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

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

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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 (pX) using acetic acid as a solvent. Several studies have been published by our group,1,2 and others5–16 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 composition2 and temperature1–2, but comparatively little discussion has been focussed on reactor geometry. This needs to be rectified because related work17–19 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-like19,23 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 pX 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.

Fig. 1 Simplified scheme of the continuous system used in this work. O2 is generated from aqueous H2O2 by high temperature decomposition in a pre-heater, PH.2 Pure xylene, an aqueous solution of the catalyst, and a mixture of O2 + H2O 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 CO2 to form carbonate. The detailed geometry of the reactor itself is changed between experiments.
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. A simplified scheme is shown in Fig. 1. Reactions were carried out in a continuous fashion. An aqueous H₂O₂ solution was passed through a coiled pre-heater at supercritical temperature long enough to achieve total decomposition of the H₂O₂ solution to form a homogeneous mixture of O₂ and supercritical water. Unless otherwise stated, the concentration of H₂O₂ in the feed solution was 2% by w/w and the flowrate was 8 mL/min. The organic flowrate was 0.06 mL/min, that is 0.5% w/w in the reactor. A mixture of CuBr₂ and NH₄Br in aqueous solution at 4 mL/min, thus giving a catalyst concentration in the reactor, expressed as the concentration of each species, Cu/NH₄/Br = 0.39/4.42/5.2 mM. Downstream of the reactor, the liquor was quenched with a solution of 1M NaOH, to neutralize the CO₂ 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 flowrate was 3.5 mL/min. 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, run time 15 min; UV detection at 230 nm). The CO₂ generated was quantified by measuring CO₃²⁻ concentration by titration of the sample with 0.2N HCl. Details of these procedures have been given elsewhere.

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

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 l₁, l₂, etc.

solution, 1.16 and 13.1 mM respectively, was fed as catalyst 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.\textsuperscript{10,21} 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\textsubscript{2}O + O\textsubscript{2}. All the outer pipes are built using Hastelloy C276 tubing, \(1/4\)” outer diameter, and 0.46 cm inner diameter. The length of the reactor from the catalytic entry point is 80 cm, with a total flowrate of 12 ml/min. As an approximation, we take the average values (i.e. \(2.8 \text{s at 380 } ^\circ\text{C and 9.7s at 330 } ^\circ\text{C}\)) to calculate the residence times of 5.8 s at 380 \(^\circ\text{C}\) and 19.2 s at 330 \(^\circ\text{C}\) using a total flow rate of 12 ml/min and the density of pure water.\textsuperscript{24} All the reactants and solvent are mixed at a \(1/4\)” mixing cross at the top of the reactor. The catalyst and organic 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:\textsuperscript{7} para-xylene (pX) \(\rightarrow\) 4-methyl-benzaldehyde (p-toluic acid, pTA) \(\rightarrow\) 4-carboxybenzaldehyde (4CBA) \(\rightarrow\) TA. Benzoic acid (BA) and CO\textsubscript{2} result from both decarboxylation and combustion (burn) mechanisms.\textsuperscript{6} Cu-based catalysts have previously been shown to be particularly active.\textsuperscript{7} Unless otherwise stated, a mixture of CuBr\textsubscript{2} and NH\textsubscript{4}Br 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 parameters.\textsuperscript{7} Yields of product, by-products and intermediates were calculated as before.\textsuperscript{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 \(^\circ\text{C}\), (entry 1), one observes a wide distribution of intermediates indicating that as previously observed,\textsuperscript{7} the catalyst is not active enough at these concentrations to complete the reaction. By contrast entries 2-4 show that, at 380 \(^\circ\text{C}\), the yield of TA is almost unchanged even when the residence time is decreased by a factor of \(\times 2\). Similarly the amounts of BA and CO\textsubscript{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.\textsuperscript{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 Reynolds’ 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\textsubscript{2}O + O\textsubscript{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\textsubscript{2}. Therefore, the hypothesis is that more efficient mixing should give higher yields of TA. The OF has been shown to give efficient mixing\textsuperscript{18,23} and is not well suited to varying the efficiency of mixing. However, the tubular reactor, TB, offers much better possibilities for testing this hypothesis.

### Table 1. Results obtained using the OF reactor.

<table>
<thead>
<tr>
<th>entry</th>
<th>T / (^\circ\text{C})</th>
<th>RT / s</th>
<th>Yield, mol %</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO\textsubscript{2}</td>
<td>TA</td>
</tr>
<tr>
<td>1</td>
<td>380</td>
<td>8.9</td>
<td>15</td>
<td>11.1</td>
</tr>
<tr>
<td>2</td>
<td>380</td>
<td>5.6</td>
<td>25-31</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>380</td>
<td>2.8</td>
<td>30</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>380</td>
<td>2.2</td>
<td>26</td>
<td>51</td>
</tr>
</tbody>
</table>

Catalyst is Cu/NH\textsubscript{4}Br = 0.15/1.7/2.0; Flow rates were varied proportionally to get the different retention times. \textsuperscript{a}Estimated residence time; \textsuperscript{b}Due to the difficulty of controlling the organic flow rate, a range of values is given in some cases.
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,\textsuperscript{26,27} (b) the position of the injection point, if it is located inside the reactor, can enhance mixing efficiency.\textsuperscript{28} (c) Buoyancy effects due to density differences can also play a role,\textsuperscript{21,22} the density of supercritical \( \text{H}_2\text{O} \) at \( 380 \) °C is only ca. 0.21 g/mL compared to >1 g/mL 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 pX feed pipes do not protrude into the T-piece (i.e. \( l_5 = 0 \), see Fig 2a). 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 feedpipes, \( l_6 \), decreases from 7 cm (TB-1) to 1 cm (TB-3). Modelling experiments to be described in a subsequent report confirm that a reduced value of \( l_5 \) 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 whereas in the larger diameter arms of the cross, it is only 0.0037 m/s. The velocity of the water stream is 0.035 m/s. In a fourth variation, pmTB, premixed pX and catalyst solutions were fed as a biphasic mixture into the reactor 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 reconnect. 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 could result in much larger changes in the efficiency of the already poor mixing.

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### Table 2: Comparison of the performance of the reactors used.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>RT( ^{a} ) /s</th>
<th>( T ) °C</th>
<th>Sel.( ^{b} ) %</th>
<th>Yield</th>
<th>CB( ^{c} )</th>
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<tbody>
<tr>
<td></td>
<td>TA</td>
<td>BA</td>
<td>CO(_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5.8</td>
<td>380</td>
<td>91</td>
<td>57</td>
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</tr>
<tr>
<td>2</td>
<td>5.8</td>
<td>380</td>
<td>41</td>
<td>20</td>
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<tr>
<td>3</td>
<td>5.6</td>
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<td>81</td>
<td>52</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>2.8</td>
<td>380</td>
<td>80.1</td>
<td>51.8</td>
<td>7.7</td>
</tr>
<tr>
<td>5</td>
<td>8.9</td>
<td>330</td>
<td>14.9</td>
<td>11.5</td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>18.9</td>
<td>330</td>
<td>57.4</td>
<td>42</td>
<td>3.1</td>
</tr>
<tr>
<td>7</td>
<td>18.9</td>
<td>330</td>
<td>60.8</td>
<td>41.8</td>
<td>2.6</td>
</tr>
<tr>
<td>8</td>
<td>18.9</td>
<td>330</td>
<td>57.6</td>
<td>29</td>
<td>2.2</td>
</tr>
</tbody>
</table>

\( ^{a} \)Estimated residence time; \( ^{b} \)Selectivity for TA; \( ^{c} \)Carbon balance closure.

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 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
CuBr₂/NH₄Br catalyst has been reported to be much less active at 330 °C. 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, CuBr₂/CoBr₂/HBr at saturated conditions. This catalyst has its highest activity at 330 °C. The results are summarized in Table 3. The results are summarized in Table 3.

**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 flowrates 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% CO₂ 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 into 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**

We thank Barry Thomas and Graham Aird for advice and Peter Fields, Richard Wilson and Mark Guyler for technical assistance. We are grateful to INVISTA for financial support.

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23. E. H. Lester, B. J. Azzopardi, Countercurrent mixing reactor for producing metal nanoparticles, e.g. nano-particulate cerium oxide, comprises additional inlet(s) diametrically opposed to first inlet and located within outlet, Patent numbers: WO2005077505-A2; EP1713569-A2; AU2005211990-A1; CN1917936-A; KR2007001999-A; US2007206435-A1; JP2007526113-W; IN20064554-P1; EP1713569-B1; DE602005014740-E; US7566436-B2; ES2327755-T3


The influence of shape and mixing effects in a continuous reactor has a dramatic influence on the aerobic oxidation of p-xylene to terephthalic acid using supercritical water as solvent.