PAPER

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 Li,[b] Edward Lester[b] and Martyn Poliakoff*[a]

In this paper we report a strong dependence of the observed performance of the catalyst on the geometry and the configuration of laboratory scale reactors in the continuous aerobic oxidation of *p*-xylene in supercritical water. Small differences, such as the length of the feed pipes protruding into the reactor, have a very large effect on the observed yields and selectivities as well as on the reproducibility of the results. Different reactor designs also exert an influence on the perceived catalyst performance. We demonstrate that these effects are consistent with the relative efficiency of mixing of the reactant streams in the different reactors. The overall conclusion is that caution is required when comparing sets of data derived from studying such reactions even in apparently similar experimental arrangements.

Introduction

Terephthalic acid (TA) is a high-volume commodity chemical. It is a main component of many types of polyester such as PET. TA is currently produced by the aerobic oxidation of *p*-xylene (*p*X) using acetic acid as a solvent. Several studies have been published by our group,[1–7] and others[8–16] on substituting acetic acid by sub- or supercritical water (SCW) on the basis of the combination of environmental and economic advantages that SCW could bring, Scheme 1.

There have been extensive reports on the optimisation of parameters such as residence time,[1] catalyst composition[7] and
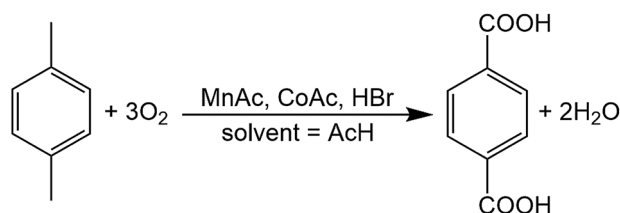
Scheme 1

[a]*School of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK. E-mail: martyn.poliakoff@nottingham.ac.uk; eduardo.velilla@nottingham.ac.uk; Fax: +44 (0)115 951 3058; Tel: +44 (0)115 951 3520*

[b]*Department of Chemical and Environmental Engineering, University of Nottingham, NG7 2RD, UK*

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temperature[1,7] but comparatively little discussion has been focussed on reactor geometry. This needs to be rectified because related work[17–20] on the synthesis of metal oxide nanoparticles in supercritical water has underlined the importance of the reactor configuration in order to control particle size and to avoid blockages. In particular Blood *et al.*[21,22] developed a visual technique to simulate the T-shaped mixing point of a reactor where an aqueous solution at room temperature is mixed with a supercritical water stream. They showed that the buoyancy of the lighter stream is important for some mixing geometries and this can affect dramatically the effectiveness of mixing and create undesirable stagnant or inhomogeneous zones. This discovery led to the invention of a nozzle-like[19,23] reactor in which the two streams encounter each other in opposed directions. The relevance of Lester's work to xylene oxidation is twofold: (i) the oxidation also involves mixing cold and supercritical water streams and (ii) the metal precursors for nanoparticles are chemically similar to the catalyst solutions used in the oxidation.

This short paper demonstrates that reactor geometry can have a significant effect on the product distribution in the oxidation of *p*X and that this effect is due, in large part, to differences in the efficiency of mixing of the various components which take part in the reaction.

Experimental

Caution: this type of oxidation is potentially hazardous, and must be approached with care and a thorough safety assessment must be made.

Our strategy has been to study the differences in performance using several reactor geometries while keeping the rest of the reaction parameters as near constant as possible.

The equipment and the experimental procedure have already been described in detail.[6,7] A simplified scheme is shown in Fig. 1. Reactions were carried out in a continuous fashion. An aqueous H_2O_2 solution was passed through a coiled pre-heater at supercritical temperature long enough to achieve total decomposition of the H_2O_2 solution to form a homogeneous mixture of O_2 and supercritical water. Unless otherwise stated, the concentration of H_2O_2 in the feed solution was 2% by w/w and the flow rate was 8 mL min^{-1}. The organic flow rate was 0.06 mL min^{-1}, that is 0.5% w/w in the reactor. A mixture of $CuBr_2$ and NH_4Br in aqueous solution, 1.16 and 13.1 mM respectively, was fed as catalyst solution at 4 mL min^{-1}, thus giving a catalyst concentration in the reactor, expressed as the concentration of each species,[7] Cu/NH$_4$/Br = 0.39/4.42/5.2 mM. Downstream of the reactor, the liquor was quenched with a solution of 1 M NaOH, to neutralize the CO_2 originating from burn and converting it to carbonate which is thus retained in solution for offline analysis. NaOH also prevents precipitation of TA and avoids consequent blockages. The NaOH solution flow rate was 3.5 mL min^{-1}. All the chemicals were purchased from Aldrich Ltd and used without further purification.

Analysis of the products was carried out by HPLC. A Waters Xterra reverse phase C18 column, maintained at 37 °C, was used (flow rate 0.7 mL min^{-1}, run time 15 min; UV detection at 230 nm). The CO_2 generated was quantified by measuring CO_3^{2-} concentration by titration of the sample with 0.2 N HCl. Details of these procedures have been given elsewhere.[6,7]

This study is based on the two basic reactor configurations shown in Fig. 2.

The Opposed Flow reactor, OF (shown in Fig. 2a) was inspired by the nozzle-like reactor developed by Lester *et al.*[19,23] The pX pipe is concentric with the catalyst pipe and both point upwards. These upward flowing streams meet the downward flowing stream of heated $H_2O + O_2$. All the outer pipes are built using Hastelloy C276 tubing, 1/4″ (6.35 mm) outer diameter, and 4.6 mm inner diameter. The inner pipes are built using

Fig. 1 Simplified scheme of the continuous system used in this work. O_2 is generated from aqueous H_2O_2 by high temperature decomposition in a pre-heater, pH.[2] Pure p-xylene, an aqueous solution of the catalyst, and a mixture of $O_2 + H_2O$ are pumped separately into the continuous reactor by means of HPLC pumps. After the reactor, the mixture is quenched with a cold solution of NaOH that neutralizes any CO_2 to form carbonate. The detailed geometry of the reactor itself is changed between experiments.

pipes of the same alloy and 1/8″ (3.18 mm) outer diameter. This configuration exploits the buoyancy of the hot stream to enhance the mixing. All the reactants should be efficiently mixed in the middle section of the reactor ($l_1 = 6.3$ cm), after which they flow upwards along the outer section of the reactor ($l_2 = 8.5$ cm) and along a 1/4″ pipe ($l_3 = 8.5$ cm) until they meet the NaOH quench.

Residence time for this reactor cannot be calculated with high accuracy since the mixing area is located somewhat imprecisely in the middle. Nevertheless, considering the dimensions, the residence time should lie between 2.3 and 3.3 s at 380 °C and between 7.4 and 11.9 s at 330 °C, using a total ambient flow rate of 12 mL min^{-1} and the density of pure water.[24] As an approximation, we take the average values (*i.e.* 2.8 s at 380 °C and 9.7 s at 330 °C).

The second configuration (TB, shown Fig. 2b) is based on a tubular design and it is the one used in all of our previous work.[3–7] All the reactants and solvent are mixed at a 1/4″ mixing cross at the top of the reactor. The catalyst and organic are delivered from opposite sides *via* 1/16″ Hastelloy pipes of 0.57 mm inner diameter. The reactive mixture then flows downwards through a tubular reactor, at the bottom of which it is rapidly cooled by the NaOH quench solution. The reactor is constructed of Hastelloy C276 tubing, 1/4″ outer diameter, and 4.6 mm inner diameter. The length of the reactor from the mixing to the quench point, l_4, was 34 cm. Based on the density of pure water,[24] a total flow rate of 12 mL min^{-1} will give calculated residence times of 5.8 s at 380 °C and 19.2 s at 330 °C.

The importance of the TB design is that it allows the mixing efficiency to be varied without altering the other aspects of the reactor, by changing the distance by which the catalyst and pX feed pipes protrude into the cross-piece.

Results and discussion

The oxidation of TA in acetic acid is known to follow a sequence of partially oxidized intermediates:[7] *para*-xylene (pX) → 4-methyl-benzaldehyde (p-tolualdehyde, pTOL) → p-toluic acid (PTA) → 4-carboxybenzaldehyde (4CBA) → TA. Benzoic acid (BA) and CO_2 result from both decarboxylation and combustion (burn) mechanisms.[6] Cu-based catalysts have previously been shown to be particularly active.[7] Unless otherwise stated, a mixture of $CuBr_2$ and NH_4Br was used as catalyst under unsaturated concentrations, *i.e.* at a concentration lower than that needed to give the maximum yield; such so-called "stressed" reaction conditions are more sensitive to the different reaction paramenters.[7] Yields of product, by-products and intermediates were calculated as before.[6,7]

The opposed flow reactor, (OF)

The first study varied residence time (by varying flow rate) for a given reactor configuration and constant feed composition. The results are gathered in Table 1. At 330 °C, (entry 1), one observes a wide distribution of intermediates indicating that as previously observed,[7] the catalyst is not active enough at these concentrations to complete the reaction. By contrast entries 2–4
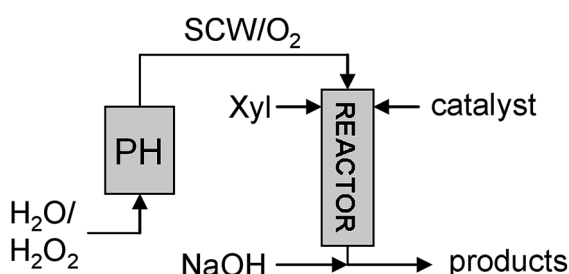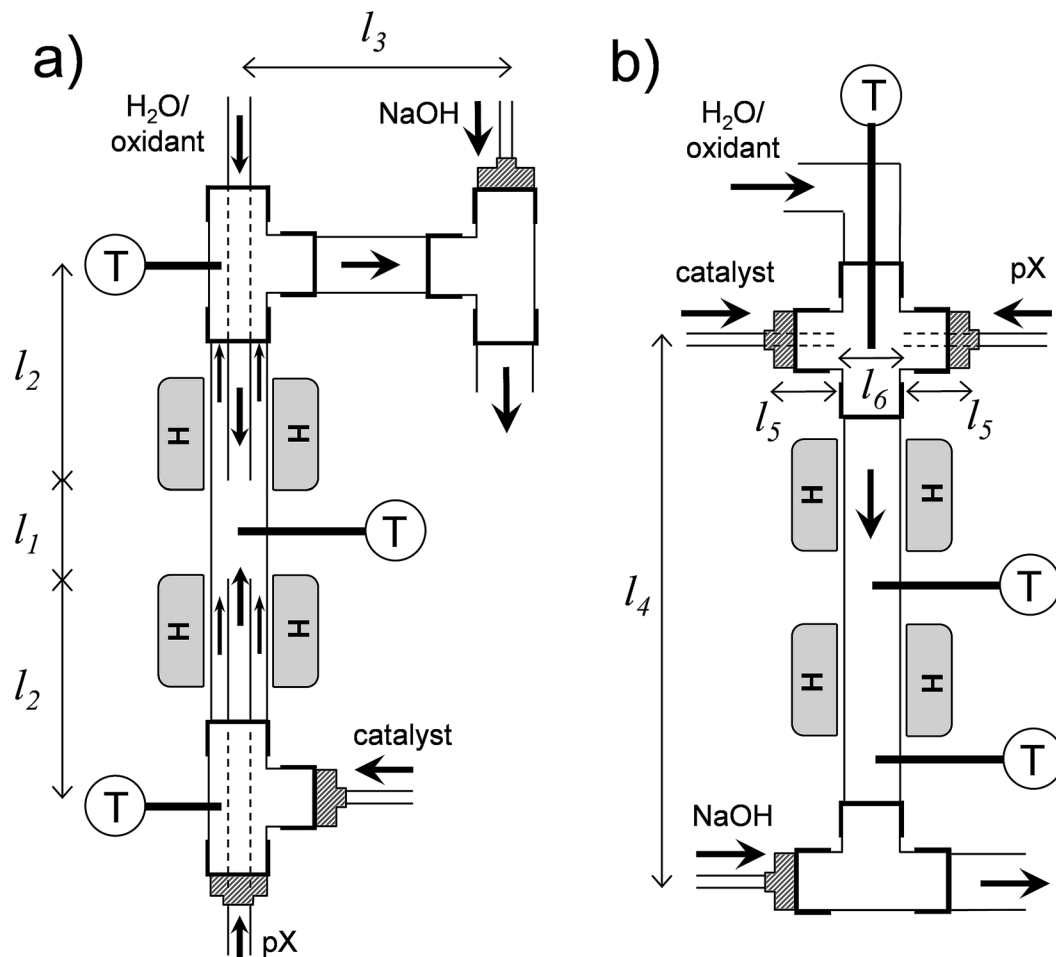
Fig. 2 The two basic configurations used in this study. (a) The Opposed Flow (OF) reactor; (b) the Tubular (TB) reactor. H are heating blocks and T are thermocouples. Important distances are labelled l_1, l_2, etc.

Table 1 Results obtained using the OF reactor[a]

| Entry | T/°C | RT[b]/s | Yield/mol% | | Selectivity | | | | |
			CO_2	TA	TA	PTA	4CBA	pTOL	BA
1	330	8.9	15	11.1	14.5	46.2	21.4	14.5	1.9
2[c]	380	5.6	25–31	52	81–84	3	1–3	0.0	13
3	380	2.8	30	52	80	5.6	2.5	0.0	12
4	380	2.2	26	51	75	11	4.3	0.0	11

[a] Catalyst is Cu/NH$_4$/Br = 0.15/1.7/2.0; flow rates were varied proportionally to obtained the different retention times. [b] Estimated residence time. [c] Due to the difficulty of controlling the organic flow rate, a range of values is given in some cases.

show that, at 380 °C, the yield of TA is almost unchanged even when the residence time is decreased by a factor of ×2. Similarly the amounts of BA and CO_2 decrease while the amounts of intermediates PTA and 4-CBA increase. These changes are not unexpected – shorter reaction time should give a less complete reaction. However, the *constant* yield of TA is surprising, suggesting that most of the TA must be formed at the beginning of the reaction along with many intermediates and, subsequently, these intermediates either burn or decarboxylate.

Potential importance of mixing

Phenix *et al.*[25] have studied the effect of mixing on the *reaction* rate of the unselective oxidation of phenol in supercritical water. In some cases, the time required to mix the organic and oxidant feeds dominated the kinetic induction time. They carried out a series of experiments varying the Reynold's number over the range of 1500–3400 and concluded that mixing is an important parameter if the Reynold's number is low *i.e.* for laminar and transitional regimes.

The high rate of the reaction that we observe in our selective oxidation experiments with OF suggests that the yield of TA may be sensitive to the efficiency of mixing of the three separate streams: high temperature $H_2O + O_2$, pX and catalyst. When the components are properly mixed, the catalyst promotes selective oxidation with formation of TA. When they are not properly mixed, the catalyst cannot operate efficiently and the oxidation becomes less selective, essentially combustion, yielding a mixture of products and CO_2. Therefore, the hypothesis is that more efficient mixing should give higher yields of TA. The OF has been shown to give efficient mixing[19,23] and is not well suited to varying the efficiency of mixing. However, the tubular

reactor, TB, offers much better possibilities for testing this hypothesis.

The mixing efficiency of a jet injected into a tubular reactor generally depends on: (a) the velocities of the jet and of the main stream.[26,27] (b) The position of the injection point, if it is located inside the reactor, can enhance mixing efficiency.[28] (c) Buoyancy effects due to density differences can also play a role;[21,22] the density of supercritical H_2O at 380 °C is only *ca.* 0.21 g mL^{-1} compared to >1 g mL^{-1} for the catalyst solution. In OF, this difference in density is exploited to improve mixing while in the TB reactors, it could hinder mixing, especially at low Reynold's numbers resulting from low fluid velocities.

Thus, to investigate the effect of mixing, we have compared four variations of the tubular reactor. TB-1, where the catalyst and *p*X feed pipes do not protrude into the T-piece (*i.e.* $l_5 = 0$, see Fig 2b). In TB-2, $l_5 = 2$ cm and, in TB-3, $l_5 = 3$ cm. This means that the gap between the ends of the feed pipes, l_6, decreases from 7 cm (TB-1) to 1 cm (TB-3). Modelling experiments to be described in a subsequent report[29] confirm that a reduced value of l_6 gives improved mixing because of the higher velocities of the fluids emerging from the narrow bore feed pipes (the velocity of the catalyst stream in the 1/16″ pipe is 0.26 m s^{-1} whereas in the larger diameter arms of the cross, it is only 0.0037 m s^{-1}, the velocity of the water stream is 0.035 m s^{-1}). In a fourth variation, pmTB, premixed *p*X and catalyst solutions were fed as a biphasic mixture into the reaction *via* a single pipe while the unused fourth arm of the crosspiece was blanked off. If the organic and catalyst are premixed at room temperature, the immiscibility of the two streams will result in an inhomogeneous feed, alternately delivering slugs of organic or catalyst solution into the reactor with poor mixing.

Therefore, we have a series of four reactors where the mixing efficiency should increase in the order pmTB < TB-1 < TB-2 < TB-3, while the other reaction parameters (temperature, residence time, *etc.*) should remain largely unchanged. Fig. 3, shows the TA yields and selectivities and selectivities for PTA and BA for experiments carried out these four configurations. The values of yield and selectivities are strongly dependent on the particular reactor as predicted on the basis of the mixing efficiency. Thus, when organic and catalyst streams are pumped into the reactor as an immiscible stream in pmTB, the TA selectivity and yield are low and the selectivity for PTA is high, 30%. By contrast, the TA selectivity and yield are greatly increased as the length of the opposed pipes protruding into the reactor is increased while the PTA selectivity decreases. The reproducibility of selectivities and yield also increases with the length of the pipes protruding. Indeed, the reproducibility for TB-3 was very good, even when the experiments were carried out 3 years apart and by different operators.

For reactors TB-1 and TB-2 results were also reproducible provided the reactors had *not* been manipulated in any way between experiments, for example, by one of the feed pipes being temporarily disconnected and reconnected. This suggests that, when using a configuration without pipes protruding significantly, the observed results could be highly sensitive to apparently trivial changes in the geometry of the reactor which
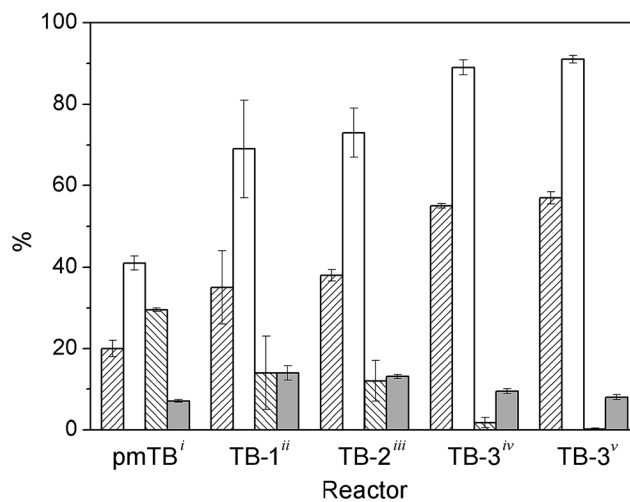

Fig. 3 Results obtained using the TB-type reactors. The catalyst is Cu/NH_4/Br = 0.15/1.7/2.0; T = 380 °C. Residence time is 5.8 s. ▨: TA yield; ☐: TA selectivity ◥: PTA selectivity; ▣: BA selectivity. [i]Average of two duplicated experiments done within few days and by different operators, [ii]average 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 separated by 3 years and carried out by different operators.

could result in much larger changes in the efficiency of the already poor mixing.

These observations are therefore consistent with the mixing of the O_2, *p*X and catalyst streams being a key factor in the overall outcome of the selective oxidation of *p*X in high temperature water.

A more quantitative comparison of the performance of some of the reactors is shown in Table 2 which includes the carbon balance closure (CB), defined as the sum of yields of all the analyzed species.

Entries 3 and 4 indicate that very similar results were obtained in OF at two different residence times. Comparison between entry 1 and entries 3, 4 shows that TB-3 gives higher TA

Table 2   Comparison of the performance of the reactors used

	Reactor	RT[a]/s	T/°C	Sel.[b]/% TA	Yield TA	BA	CO_2	CB[c]
1	TB-3	5.8	380	91	57	5	22	84
2	pmTB	5.8	380	41	20	3.5	18	68
3	OF	5.6	380	81–84	52	8	25–31	88–94
4	OF	2.8	380	80.1	51.8	7.7	30	95
5	OF	8.9	330	14.9	11.5	1.5	14.5	91
6	TB-1	18.9	330	57.4	42	3.1	21	94
7	TB-3	18.9	330	60.8	41.8	2.6	21.1	89.9
8	pmTB	18.9	330	57.6	29	2.2	18	69

[a] Estimated residence time. [b] Selectivity for TA. [c] Carbon balance closure.

Table 3 Comparison[a] between TB and OF using higher reactant concentrations and Cu/Co/H/Br catalyst. $T = 330\ °C$ and $p = 230$ bar

	Reactor	RT[d]/s	Sel.[e] %TA	Yield			
				TA	BA	CO_2	CB[f]
1[b]	TB-1	19.1	56(4)	41(2)	3(1)	8.5(1)	87(3)
2[b]	OF	8.3	74(2)	59(2)	5(2)	8	93(5)
3[c]	OF	17.3	89.4	62.8	3.4	10	81

[a] This experiment was performed with higher concentrations. The flow rates were used: water/oxidant: 0.80 mol L^{-1} at 9.7 mL min^{-1}; catalyst: $CuBr_2$/$CoBr_2$/HBr, 9.1/54.1/25.5 mmol L^{-1} 20 mL min^{-1}; p-xylene: 0.29 mL min^{-1}. [b] Average of two duplicate experiments. Values between brackets are standard deviations. [c] For this run, the total flow rate was reduced to give higher residence time. [d] Estimated residence time. [e] Selectivity for TA. [f] Carbon balance closure.

selectivity and lower CO_2 yield than does OF. In fact OF does not provide a significant improvement over TB-3 under these reaction conditions. An important fact to be taken into account is that the carbon balance is generally higher for OF at 380 °C. On the other hand, higher CO_2 and BA yields are also associated with OF.

At 330 °C, the TA selectivities and yields are generally lower than for 380 °C. This is to be expected since the $CuBr_2$/NH_4Br catalyst has been reported to be much less active at 330 °C.[7] However, at 330 °C, the differences between reactors were not as large as at 380 °C; TB-1 and TB-3 gave similar values. At 330 °C, pmTB still gives lower TA yield than TB-3 but the difference is much less than at 380 °C. OF gives much worse results than TB-3 probably because the residence time is significantly lower in OF. These results are consistent with the idea of the mixing efficiency influenced by buoyancy effects, because at 330 °C, the difference between the hot water stream (0.68 g mL^{-1}) and the catalyst solution (1.01 g mL^{-1}) is not as large as at 380 °C (0.21 g mL^{-1} and 1.01 g mL^{-1} respectively), and presumably, buoyancy effects are less important at 330 °C.

A series of experiments was performed to investigate how the performance of TB-1 and OF compared when the reaction was carried out with the catalyst, $CuBr_2$/$CoBr_2$/HBr at saturated conditions. This catalyst has its highest activity at 330 °C.[7] The results are summarized in Table 3.

Comparison between entries 1 and 2 in Table 3 shows that, with this catalyst, OF performed better than TB-1 even at lower residence times. When the flow rates were reduced to get comparable residence times (entry 3), TA selectivity and yield of 89 and 63% respectively were achieved with relatively low combustion (10% CO_2 yield). These experiments show that, although mixing is important, other factors such as concentration and the nature of the catalyst also play a significant role in determining the overall performance of a reactor.

Conclusions

The experiments described in this paper emphasize the role of mixing in this selective oxidation reaction. Although a bench-scale continuous reactor is a convenient way to study such reactions, one must be aware that the detailed geometry of the reactor may have a strong influence on the results. Apart from the shape of the reactor, other factors such as mixing efficiency, temperature and velocity of the mixing streams can have a significant influence. The type of flow regime is likely to be of importance in the bench-scale reactors; in a scaled-up system, turbulent flow is preferred and some of these factors will have less influence but they need to be taken in to account on the laboratory scale.

We believe that the results presented here are important because, if green chemistry is to have real impact, it needs to tackle the manufacture of bulk chemicals such as TA. However, conducting high pressure/high temperature oxidation reactions in a laboratory is a relatively specialized task and is never likely to be carried out in more than a limited number of laboratories. Therefore it is particularly important that the limitations and problems of performing such reactions on a small scale are widely understood. Otherwise, undue significance may be given to specific sets of results without realising that they could be the consequence of the reactor design rather than an inherent reflection of the underlying chemistry.

Acknowledgements

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