geometry and Mixing in Laboratory Scale Continuous Reactors.†

Eduardo Pérez,*[a] Morgan L. Thomas,[a] Duncan Housley,[a] Paul A. Hamley,[a] Joan Fraga-Dubreuil,[a] Jun
5 Li,[b] Edward Lester,[b] and Martyn Poliakoff*[a]

SUPLEMENTARY DATA

Experimental section

The scheme of the oxidation rig (using reactor configuration = TB as example) is shown in Figure S1. All the experiments were
10 conducted using tubular continuous flow reactors. The continuous oxidation was carried out in high temperature water (HTW),
either sub- or supercritical, using aqueous solutions as catalysts. Concentration of p-xylene is relatively diluted (0.5% organic
w/w). An aqueous solution of H_2O_2 of 2% vol. was used as the source of O_2. That solution is driven via a reciprocating pump,
which allows for accurate control of the O_2:substrate ratio. The H_2O_2 solution was pumped into the system and decomposed in a
coiled pre-heater under the required experimental conditions to generate a homogeneous mixture of O_2 and SCW. The residence
15 time in the pre-heater was long enough to achieve total decomposition of H_2O_2.

For most of the experiments displayed in Tables 1-2 and Figure 3, the volumetric flow rate through the rig was 12 mL/min. The
water/H_2O_2 flowrate was 8 mL/min; the catalyst flowrate was 4 mL/min and the organic flowrate was 0.06 mL/min. Catalyst
strength is typically 7.7 mM feed (2.6 mM in reactor). For OR, the residence time should lie between 2.3 and 3.3 at 380 ºC and
20 between 7.4 and 11.9 s at 330 ºC, as an approximation, we take the average values (i. e. 2.8 s at 380 ºC and 9.65 s at 330 ºC). For
TB, residence times are calculated, 5.8 s at 380 ºC and 19.2 s at 330 ºC. For some entries, residence times are varied from these
values, the proportion water/H_2O_2:catalyst:organic flowrates is kept 8:4:0.06 mL/min and total flowrate is modified in each case
to match the reported residence times. At the reactor outlet, the mixture was quenched with a solution of NaOH 1M to prevent
precipitation of TA and to keep CO_2 in solution in the form of carbonate. Quench solution flowrate: 3.5 mL/min. All the
25 chemicals were purchased from Aldrich Ltd and used without further purification.
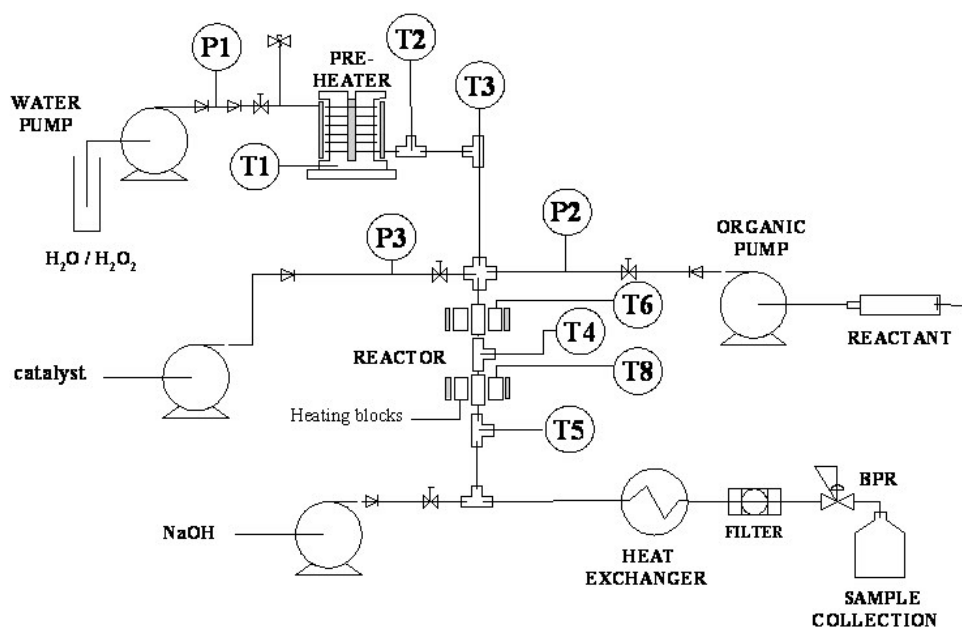

Figure S1. Configuration of the continuous aerobic oxidation reactor. P1-3 pressure transducers.
T2-5: log temperatures. T1, T6 and T8: control temperatures.

30 All the reactors were made of Hastelloy C276 pipe ¼ inch. external diameter and 0.46 cm inner diameter. For TB, the catalyst and
organic were delivered from the sides by 1/16 inch hastelloy alloy pipes of 0.57 mm inner diameter.

**CAUTION: This type of oxidation is potentially hazardous, and must be approached with care and a thorough safety
assessment must be made.** The apparatus is regularly hydrostatically pressure tested. Before every run, water was pumped at 230

bar and room temperature at the desired flowrates. It was then heated. Once the operating temperature had been reached, the pumps for the reactants were started. Typically, an experiment was run for 40 minutes. The products were collected for sequential periods of 5 min and analysed.

5 Analysis of the products was done by HPLC. A Waters Xterra reverse phase C18 column, maintained at 37 °C, was used (flow rate 0.7 mL/min, run time 15 min; UV detection at 230 nm). Solvents acetonitrile (ACN) and CH_3CO_2Na/CH_3CO_2H buffer were used. The method was as follows: isocratic method (16.7% ACN) for the first 4 minutes; 4-8 min, gradient method (16.7 to 40% ACN); back to isocratic method (16.7% ACN) for the last 7 minutes. The stock buffer solution was prepared by dissolving 15 g CH_3CO_2Na anhydrous in 250 mL de-ionised water, before adding CH_3CO_2H (50% v/v, 100 mL). The pH was adjusted to 3.9 with
10 5% CH_3CO_2H, before diluting to 500 mL. The dilute buffer was prepared by diluting 30 mL of the stock buffer solution to 500 mL with de-ionised water. The following species are quantified by HPLC: Terephthalic acid (TA), 4-methyl-benzaldehyde (p-tolualdehyde, pTOL), 4-hydroxymethyl benzoic acid (HMBA), p-toluic acid (PTA), 4-carboxybenzaldehyde (4CBA), benzoic acid (BA). The selectivity for each compound was calculated as the concentration of that compound divided by the sum of those of the six aromatic compounds. The yield of TA, Y_{TA}, was calculated by Equation 1

$$15 \quad Y_{TA} = 100 \frac{[TA]}{[pX]} \tag{1}$$

where [pX] is the molar concentration of pX in the sample if the conversion had been 0. i.e. allowing for dilution. $[pX] = (F_{pX} \times \rho_{pX})/(F_{total} \times M_{pX})$, where F_{pX}, F_{total} are the flowrates of pX and the total flow after quench; ρ_{pX} and M_{pX} are the density and molar mass of pX respectively.

20 The analysis for phenols and benzene was not done because they are present only in very small amounts. Phenols are present in very small amounts because they are oxidized much more rapidly than pX. Benzene is present in very small amounts because it would require the consecutive decarboxylation of terephthalic acid to benzoic acid and then benzoic acid to benzene.

CO_3^{2-} concentration was measured by titration of the sample with HCl 0.2N. The difference between the first two titres was used
25 to calculate the carbonate concentration. The first titre accounts for the excess OH^- and the second for the protonation of CO_3^{2-} to HCO_3^-. An autotitrator METROHM (785 DMP titrino) was used.

Results

Table S1 show the dependence of the results on the length of the pipes protruding for a TB reactor. These are the original data for the Figure 3. apart from the effects described in the paper, we can see the presence of small amount of intermediates for
30 configurations different than TB-3. Also, a big error is associated to those values.

Table S1 Results obtained using the TB-type reactors.

| entry | Reactor | Yield, mol % | | Selectivity | | | | | |
		CO_2	TA	TA	PTA	4-CBA	HMBA	pTOL	BA
1[i]	pmTB	17.6 (0.4)	20 (2)	41 (1.7)	29.5 (0.4)	9(4)	2.4 (0.4)	12 (0.9)	7.1 (0.3)
2[ii]	TB-1	29 (1)	35 (9)	69 (12)	14(9)	3(3)	0	0	14 (1.8)
3[iii]	TB-2	26 (0.8)	38 (1.4)	73 (6)	12(5)	3(2)	0	0	13.1 (0.5)
4[iv]	TB-3	24.1 (0.4)	55 (0.6)	89 (1.8)	1.8 (1.2)	0	0	0	9.5 (0.6)
5[v]	TB-3	22 (3)	57 (1.5)	91 (0.9)	0.2 (0.3)	0	0	0	8 (0.6)

The catalyst is $Cu/NH_4/Br = 0.15/1.7/2.0$; T=380 °C. Residence time is 5.8 s. [i]Average of two duplicated experiments done within few days and by different operators. [ii]Average of five duplicated experiments each after a manipulation of the reactor. [iii]Average of two duplicated experiments each after a manipulation of the reactor. [iv]Average of three duplicated experiments each after a manipulation of the reactor. [v]Average of two duplicated experiments
35 separated by 3 years and carried out by different operators. Values between brackets are standard deviations.

In order to lower the CO_2 yield by improving the oxygen distribution along the reactor, two small holes were drilled at 2.5 cm from the end of the water/oxidant pipe. The concentration of oxygen and the flowrate are modified. Results are gathered in table S2.

40 **Table S2** Results obtained using the drilled Opposed Flow reactor (dOF).

| entry | $[O_2]$ [a] | Residence time / s | Yield, mol % | | Selectivity | | | | | |
			CO_2	TA	TA	PTA	4-CBA	HMBA	pTOL	BA
1	1.5	2.8	29.0	53.1	76.7	8.5	3.7	0.0	0.0	11.1
2	1.5	4.1	27.7	56.3	82.1	3.7	2.6	0.0	0.0	11.6

3	3.0	1.7	28.3	41.6	61.9	19.4	6.6	3.3	0.0	9.9
4	3.0	2.8	35.1	48.6	81.6	4.5	1.4	0.0	0.0	12.5

Temperature is 380 ºC. Feed is the same than for previous experiments except the water/oxidant one where O_2 concentration and flowrates are varied.
[a]Concentration relative to the stechiometric amount to oxidize all the pX.

As shown in entry 1, and comparing it to entry 3 in table S3, dOF gives slightly better results than OF in terms of TA and CO_2 yield but TA selectivity is slightly lower. Increasing residence time (entry 2) leads to better TA yield and selectivity as well as fewer amounts of intermediates and CO_2. dOF may suppose an improvement to OF but O_2 concentration and water flowrate must be chosen carefully. A double oxygen concentration decreases TA yield and gives much higher burn.

Table S3 shows a comparison of the performance of some of the reactors used. Those data are the table 2 expanded. Notice that secetivity for intermediates is higher for OF reactors than for TB reactors. Amount of 4-CBA is relatively high at 330 ºC.

Table S3 Comparison of the performance of the reactors used.

				Yield, mol %		Selectivity						CB[b]
entry	Reactor	T / ºC	RT[a] / s	CO_2	TA	TA	PTA	4-CBA	HMBA	pTOL	BA	
1	TB-3	380	5.8	22	57	91	0.2	0	0	0	8	84
2	OF	380	5.6	25-31	52	81-84	3	1-3	0	0	13	88-94
3	OF	380	2.8	30	51.8	80.1	5.6	2.5	0.0	0.0	11.8	95
4	dOF	380	2.8	29	53.1	76.7	8.5	3.7	0.0	0.0	11.1	98
5	TB-1	330	18.9	21	42	57.4	18.5	19.7	0.0	0.0	4.3	94
6	TB-3	330	18.9	21	41.8	60.8	21.4	14.0	0.0	0.0	3.7	89.9
7	pmTB	330	18.9	18	29	57.4	16.8	19.7	0.0	1.5	4.3	69
8	OF	330	8.9	14.5	11.5	14.9	45.9	21.3	1.5	14.5	1.9	91

[a]Estimated residence time; [b]Carbon balance closure.

Finally, Table S4 gives the expanded data for Table 3. At high concentrations of reactants, High TA yield and selectivity are obtained with a relatively low amount of CO_2 and BA formed using TB and long enough residence time (see entry 3). Low amounts of intermediates are also obtained.

Table S4 Comparison between TB and OF using higher reactant concentrations and Cu/Co/H/Br catalyst. T = 330 ºC.

			Yield, mol %		Selectivity						CB[d]
entry	Reactor	RT[c] / s	CO_2	TA	TA	PTA	4-CBA	HMBA	pTOL	BA	
1[b]	TB-1	19.1	8.5(1)	41 (2)	56(4)	27 (0.3)	9.3 (1.3)	2 (3)	1.0 (1.3)	4.1 (1.1)	87 (3)
2[b]	OF	8.3	8	59 (2)	74(2)	14.1 (0.4)	6.3 (1.2)	0	0.3 (0.4)	6(2)	93 (5)
3[a]	OF	17.3	10	62.8	89.4	3.2	1.7	0	0.9	4.8	81

[a]Total flowrate was reduced to give higher residence time; [b] average of two duplicate experiments. Values between brackets are standard deviations; [c]Estimated Residence time. [d]Carbon balance closure