

Industrial Synthesis of Terephthalic Acid in Near/Supercritical Water



**The University of
Nottingham**

UNITED KINGDOM • CHINA • MALAYSIA

Samuel Duncan Housley

BA(Hons) Cantab, MA, MBA

School of Chemistry

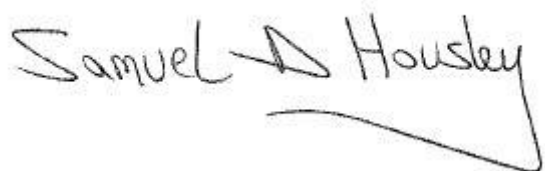
**Thesis submitted to the University of Nottingham for
the degree of Doctor of Philosophy, September 2017**

Declaration

I, Samuel Duncan Housley, declare that this thesis is the result of my own work which has been mainly undertaken during my period of registration (January 2010 to December 2015) for the degree of PhD at the University of Nottingham.

Where any work has been carried out in collaboration, the relevant researcher or researchers have been acknowledged.

The Thesis has not been accepted in partial or complete fulfilment of any other degree or personal qualification.

A handwritten signature in black ink that reads "Samuel Duncan Housley". The signature is written in a cursive style with a large, sweeping underline.

Samuel Duncan Housley, 1st of September 2017

Dedication

This thesis is dedicated to my late father,

Dr. Samuel Housley

1924 – 1987

Abstract

Terephthalic acid is an industrial commodity chemical produced as an intermediate in the manufacture of polyethylene terephthalate polymer used in the manufacture of polyester textiles, plastic bottles and packaging material. This thesis undertakes an industrial assessment of an alternative process technology for the manufacture of this intermediate. It is divided into nine Chapters which can be summarised as follows.

Chapter 1 discusses current industrial TA processes. TA is produced by the autoxidation of *p*-xylene (*pX*) with air oxidant in acetic acid solvent, using a homogeneous catalyst at a temperature of around 160 - 220 °C. The TA precipitates as a crude material containing contaminants and must be further purified to a purer grade material suitable for making polymer. The chapter considers the problems with the current processes and introduces *pX* oxidation in near critical or supercritical water (N/SCWO). It considers the difficulties in introducing new processes and displacing established, incumbent technology. The chapter finally considers the aims of this PhD project.

Chapter 2 reviews the state of the art of N/SCWO at the commencement of this project. This includes total oxidation and synthetic oxidations including *pX* N/SCWO.

Chapter 3 describes the experimental rigs, methods and analysis used in this project. It covers assessments, validations and improvements that were made.

Chapter 4 describes mixing aspects. The reaction requires the mixing of SCW and NCW streams and this was challenging due to their significant density difference. It was best achieved by the downward injection of the SCW stream into a rising NCW stream, an arrangement that exploits the buoyancy of the less dense stream to aid efficient mixing. A methodology was developed to assess the likely performance of a mixer under actual process conditions based on the turbulence, density difference and momentum ratio of the streams to be mixed.

Chapter 5 describes the influence of residence time distribution on the reaction outcomes. The reaction was undertaken in tubular and continuous stirred tank reactors and the outcomes were compared and related to their industrial significance.

Chapter 6 considers chemistry aspects. TA is produced by *pX* N/SCWO at a temperature around 300 – 400 °C and a pressure around 200 bar. The TA remains in solution during the oxidation. The N/SCWO can be catalysed by several transition metal bromides and Cu/Co/Br with a Co/Cu ratio of 85/15 was found to be the most effective. The process produces similar by-products to the acetic acid based process of carbon oxides and other aromatics but in higher amounts. Optimum TA yields were obtained under turbulent plug flow conditions using low temperature (~300 °C), high catalyst concentration and minimising oxygen concentration.

Chapter 7 considers the evolution of aromatic mass accountability and TA yield during the project and relates this to key reactor and chemistry developments. It was important to weld reactor joints to avoid yield losses through leaking compression joints and to accurately pump the *pX*. Reactors were constructed of Hastelloy C-276 though this material corrodes slowly under N/SCWO conditions and would not be suitable for commercial deployment. A high aromatic mass balance of up to 100 % has been obtained with a maximum yield of ~90 % of TA.

Chapter 8 considers the economics and value of the *pX* N/SCWO process relative to the acetic based process. The N/SCWO eliminates losses of acetic acid and generates higher grade steam from the reaction exotherm at the higher temperature. However, these gains trade off against the lower yield of TA obtained. The high make of by-products prevents significant process simplification and capital reduction compared to the acetic acid based process.

Chapter 9 reviews the extent to which the aims of the project were achieved and draws conclusions. The yield and quality of the TA obtained in the N/SCWO process is currently short of that needed for commercial deployment of the technology. Any future work will need to address these limitations and to further address materials of construction issues.

Acknowledgements

I'd like to acknowledge and thank the many people and organisations without whose help this project and thesis would not have been possible.

With thanks to my Industrial Sponsor who provided financial support and facilities and agreed to make the data available for publication but have chosen to remain anonymous.

With thanks to the University of Nottingham and especially to my PhD supervisors Professor Martyn Poliakoff and Professor Peter Licence for their tireless support, enthusiasm and encouragement. Also thanks to other faculty members and students for their support and advice especially Professor Edward Lester, Dr Paul Hamley, Professor Sandy Blake, Dr Eduardo Cepada Verdugo, Dr Joan Fraga-Dubreuil, Dr Eduardo Velilla, Dr Tom Huddle and Mrs Diane Mann. And to my Fellow PhD students for their encouragement and friendship particularly Yan Chong, Morgan Thomas, Gurbuz Comak and Laura Schofield.

Also thanks to Dr Walt Partenheimer (retired) who consulted and guided on chemistry matters.

Finally, with special thanks to my wife Vanessa and my daughter Natasha and son Adam for their understanding, patience and support throughout.

Contents

Declaration.....	ii
Dedication.....	iii
Abstract.....	iv
Acknowledgements.....	vi
Contents.....	vii
Abbreviations.....	xv
Definitions of Hydrodynamic Groups.....	xviii
1 Introduction to the Terephthalic Acid Processes and to High Temperature Water Oxidation.....	1-1
1.1 Introduction.....	1-1
1.2 The Conventional Terephthalic Acid Processes.....	1-3
1.3 The Chemistry of the Autoxidation of <i>p</i> -Xylene.....	1-8
1.3.1 The Main Reaction Pathways	1-8
1.3.2 Aromatic Over Oxidation Reactions.....	1-14
1.3.3 Colour Forming Reactions.....	1-16
1.3.4 Acetic Acid Oxidation Reactions.....	1-18
1.3.5 Catalyst Structure and Mechanisms.....	1-21
1.3.6 Problems with the Conventional Terephthalic Acid Process and an Alternative Approach.....	1-24
1.3.7 Final Comments on the Chemistry.....	1-24
1.4 Introduction to <i>p</i> -Xylene Oxidation in High Temperature Water....	1-25
1.4.1 The Properties of Near Critical and Supercritical Water....	1-25
1.4.2 Chemistry in Near Critical and Supercritical Water.....	1-26
1.5 Challenges in the Introduction of New Process Technology.....	1-29

1.5.1	Bio-Derived Terephthalic Acid.....	1-30
1.5.2	<i>p</i> -Xylene Spray Process.....	1-33
1.6	Structure of the Project.....	1-34
1.7	Aims of the Project.....	1-35
1.8	Structure of the Thesis.....	1-37
1.9	References.....	1-39
2	<i>p</i>-Xylene Near/Supercritical Water Oxidation; The State of the Art.....	2-1
2.1	Overview.....	2-1
2.2	Literature Review of Near /Supercritical Water Chemistry.....	2-1
2.2.1	Related Applications of SCW.....	2-1
2.2.2	Chemical Synthesis in N/SCW.....	2-2
2.2.3	Xylene N/SCWO Chemistry.....	2-2
2.2.4	Reactors and Mixing in N/SCW Systems.....	2-10
2.2.5	<i>p</i> -Xylene N/SCWO Process Synthesis.....	2-12
2.3	N/SCWO Experimental Facilities.....	2-13
2.3.1	The University of Nottingham N/SCWO Rigs.....	2-13
2.3.2	The IP1 and K5 N/SCWO Rigs.....	2-19
2.4	Xylene SCWO Chemistry.....	2-24
2.4.1	Formulations and Reactor Performance.....	2-25
2.4.2	Product Work Up and Analysis Techniques.....	2-26
2.5	Critique of the State of the Art.....	2-27
2.5.1	Material Balance and Analysis.....	2-27
2.5.2	Rig Design.....	2-33
2.5.3	Reactor Flow Regime.....	2-39
2.5.4	Reactor Residence Time.....	2-46

2.5.5	Reactor Orientation and Mixer Design.....	2-48
2.5.6	Chemistry Formulations and Analysis.....	2-51
2.5.7	Economic Issues.....	2-54
2.5.8	Materials Issues.....	2-54
2.5.9	Critique Summary.....	2-55
2.6	Detailed Aims and Tasks for this Project.....	2-56
2.6.1	Reactor Design and Mixing Issues.....	2-56
2.6.2	Chemistry Issues.....	2-58
2.6.3	Reactor Materials Issues.....	2-59
2.6.4	Process Integration and Economic Issues.....	2-59
2.7	References.....	2-60
3	Equipment and Experimental.....	3-1
3.1	The Basis of Safety of the Rigs.....	3-1
3.2	Rig Design.....	3-2
3.3	The Oxygen Feed System.....	3-4
3.3.1	Feed Vessels and Low Pressure Pipework.....	3-4
3.3.2	Pumps.....	3-7
3.3.3	Pre-heaters.....	3-9
3.4	The Catalyst Feed System.....	3-14
3.4.1	Feed Vessels.....	3-14
3.4.2	Pumps.....	3-15
3.4.3	Mass Flow Meters.....	3-18
3.5	The <i>p</i> -Xylene Feed System.....	3-18
3.5.1	Feed Vessels.....	3-18
3.5.2	Pumps.....	3-18
3.5.3	Mass Flow Meters.....	3-19

3.6	Reactors.....	3-20
3.7	Quench System.....	3-20
3.7.1	Feed Vessels.....	3-20
3.7.2	Pumps.....	3-21
3.7.3	Quench Point Design.....	3-21
3.7.4	Cooler.....	3-22
3.8	Pressure Let Down System.....	3-23
3.8.1	Back Pressure Regulators.....	3-23
3.8.2	Filters.....	3-24
3.9	Product Collection System.....	3-25
3.9.1	Gas Liquid Separator and Gas Analysis.....	3-25
3.9.2	Sample Points and Sampling.....	3-27
3.10	Experimental Procedures.....	3-27
3.10.1	Pressure Testing.....	3-28
3.10.2	Formulations.....	3-28
3.10.3	Start-Up Procedure.....	3-31
3.10.4	Shutdown Procedure.....	3-32
3.10.5	Analytical Procedures.....	3-33
3.10.6	Data Reporting Conventions and Error Assessment.....	3-34
3.11	References.....	3-36
4	Mixer Design and Development.....	4-1
4.1	Overview.....	4-1
4.2	The Effects of Poor Mixing.....	4-1
4.2.1	Low Oxygen Concentration Regions.....	4-3
4.2.2	High <i>p</i> -Xylene Concentration Regions.....	4-4
4.2.3	Low Catalyst Concentration Regions.....	4-4

4.3	Literature.....	4-4
4.4	Mixer Characterisation.....	4-4
4.5	Mixer Scale Up.....	4-12
4.6	References.....	4-14
5	The Optimisation of Residence Time Distribution.....	5-1
5.1	Reaction Concentration Profiles.....	5-1
5.2	Heat Removal Considerations.....	5-5
5.3	Conversion and Recycle.....	5-6
5.4	Effect on By-Products.....	5-6
5.5	The Engineering of a Plug Flow Reactor.....	5-7
5.6	The Engineering of a Back Mixed Reactor.....	5-8
5.6.1	Jet Mixed Reactors.....	5-8
5.6.2	Thermosiphon Reactor.....	5-10
5.6.3	Stirred Tank Reactor.....	5-11
5.7	Summary of Hydrodynamic Regimes Achieved.....	5-13
5.8	Experimental Studies.....	5-14
5.8.1	Introduction.....	5-14
5.8.2	The Transition from Laminar to Turbulent Flow in a Stirred Tank Reactor.....	5-15
5.8.3	The Transition from Laminar to Turbulent Flow in a Tubular Reactor.....	5-18
5.8.4	The Comparison of Tubular and Stirred Tank Reactors.....	5-21
5.8.5	The Comparison of Minor Components in NCWO and the Acetic Acid Based Process.....	5-25
5.9	Scale Up Considerations.....	5-26
5.10	Implications for Process Design.....	5-27

5.11	References.....	5-28
6	Chemistry Studies.....	6-1
6.1	Introduction.....	6-1
6.2	Stability of TA in NCW/SCW/O ₂ Environments.....	6-2
6.3	<i>p</i> -Xylene Concentration.....	6-10
6.4	Other Chemistry Studies.....	6-16
6.4.1	Catalyst Studies.....	6-16
6.4.2	Conversion.....	6-19
6.4.3	Oxygen Addition Strategies.....	6-20
6.4.4	Residence Time.....	6-20
6.4.5	Temperature Studies.....	6-23
6.4.6	Phase Studies.....	6-23
6.4.7	Quench.....	6-26
6.4.8	Residual Hydrogen Peroxide.....	6-26
6.5	References.....	6-28
7	The Evolution of <i>p</i>-Xylene Near/Supercritical	
	Water Oxidation.....	7-1
7.1	Introduction.....	7-1
7.2	The Commissioning of and Improvements to the IP1 Rig.....	7-1
7.2.1	Commissioning of the IP1 Rig.....	7-1
7.2.2	Improvements to the IP1 Rig.....	7-3
7.3	The Commissioning of the Kinetics Rig.....	7-6
7.4	Evolution of the Kinetics Rig and Reactor.....	7-6
7.5	The Progression of Aromatic Material Balance and TA Yield.....	7-15
7.6	References.....	7-18

8	The Economics of <i>p</i>-Xylene N/SCWO	8-1
8.1	Introduction	8-1
8.2	Review of Process Economics Literature	8-1
8.3	Capital Cost Aspects	8-3
8.4	Variable Cost Aspects	8-5
8.5	Assessing the Commercial Viability of <i>p</i> -Xylene N/SCWO Technology	8-8
8.6	References	8-10
9	Conclusions and Recommendations	9-1
9.1	Introductory Remarks	9-1
9.2	Review of Project and Thesis	9-2
9.3	Conclusions and Recommendations	9-4
	9.3.1 Technical Perspective	9-4
	9.3.2 Areas for Further Work	9-4
	9.3.3 Commercial Perspective	9-9
9.4	References	9-10

Appendix 1 Papers

Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 1: comparison with *ortho*-xylene and the role of the catalyst.

Eduardo Pérez, Joan Fraga-Dubreuil, Eduardo Garcia Verdugo, Paul A Hamley, W Barry Thomas, Duncan Housley, Walt Partenheimer and Martyn Poliakoff.
Green Chem., 2011, **13**, 2389-2396.

Selective aerobic oxidation of *para*-xylene in sub and supercritical water. Part 2: the discovery of better catalysts.

Eduardo Pérez, Joan Fraga-Dubreuil, Eduardo Garcia Verdugo, Paul A Hamley, Morgan L Thomas, Yan Chong, W Barry Thomas, Duncan Housley, Walt Partenheimer and Martyn Poliakoff.
Green Chem., 2011, **13**, 2397-2407.

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, Morgan L Thomas, Duncan Housley, Paul A Hamley, Joan Fraga-Dubreuil, Jun Li, Edward Lester and Martyn Poliakoff.
RSC Adv., 2016, **6**, 11289-11294.

The use of dimensionless groups to analyse the mixing of streams with large density differences in sub- and supercritical water.

Duncan Housley, Thomas Huddle, Edward Lester and Martyn Poliakoff.
Chem. Eng. J., 2016, **287**, 350-358.

Abbreviations

4-CBA	4-carboxybenzaldehyde
% w/w	percentage weight per weight
BA	benzoic acid
BPR	back pressure regulator
BPTC	biphenyl tricarboxylic acid
BrTA	bromoterephthalic acid (ring brominated)
CEBC	Center For Environmentally Beneficial Catalysis (The University of Kansas)
CTA	crude terephthalic acid
CSTR	continuous stirred tank reactor (idealised)
C_v	specific heat capacity (at constant volume)
DCA	dicarboxyanthraquinone
DCF	dicarboxyfluorenone
DMT	dimethyl terephthalate
DoE	U.S. Department of Energy
EG	ethylene glycol
EXAFS	extended X-ray absorption fine structure
exc.	excluding
FDC	furan dicarboxylic acid
FID	flame ionisation detector
GC	gas chromatography
GCMS	gas chromatography mass spectroscopy
GLS	gas liquid separator
G_r	Grashof number (the ratio of buoyancy to viscous forces)
HPLC	high pressure liquid chromatography
hr	hour
HTW	high temperature water
I.D.	inner diameter (of tubing)
inc.	including
IP1	Data scouting rig 1
iPA	<i>iso</i> -phthalic acid (1,3-dicarboxybenzene)

ISBL	inside battery limits (see section 8.3)
K_w	ionic product of water
K5	kinetic data gathering rig 5
KIST	Korea Institute of Science and Technology
<i>mX</i>	<i>meta</i> -xylene
LAI	light absorption imaging
MTA	medium grade terephthalic acid
MEG	mono ethylene glycol
MLT	multi-component-continuous gas analyser (Fisher Rosemount)
min(s)	minute(s)
MoC	material of construction
mol	mole
NCL	National Chemical Laboratory (of the Indian Government in Pune)
NCW	near critical water
NCWO	near critical water oxidation
NMR	nuclear magnetic resonance
N/SCWO	near/supercritical water oxidation
NIST	National Institute of Standards and Technology
NA	not applicable
NR	not reported
O.D.	outer diameter (of tubing)
<i>oPA</i>	<i>ortho</i> -phthalic acid (1,2-dicarboxybenzene)
OSBL	outside battery limits (see section 8.3)
<i>oX</i>	<i>ortho</i> -xylene
p	pence
PC	personal computer
P_e	Péclet number (the ratio of rate of advection to rate of diffusion)
PEEK	poly ether ether ketone
PET	polyethylene terephthalate
PFR	plug flow reactor (idealised)
PhD	Doctor of Philosophy (Degree)
P&ID	process and instrument diagram
ppm	parts per million
PTA	pure terephthalic acid

PTFE	polytetrafluoroethylene
<i>p</i> Tol	<i>para</i> -toluic acid (4-methylbenzoic acid)
PVC	polyvinyl chloride
<i>p</i> X	<i>para</i> -xylene
Re	Reynolds number (the ratio of inertial to viscous forces)
Ri	Richardson number (the ratio of inertial to buoyancy forces)
RMB	Chinese Yuan Renminbi (currency)
RTD	residence time distribution
s	second(s)
SCW	supercritical water
SCWO	supercritical water oxidation
SRI	SRI International (Business consultancy)
STR	stirred tank reactor (non-idealised)
STY	space time yield
TA	terephthalic acid (1,4-dicarboxybenzene)
TBR	tubular reactor
te	metric tonne
te/yr	metric tonnes per year
TM	trimellitic
TMA	trimellitic acid (1,2,4-tricarboxybenzene)
TMFM	thermal mass flow meter
U.K.	United Kingdom
U.S.	United States
UoN	University of Nottingham
wrt	with respect to
XANES	X-ray absorption near edge structure
XRF	X-ray fluorescence
ϵ	Dielectric constant
σ	Standard deviation

Definitions of Hydrodynamic Groups

To characterise the flow and mixing regimes in a mixer for a given set of operational conditions, it is important to assess the relative magnitude of the various forces present. This can be done using dimensionless numbers, which address the following considerations:

- The inertial forces compared to the viscous forces. This will determine if there is sufficient kinetic energy in the system to generate turbulent flow and therefore efficient mixing. This can be assessed by the **Reynolds number**:

$$Re = \frac{\rho v D_H}{\mu}$$

where ρ is the density in kgm^{-3} ; v is the mean velocity of the fluid in ms^{-1} ; D_H is the hydraulic diameter of the pipe in m; μ is the dynamic viscosity of the fluid in $\text{kgm}^{-1}\text{s}^{-1}$.

- The buoyancy forces compared to the viscous forces. This considers where there is enough potential energy in the system to create turbulence. This is assessed by the **Grashof number**:

$$Gr = \frac{g\beta(T_s - T_\infty)D_H^3}{\nu^2}$$

where g is the acceleration due to Earth's gravity in ms^{-2} ; β is the volumetric thermal expansion coefficient, approximately equal to $1/T$ for ideal fluids; T_s is the surface temperature and T_∞ is the bulk temperature in K; D_H is the hydraulic diameter of the pipe in m; ν is the mean velocity of the fluid in ms^{-1} . Using the pseudo fluid method, buoyancy is simulated through a difference in densities between the two mixing fluids, and in a real high temperature reactor the density of each fluid flow directly correlates to its temperature. As such we can use an analogous form of the equation to generate an approximate Grashof number; T_s and T_∞ can be

exchanged with the respective densities of the two fluids (ρ_1 and ρ_2) and β can be defined as $1/\rho_1$. The Grashof number then becomes:

$$G_r = \frac{g\Delta\rho D_H^3}{\rho\nu^2}$$

- The inertial forces compared to the buoyancy forces. This will determine if the system is prone to flow stratification. This is assessed by the **Richardson number**:

$$R_i = \frac{G_r}{R_e^2}$$

- The rate of advection and the rate of diffusion, measured by the **Péclet number**. The **diffusive mixing length** of the system can be assessed as the product of the Péclet number and the length scale:

$$P_e L = \frac{L^2 \nu}{D}$$

where L is the characteristic length in m; ν is the local flow velocity in ms^{-1} ; D is the mass diffusivity in m^2s^{-1} .

- The **relative momenta** of the streams will indicate the extent of flow penetration and reduce the diffusive mixing length required. This can be considered as the momenta ratio in either a local or global scale. The localised measure considers the situation in the immediate vicinity of a point in the flow while the globalised measure considers the totality of the two impinging flows:

$$M_{rl} = \frac{\rho_1 \nu_1}{\rho_2 \nu_2} \qquad M_{rg} = \frac{\rho_1 \nu_1 A_1}{\rho_2 \nu_2 A_2}$$

Where ρ is the density in kgm^{-3} ; ν is the mean velocity of the fluid in ms^{-1} ; A is the cross sectional wetted area in m^2 .

- **Dispersion number** measures the extent of axial dispersion:

$$D_i = D/vd_t$$

Where D is the mass diffusivity in m^2s^{-1} , v is velocity in ms^{-1} ; d_t is the tubing diameter in m.

- The momentum diffusivity (viscosity) to the mass diffusivity, measured by the **Schmidt number** and used to characterise fluid flows in which there are simultaneous momentum and mass diffusion convection processes. It physically relates the relative thickness of the hydrodynamic layer and mass-transfer boundary layer. It is defined as:

$$Sc = \mu/\rho D$$

where μ is fluid dynamic viscosity in Nms^{-2} ; ρ is fluid density in kgm^{-3} ; D is the mass diffusivity in m^2s^{-1} .

1 Introduction to the Terephthalic Acid Processes and to High Temperature Water Oxidation

1.1 Introduction

The autoxidation of *p*-xylene (*p*X) to terephthalic acid (TA), using acetic acid as solvent, is a reaction of huge industrial importance.¹⁻³ The reaction is shown in Figure 1-1. TA is a chemical intermediate in the production of the polyester polymer polyethylene terephthalate (PET)^{4, 5} which is produced by the condensation polymerisation of TA with mono ethylene glycol (MEG). Polyester polymer is used for the manufacture of textile fibres, plastic bottles and packaging film. The current worldwide capacity for TA is approximately 50 million tonnes per annum, with an annual value > \$50 billion (\$5 x 10¹⁰).

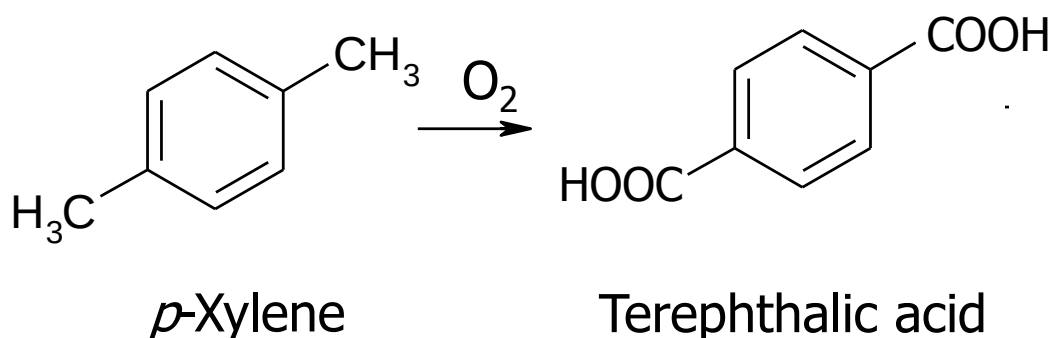


Figure 1-1. The oxidation of *p*X to TA.

The annual growth rate for TA demand and capacity is ~5 - 7 % and this is unusually high for a large scale, commoditised chemical intermediate. There are several factors that are driving this growth. Both the TA and PET processes are very efficient, the former achieving 97 % yields; by comparison the process for intermediates for polyamides achieves ~80 %. Thus, PET can be manufactured relatively cheaply, it can be recycled and it has multiple uses as noted above. Asian middle classes are growing rapidly and creating strong demand for PET products. In textile applications PET fibres compete with cotton; cotton plants are thirsty for water and this has created environmental problems, an extreme

example being the progressive disappearance of the Aral Sea in Central Asia through over irrigation. Chemically, PET contains only C, H, O whereas PVC contains Cl and polyamide contains N. On incineration, Cl and N containing waste can form polychlorinated dibenzodioxins and nitrogen oxides respectively that are harmful substances that require abatement. PET is lighter than glass and is less likely to break so its use reduces transport costs. It has adequate barrier properties for carbonated water and is suitable for food contact. Due to these many factors, PET is gradually displacing cotton, glass, other polymers and (to a lesser extent) aluminium in fibre and packaging applications.

PET does however have some weaknesses. Its barrier properties are inadequate for beer which requires a very high barrier to atmospheric oxygen ingress. It is not bio degradable and persists in the environment particularly cluttering beaches and presenting hazards to wildlife.

The large market size and high growth of TA provides a high economic incentive for cost reductions through process improvement. In 1998 Holliday⁶ showed that *p*X autoxidation can also be undertaken using high temperature, near critical water (NCW) as an alternative solvent (to acetic acid). NCW is advantageous for this process because:

- The reactions proceed rapidly at high temperatures potentially enabling process intensification and the deployment of smaller reactors.
- The reaction exotherm is released at higher temperature which is more thermodynamically efficient.
- Substrate and oxygen miscibility with the solvent is high under these conditions.
- The tendency for the (acetic acid) solvent to be oxidised to carbon dioxide is eliminated.

This PhD study aims to assess whether *p*X oxidation in near critical or supercritical water provides an alternative process to produce TA that is economically advantageous compared to the conventional acetic acid based process that is currently used in the industry.

1.2 The Conventional Terephthalic Acid Processes

There are several TA processes that are deployed commercially and these are described in detail by technology and market analysis companies such as SRI/IHS and Nexant and in numerous patents. They fall into three main categories, modern pure TA processes,^{3, 7} older dimethyl terephthalate (DMT) processes^{3, 8, 9} and medium grade TA processes.^{10, 11} They all comprise of similar oxidation plants but differ in their subsequent purification steps and are described in the following paragraphs.

pX autoxidation, using molecular oxygen (sparged as air) as the oxidant, is carried out in a boiling acetic acid and water solvent that comprises ~88 - 92 % acetic acid and ~8 – 12 % water by weight, at a temperature in the range 160 – 200 °C using air as the oxidant. The melting and boiling properties of the main components are given in Table 1-1. A pressure of ~8 – 16 bar_a (the exact pressure required is determined by the required temperature and solvent water content) is applied to enable the solvent to be superheated above its atmospheric boiling temperature. The pressure reduces the volumetric flow rate of the air and the acetic acid and water vapour that is produced. Partial dimerisation of the acetic acid in the vapour phase occurs and this further reduces the volumetric flow rate of vapour. A homogeneous, liquid phase catalyst is used, usually comprising cobalt, manganese and bromide though additional components have been claimed.¹²

Table 1-1. Melting and boiling points of the main components in *pX* autoxidation to TA at atmospheric pressure.

Component	Boiling point °C	Melting point °C
Acetic acid	118 - 119	16 - 17
Water	100	0
<i>pX</i>	138.4	13.2
TA	Sublimes at 402	300

The TA product is highly insoluble and precipitates from the reactor liquor as a slurry of white crystalline powder known as crude terephthalic acid (CTA). The exact chemical yields from industrial TA processes are commercially sensitive information. However, the reaction is highly selective and gives ~98 – 99 %

yield of TA. The overall industrial process yield is lower because of unrecovered physical losses of TA and these vary for different processes; however, the overall yield is still very high for a large scale industrial process. This high yield occurs for two reasons. Firstly, the precipitation of the TA removes it from the liquid phase reaction environment thus protecting it from degradation. Secondly, the high stability of the aromatic nucleus limits the degree of undesirable side reactions even in the aggressive conditions that are used to drive the reaction to high conversion. Autoxidations proceed by free radical mechanisms and for such reactions the relative rates are strongly dependent upon the C-H bond strength. The high stability of the aromatic nucleus is due to the large difference in C-H bond strength in the ring compared to the pendant methyl groups.

The process is carried out both in large continuous stirred tank reactors (CSTR) and in bubble columns. The process conditions and the reactor configurations have been extensively studied and optimised.¹² Other reaction schemes have been described in the literature including a solution process (*i.e.* a process in which the TA remains in solution) employing a plug flow reactor¹³ and a hybrid process using a solution plug flow reactor followed by a crystallising CSTR reactor.¹⁴ However, these processes have not, to date, been commercialised at industrial scale.

The autoxidation of *p*X proceeds through a series of intermediates as illustrated in Figure 1-2. These are the main reaction intermediates but not all of them, since alcohols, acetates, benzylic bromides and other intermediates are also seen in relatively small amounts. A figure detailing all of the intermediates is available elsewhere.¹⁵

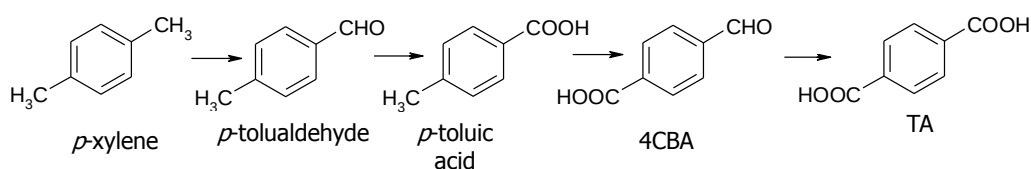


Figure 1-2. The predominant reaction pathway and intermediates for the conversion of *p*X to TA.

The reaction time (for 50 % conversion) of *p*X to *p*-toluic acid is of the order of 6 s. The oxidation of *p*-toluic acid to TA is more difficult, probably due to the electron withdrawing nature of the carboxylic acid group, and the reaction time is an order of magnitude longer at around 60 s.^{12, 16}

In view of these reaction timescales it is surprising that the reactor residence time employed in the various industrial processes are in the range 30 - 120 minutes. The residence time required depends on the temperature used, with longer times required at lower temperatures. These long residence times, combined with the high (industrial scale) throughputs, lead to the reactors being very large. The process requires titanium lined carbon steel reactors and the large vessels employed are close to the limits of fabrication feasibility. The reasons for needing this long residence time, when the reactions are relatively fast, are to be found in issues of product purity.

The intermediate 4-carboxybenzaldehyde (4-CBA) has a similar chemical conformation to that of TA and is prone to co-crystallising with the TA in the reactor. The TA produced is thus impure and is known as crude terephthalic acid (CTA). The CTA slurry is flashed cooled down to lower temperature and pressure in a series of vessels in which further crystallisation occurs and reaches a temperature of ~ 140 °C in the final flash stage.

4-CBA is a monoacid and is therefore a chain stopper in the subsequent condensation polymerisation of TA, with MEG, to make PET polymer. This limits the molecular weight of polymer that can be obtained and adversely affects its processing properties. It is therefore necessary to reduce the 4-CBA concentration in the CTA crystals down to a low level to produce purified terephthalic acid (PTA). CTA typically contains ~2000 - 5000 ppm of 4-CBA and the product specification for purified terephthalic acid (PTA) is < 25 ppm. There are two technologies that can achieve this level of 4-CBA reduction, distillation and hydrogenation/crystallisation. A third process, digestion can be used to obtain a medium grade of terephthalic acid (MTA) that contains a higher level of 4-CBA.

- To purify by distillation, CTA is esterified to liquid dimethyl terephthalate (DMT) ^{3, 17} which is distilled. The purified DMT is then easily hydrolysed back to TA. This process produces the purest PTA and is practiced on an industrial scale. However, distillation is energy intensive and expensive so is being displaced by crystallisation technology.
- To purify TA by crystallisation, the CTA is dissolved in high temperature water (at ~280 °C) under pressure. Prior to crystallisation it is necessary to reduce the 4-CBA level in solution because of its tendency to co-crystallise with the TA. The solution is therefore hydrogenated over a supported palladium catalyst which both hydrogenates 4-CBA back to *p*-toluic acid and reduces the level of some undesirable coloured by-products, an aspect described more fully in Section 1.3.3. The resulting hydrogenated solution is then flashed crystallised by reducing its pressure and temperature over several flash crystallisation vessels and PTA solid is obtained at ~99.9 % purity. Most of the PTA currently manufactured is produced by this process.
- To purify by digestion, the CTA is heated to ~200 – 240 °C in acetic acid/water and sparged with a gentle air feed. Crystal turnover (*i.e.* dissolution and recrystallisation) gradually releases the 4-CBA into solution where it is oxidised to TA. This process produces MTA that contains ~200 – 400 ppm 4-CBA. Such material can be used to make PET but requires more care to do so. It does not meet the (internationally accepted) PTA specification and cannot be sold as such. MTA processes tend therefore only to be employed by integrated TA/PET producers who polymerise their own MTA material.

The hydrogenation and crystallisation process has become the dominant industry technology. However, it has limited capacity to reduce the 4-CBA content of the crude TA and it is therefore necessary to limit this content of the crystals to around 2000 - 5000 ppm in the oxidation reactor. This is achieved by driving the reaction to very high TA conversions, with a low standing concentration of the 4-CBA intermediate in the reactor liquor thus limiting the degree of 4-CBA co-crystallisation. CSTRs are not well suited to achieve high conversions and

require long residence times for this. Thus, for high industrial scale throughputs, large vessels are required.

A further difficulty is that the oxidation reaction liquor contains bromide as a component of the catalyst which is aggressively corrosive. The materials of construction need to be titanium at higher temperatures and varying grades of stainless steels at lower temperatures. These materials and the large vessel size lead to very high capital costs and a high inventory of hazardous materials, *i.e.* flammable solvent and oxygen. This is clearly far from ideal.

The oxidation of *p*X to TA produces considerable heat (~12.3 MJ/kg) and two moles of water per mole oxidised. The water is miscible with the acetic acid solvent. The heat of reaction is removed by allowing the reactor to boil and evaporating solvent that contains both acetic acid and water. These solvent components are partially separated by either conventional distillation, azeotropic distillation (using an additional component such as *n*-propyl acetate) or by rectification and an acetic enriched solvent stream is returned to the reactor. Thus, the water content of the oxidation reactor solvent can be controlled and can be in the range of ~5 – 16 % by mass. The heat is captured as various grades of steam and is used to heat the water solvent used in the purification plant. Very large inventories of acetic acid/water solvent are used and this and the dissolved (Co/Mn/Br) catalyst are therefore recycled. The solvent is separated from the CTA by conventional separation techniques such as centrifugation and/or filtration. Minor component by-products also accumulate in the solvent and it is therefore necessary to limit their concentration build up by taking a solvent purge. This purge contains catalyst components and the metals are recovered by precipitating them as insoluble salts such as oxalates^{18, 19} or carbonates²⁰ and these are recycled back to the oxidation reactor where they breakdown. The bromide in the purge is not recovered and is passed to an effluent treatment plant. Some of the minor components, *e.g.* benzoic acid, can be recovered by crystallisation or solvent extraction for sale. The remaining minor components are concentrated up by evaporation and sent to effluent treatment.

The CTA is re-slurried in water and then purified by hydrogenation and flash crystallisation as previously described. The PTA produced is separated from the

water by conventional separation techniques such as centrifugation and/or filtration and the water is sent to an effluent treatment plant and then recycled to the process. The PTA is dried in a rotary kiln drier or hot air drier and pneumatically conveyed to storage silos. It is ultimately further conveyed to facilities for packing into bags, intermediate bulk containers, road tankers or rail cars.

1.3 The Chemistry of the Autoxidation of *p*-Xylene

The chemistry of the autoxidation of *pX* in acetic acid/water solvent using cobalt/manganese/bromide catalyst has been extensively studied and is the subject of an extensive literature.^{12, 21-45} Mechanistic aspects are considered in the following reviews.^{26-28, 43-60} A good overall review is provided by Partenheimer¹² and the main aspects are summarised in the following sections.

1.3.1 The Main Reaction Pathways

The main reaction pathway proceeds through a series of chemical intermediates, as shown in Figure 1-2, and these can be detected in the reaction slurry by HPLC analysis.⁶¹ The reactions proceed by free radical chain mechanisms involving initiation, propagation and termination steps. Indication of a free radical chain mechanism is given by:

- The initial rate of the reaction can be affected by light.
- Very small quantities of substances can either:
 - initiate the reaction (*e.g.* acetaldehyde or *m*-chloroperbenzoic acid.²⁶)
 - Inhibit the reaction (*e.g.* phenols, primary amines or sulfides.¹²)

The initial initiation is thought to occur from traces of peroxide in the acetic acid.²⁸ This can thermally or catalytically dissociate to form peroxide radicals that can then abstract hydrogen from *pX* to form benzylic radicals. Benzylic radicals react with oxygen to form primary peroxide radicals and these can propagate by further hydrogen abstraction thus forming additional benzylic

radicals and peroxides as shown in Figure 1-3. The role of the catalyst is shown in Figure 1-4 and Figure 1-5.

The primary benzylic peroxides can oxidise Co^{II} to Co^{III} and are reduced to aromatic aldehyde intermediates.²⁶ Co^{III} undergoes rapid reduction by Mn^{II} back to Co^{II} and this is an important reaction because Co^{III} is a highly effective catalyst for decarboxylation of aromatic carboxylic acids,⁶² an undesirable reaction leading to yield loss and discussed in more detail in the next section.

Mn^{III} (and less importantly Co^{III}) can oxidise bromide to a bromine radical, the Mn^{III} being reduced back to Mn^{II} . The bromine radical is a highly efficient chain propagator as it can hydrogen abstract from additional methyl aromatics and aromatic aldehydes. Thus, the catalyst system forms a highly effective redox cascade. The rate limiting step in the scheme is the reduction of Mn^{III} to Mn^{II} by bromide. Thus, at a given moment, the predominant forms of Co and Br in the catalyst are Co^{II} and bromide. The ratio of Mn^{II} and Mn^{III} in the active system is difficult to predict and is probably sensitive to the catalyst ratios and process conditions.

The aromatic aldehydes formed can be further oxidised as illustrated in Figure 1-6. Propagating radicals can abstract the hydrogen from the aldehyde to form aroyl radicals (*p*-methylbenzenecarbonyl radicals). These radicals react with oxygen to form peroxide radicals which can in turn propagate by hydrogen abstraction to form peroxy acids. The aromatic peroxy acids can be reduced by Co^{II} to aromatic carboxylic acids, which are the desired product.

Thus, the peroxide radicals and bromine radicals are the main propagating radicals, both of which can hydrogen abstract from *p*X and aromatic aldehydes, to form further benzylic and aroyl radicals. The bromine radicals are the more effective propagating species, illustrated by the observation that non-catalysed *p*X oxidation cannot be driven to high TA yields. *p*-Toluic acid is more difficult to oxidise than *p*X and can only be converted to TA at low yield when the catalyst contains no bromide.

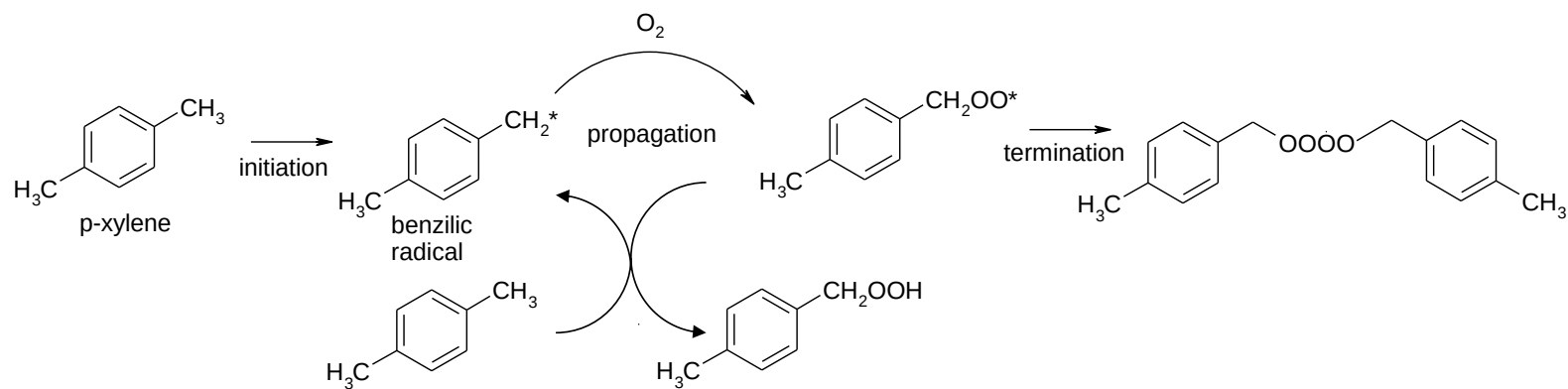


Figure 1-3. The free-radical chain mechanism for the autoxidation of *pX*.⁶³ The termination product shown will be unstable.

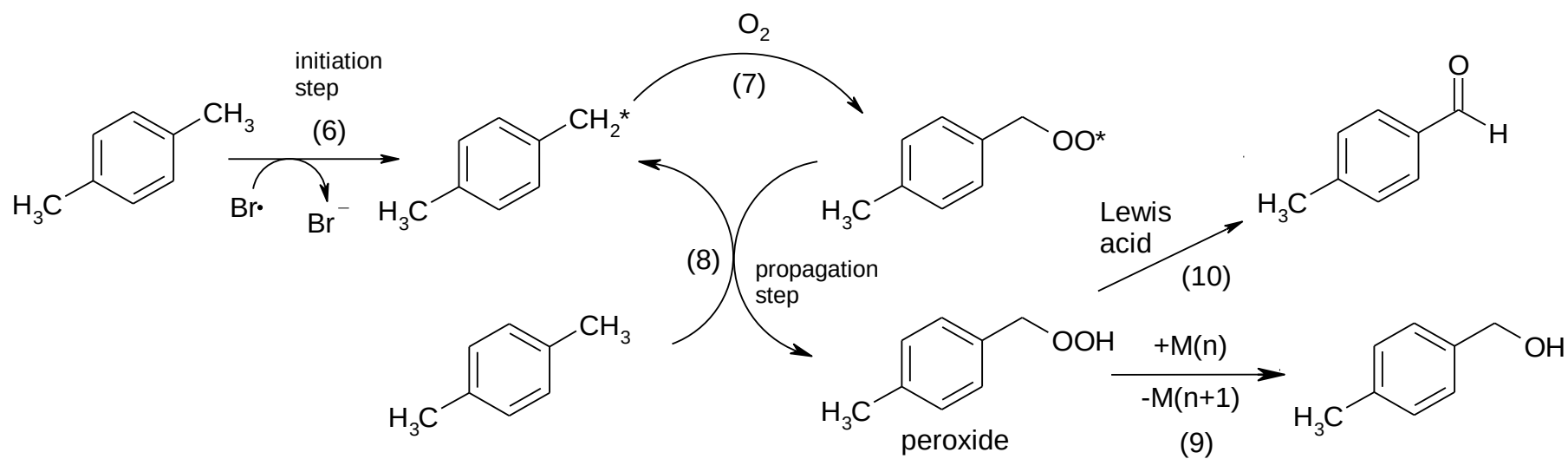


Figure 1-4. The role of catalyst in the autoxidation of $p\text{X}$.^{2, 3, 15}

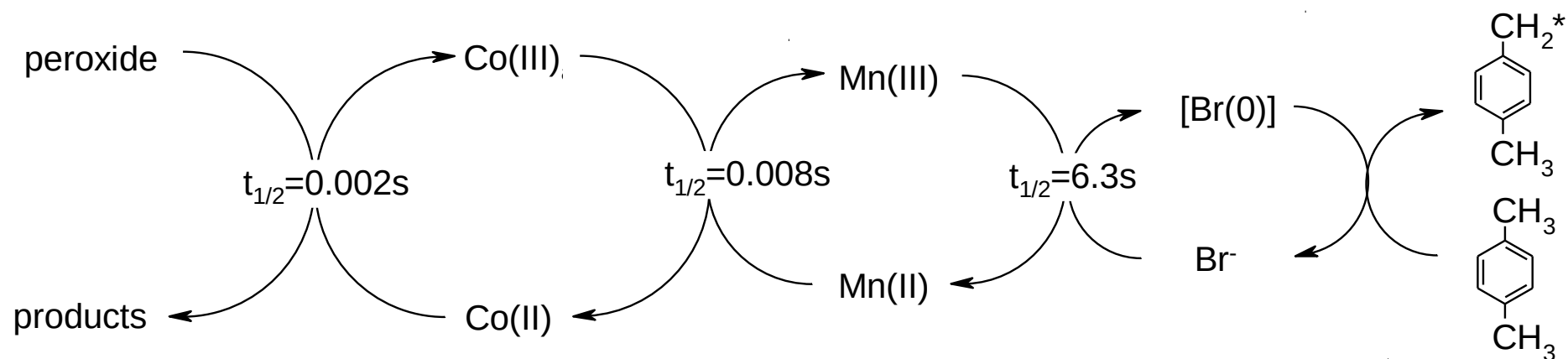


Figure 1-5. Catalyst redox cascades in the autoxidation of *p*X. The size of the loops illustrates the degree of change in the oxidation potential in the step. Peroxides rapidly oxidise Co^{II} being reduced to the aromatic acid products. Mn^{II} rapidly returns the Co^{III} to its lower oxidation state. The reduction of Mn^{III} by bromide to produce a bromine radical is a slower reaction and is the rate limiting step. Thus, appreciable Mn^{III} can build up in the system. The scheme is as reported by Partenheimer¹⁵ and the time constants ($t_{1/2}$) have been adapted to the industrial condition.

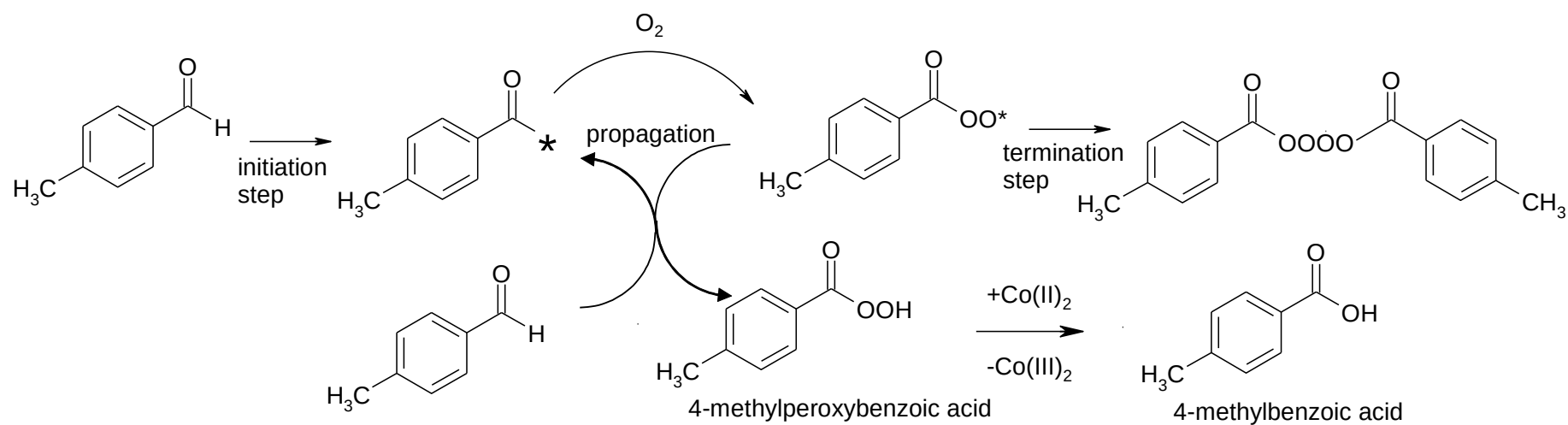


Figure 1-6. The catalytic autoxidation of *p*-tolualdehyde to *p*-toluic acid. It is thought that the reaction is started by initiation by trace amounts of peroxides in the acetic acid. Propagation is by peroxide radicals and bromide radicals. The redox reaction of peroxides and Co^{II} forms the aromatic acid products and Co^{III}.^{3, 63} The metals can be present as dimers as discussed in Sections 1.3.2 and 1.3.5.

The balance of propagation over termination determines if the reaction can proceed and the 'chain length' (*i.e.* number of consecutive propagation steps) that it can achieve. The rate and selectivity of these autoxidations are very sensitive to the presence of small amounts of catalysts; reference ⁶⁴ describes experiments where small amounts of Co/Mn/Br were added to an uncatalyzed oxidation of benzaldehyde which resulted in a large decrease in by-products. This indicates that the chain length of methyl aromatic autoxidations is very short, 5 - 10 probably being a reasonable estimate.

1.3.2 Aromatic Over Oxidation Reactions

As discussed in the previous section, methyl aromatic autoxidations are much more selective when a metal bromide catalyst is present. The reasons for this can be appreciated by consideration of the possible side reactions as illustrated in Figure 1-7.

The catalytic routes rely on oxidisable metal dimers, to reduce organic peroxides (Figure 1-7, reaction 2) and these reactions are highly selective. Non-catalytic routes do not have this pathway and rely on either thermal scission of peroxides to form alkoxy radicals or carboxylic acid radicals plus hydroxyl radicals (reaction 1) or the formation and subsequent dissociation of a Baeyer-Villiger intermediate (reactions 3 & 4). These reactions are much less selective because:

- Hydroxyl radicals are highly energetic species that react unselectively with any organic species with abstractable hydrogen atoms and many inorganics.⁶⁵ The products formed, such as phenols, are further oxidised to carbon dioxide and carbon monoxide.
- The Baeyer-Villiger chemistry also forms aryl formates (reaction 5) then formic acid and phenols (reaction 9).⁶⁶ In this system the formic acid oxidises to CO₂ and CO and the phenols oxidise, initially to quinones (reaction 11)⁶⁷ and ultimately to CO₂ and CO (reaction 13).

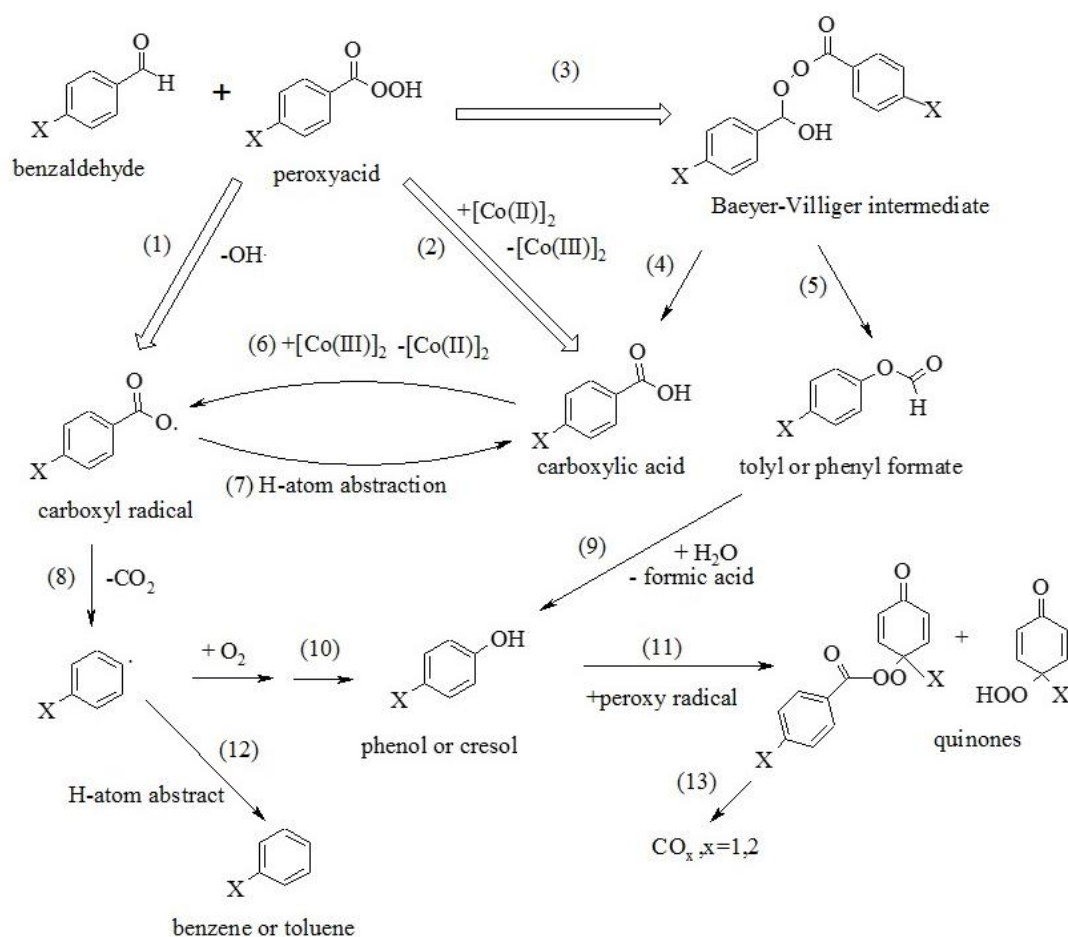


Figure 1-7. Over oxidation mechanisms and pathways for the Co/Mn/Br catalysed oxidation of *p*X in acetic acid.¹⁵

There are many reactions by which CO_2 and CO can be formed.⁶² Again these are illustrated with reference to Figure 1-7. These can include:

- Hydrogen abstraction from an acid group to form an acid radical (reaction 6) that then decarboxylates to an aryl radical (reaction 8). This is catalysed by Co^{III} . The aryl radicals will oxidise to phenols (reaction 10), quinones (reaction 11) and ultimately CO_2 and CO (reaction 13).
- Other sources of phenols (and hence ultimately of CO_2 and CO) are the attack of hydroxyl radicals on the ring of aromatics and Baeyer Villiger chemistry⁶⁶ (reactions 3, 5, 9).
- Thermal decomposition of peroxides to a carboxyl radical (reaction 1) and subsequent decarboxylation (reaction 8).

- Thermal decarboxylation of aromatic acids.⁶⁸ The ease of decarboxylation increases with the number of carboxylic acid groups, thus trimellitic acid > TA > *p*-toluic acid. However, at the acetic acid process temperature (~160 – 200 °C), this is a minor route to CO₂ and CO.
- Decarbonylation of RC•O radicals. This is much more favoured for aliphatic aldehydes than aromatic, the former arising when the aromatic rings are ruptured (*e.g.* of a quinone formed from a phenol) and the carbons are unzipped one at a time by successive hydrogen abstractions, oxidations and (aliphatic) decarboxylations and decarbonylations. Decarbonylation of aliphatic aldehydes is probably the major source of (aromatically derived) carbon monoxide in the system.⁶⁹
- Carbon dioxide and carbon monoxide also derive from the oxidation of acetic acid and these reactions are discussed in Section 1.3.4.

1.3.3 Colour Forming Reactions

Benzylic radicals are on the desired reaction path. However, they can also undergo undesired reactions by cross linking with other aromatics. This will initially form species with the cross link between the aromatic centres with a methylene bridge. This bridge will subsequently be oxidised to a ketone group. The major species of this type are 2,6-dicarboxyanthraquinone (DCA) and 2,4',5-tricarboxybenzophenone.⁶¹ These species are highly coloured and thus undesirable since PET polymer needs to be colourless.⁷⁰ These pathways are illustrated in Figure 1-8. By-products of this type can also be formed *via* a Friedel-Crafts reaction of a benzylic bromide.

Other possible by-products from benzylic radicals include benzils and stilbenes as illustrated in Figure 1-9.

Aryl radicals (*e.g.* the 4-methylphenyl radical or the 4-carboxyphenyl radical) can be formed by several routes, such as the metal-catalysed decarboxylation of a substituted benzoic acid or a decarbonylation of an aroyl radical. Aryl radicals have several potential fates:

- They react with oxygen to form phenols which are subsequently oxidised to quinones and then to CO₂ and CO (as was discussed in the previous Section 1.3.2).
- They abstract hydrogen from another species (such as *pX*) to form toluene (if the 4-methylphenyl radical) or benzoic acid (if the 4-carboxyphenyl radical). The toluene would subsequently be oxidised to benzoic acid.
- They react with di-substituted aromatics to give a 2,4',5-substituted biphenyl as illustrated in Figure 1-10. Further reactions lead to fluorenones, benzocoumarines and biphenyls. The major species of this type are 2,4',5-tricarboxybiphenyl (BPTC) and 2,6-dicarboxyfluorenone (DCF). DCF is a highly coloured (yellow) by-product and is thus undesirable.
- They react with mono-substituted aromatics (such as benzoic acid) to give bi-substituted biphenyls. The major species of this type is 4,4'-diphenic acid (4,4'-dicarboxybiphenyl).

Ring brominated bromoterephthalic acid (BrTA) is generally only observed as a trace by-product in the acetic based process.⁶¹ This suggests that electrophilic addition is not a significant mechanism in this process and that little if any of the bromine is present as elemental bromine.

The most highly coloured by-products are fluorenones (*e.g.* DCF) and anthraquinones (*e.g.* DCA) which can co-crystallise with the TA and impart colour to the product. DCF is the more significant as it is formed in larger quantities. The tendency to colour is reduced in the purification plant by hydrogenation of the ketone groups in these species back to methylene bridges forming fluorenes and anthracenes which are less conjugated and uncoloured.

1.3.4 Acetic Acid Oxidation Reactions

Acetic acid is the solvent of choice for this system due to its high chemical stability and the high catalyst activity in this solvent. However, the acetic acid can undergo oxidation reactions to form CO₂ and CO.⁶² Hydrogen abstraction can occur from both the methyl group and from the acid group. This forms

carboxymethyl radicals ($\cdot\text{CH}_2\text{COOH}$) and methylcarboxy radicals ($\text{CH}_3\text{COO}\cdot$) respectively. The former can add oxygen to form carboxyperoxide radicals ($\cdot\text{OOCH}_2\text{COOH}$) and these will ultimately likely form CO_2 and CO . The latter can undergo decarboxylation to methyl radicals and CO_2 . The presence of methyl radicals in the system is strongly indicated by the detection of products that likely occur from further reaction of these radicals. These include:

- Methane. The formation of some methane provides strong evidence for the presence of methyl radicals as these can abstract a hydrogen atom from other organic species such as $p\text{X}$ to form the methane.
- Trimellitic acid (1,2,4-tricarboxybenzene) (TMA) formed by the attack of methyl radicals on 1,4-disubstituted aromatics followed by oxidation of the methyl groups to carboxylic acids.⁶¹
- Small amounts of methanol formed by the reaction of methyl radicals with oxygen to form peroxides followed by the reduction of the peroxide by the mechanisms described earlier.
- Larger amounts of methyl acetate formed by the esterification of methanol with acetic acid.⁷¹

Methyl bromide is also observed as a product but is not thought to be formed from methyl radicals; a possible mechanism for its formation is discussed in the next section. It is a potent greenhouse gas and is therefore destroyed in a catalytic combustion unit prior to atmospheric discharge of the oxidation reactor off-gas.

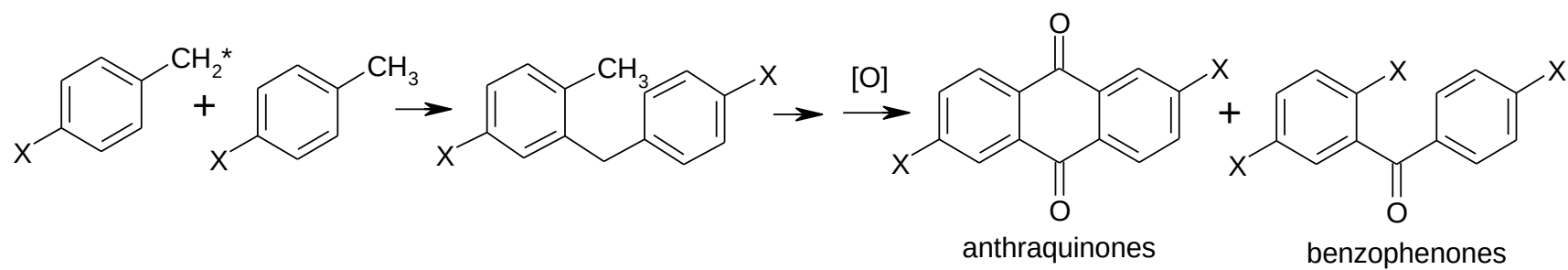


Figure1-8. Formation pathway of anthraquinones and benzophenones.^{61, 63}

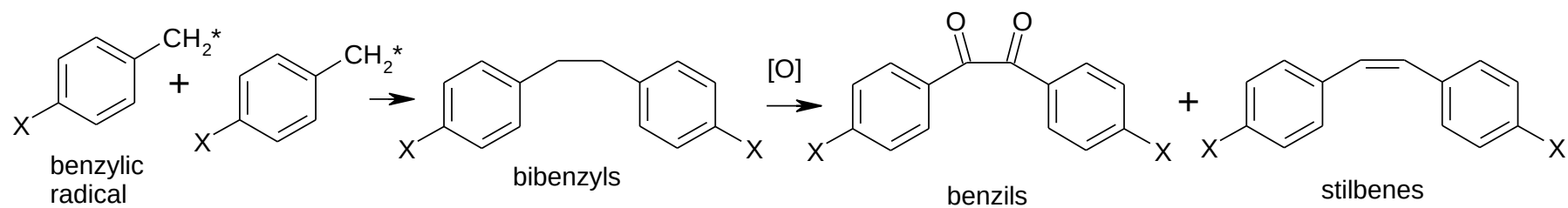


Figure 1-9. Formation pathway of benzils and stilbenes.^{61, 63}

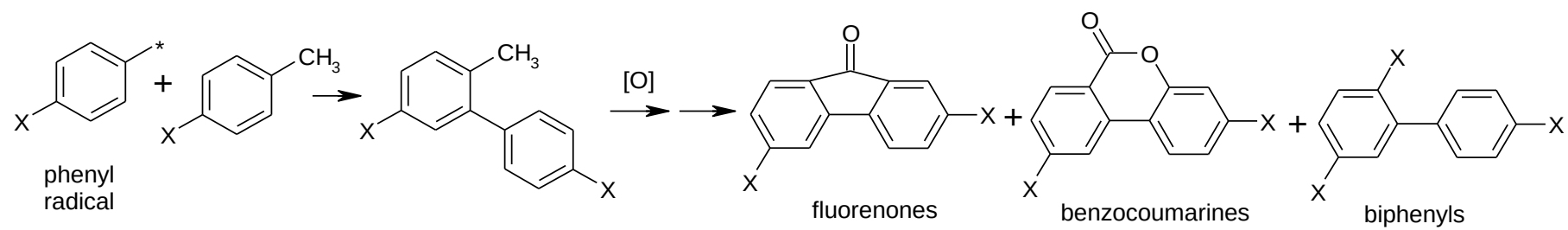
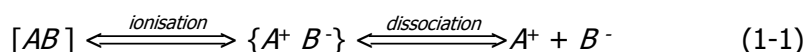


Figure 1-10. Formation pathway of fluorenones, benzocoumarines and biphenyls.^{61, 63}

1.3.5 Catalyst Structure and Mechanisms

The catalyst in the acetic acid process is homogeneous and comprises a mix of cobalt, manganese and bromide salts. The structure of the metal species in acetic acid is complex and a good review has been undertaken by Partenheimer.³⁵

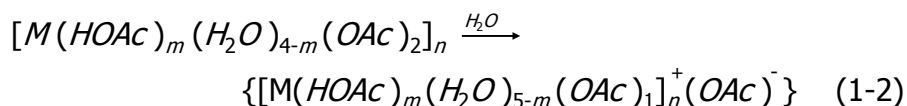
In acetic acid, one must distinguish between ionisation of metal salts to form an ion pair and the subsequent dissociation to free ions:



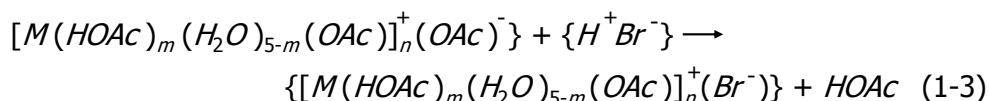
where curly brackets { } indicate undissociated ion pairings and square brackets [] indicate the metal coordination sphere. In this system, the concentration of the dissociated species is very small.⁷²⁻⁷⁴

Solid state crystal studies have shown that both cobalt and manganese have octahedral structures^{75, 76} but that cobalt is mononuclear and manganese is polynuclear. In anhydrous acetic acid, ion-migration experiments⁷⁷ show that > 95 % of the metal species are uncharged suggesting structures such as $[M(\text{HOAc})_4(\text{OAc})_2]_n$ and the ion pairings $\{[M(\text{HOAc})_5(\text{OAc})]^+(\text{OAc})^-\}_n$. The formation of the uncharged species is unsurprising because the dielectric constant of anhydrous acetic acid is low ($\epsilon = 6.2$). Some authors report mononuclear structures (*i.e.* $n = 1$)^{77, 78} while others report dimers ($n = 2$).⁷⁹⁻⁸¹ Possible structures for dimers are suggested by Partenheimer³⁵ where acetate can act as a bridging ligand between the two metal ions. These dimers can be homo or hetero with regards to the metals (*e.g.* Co/Co, Mn/Mn or Co/Mn dimers).

The addition of water to the system results in acetic acid ligands being replaced by water ligands. Partenheimer³⁵ used the data of others^{82, 83} to calculate the distribution of $[M(\text{HOAc})_m(\text{H}_2\text{O})_{4-m}(\text{OAc})_2]_n$ species as a function of water content. This analysis suggested a distribution of 2 % of $m = 3$, 18 % of $m = 2$, 38 % of $m = 1$ and 42 % of $m = 0$ in 90/10 acetic acid/water solvent by mass, at room temperature. These species can undergo the following ionisation to ion pairings:



Studies on the addition of hydrobromic acid ⁷³ indicate that an acid base neutralisation reaction occurs between HBr and the stronger acetate base. If > 5 % water is present, very little of the bromide enters the coordination sphere and the predominant species is the ion-paired bromide salt:



It is unlikely that dissociation occurs to produce free bromide in solution because of the low dielectric constant of acetic acid.⁷²⁻⁷⁴ Although experimental data on the effect of elevated temperature is not available, the effect of temperature will probably be to disrupt any hydrogen bonding within and between water and acetic acid and further lower the dielectric constant.⁸⁴ This will reinforce the tendency to form ion pairings and for ions to enter the coordination spheres of the metals.

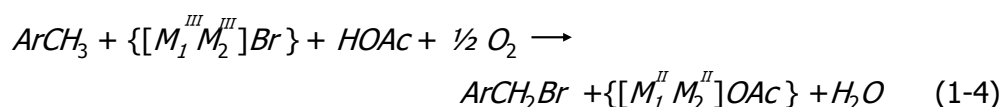
It is known that metal/bromide catalysts require carboxylic acid solvents, particularly acetic acid and that excess water will lower their activity.⁸⁵⁻⁹⁰ NMR studies have shown that the acetic acid – metal bond is weak (24.7 kJ/mol for Co and Mn).⁹¹⁻⁹⁴ Acetate ligands are thus weak and labile and can be displaced by other weak ligands such as peroxides, peroxy acids and oxygen. Thus, all the elements of substrate (*i.e.* aromatics), oxidant (*i.e.* oxygen), catalyst components (cobalt, manganese and bromide) can be present within an ion paired complex simultaneously and a rapid, coordinated redox cascade is able to occur as is illustrated in Figure 1-5.^{12, 27, 46}

Despite the efficiency of the desired reaction in the coordination complex, other less desirable reactions also occur:

- The decarboxylation of aromatic acids and of acetic acid.⁶²
- The formation of benzylic bromides.^{89, 95}
- The formation of methyl bromide.^{96, 97}

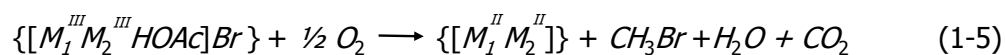
The decarboxylation of carboxylic acids is catalysed by Co^{III} . Thus, an important role of the Mn^{II} is to rapidly reduce the Co^{III} to Co^{II} before it can perform these undesirable side reactions. It is possible that monomeric and dimeric catalyst metal structures such as $[\text{Co}^{\text{III}}]$, $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}]$ and $[\text{Co}^{\text{III}}\text{Mn}^{\text{III}}]$ (the ligands have been omitted) where Mn^{II} is not readily available to reduce the Co^{III} could be disproportionately responsible for these undesirable reactions.

The metal dimers can be oxidised by one electron oxidants such as a peroxide radical or peroxy acid radical, or by two electron oxidants such as peroxides or peroxy acids. One electron oxidation gives $[\text{M}^{\text{II}}\text{M}^{\text{III}}]$ complexes which are useful catalytic species. Two electron oxidation gives $[\text{M}^{\text{III}}\text{M}^{\text{III}}]$ complexes which are less useful for the desired reactions. A possible side reaction of these complexes is a concerted two electron, single step oxidation to form benzylic bromides.^{35, 89}



There are two benzylic bromides that are formed, α -bromo-*p*-xylene and α -bromo-*p*-toluic acid. Benzylic bromides are a catalytically inactive form of bromine but are hydrolysed slowly, a process that restores the bromine to a catalytically useful form. α -Bromo-*p*-xylene is hydrolysed ~20 times faster than α -bromo-*p*-toluic. It is therefore the α -bromo-*p*-toluic which can lock up a sizeable proportion of the bromine in the system in a catalytically non-useful form, and this proportion is believed to be high, *i.e.* > 90 %. Under some process conditions the proportion of inactive bromine can approach 100 % and the catalyst system begins to fail.

Methyl bromide is probably formed by a similar two electron oxidation involving acetic acid:



1.3.6 Problems with the Conventional Terephthalic Acid Process and an Alternative Approach

In the conventional TA process, the TA produced precipitates out incorporating a significant amount of the intermediate 4-CBA within the crude crystals. The 4-CBA level is lowered in the purification process by dissolution of the crystals in high temperature water, hydrogenation of the 4-CBA to *p*-toluic acid over a fixed bed catalyst and recrystallisation. The activity of the catalyst limits the amount of 4-CBA that can be removed from the crude TA by this method. It is thus necessary to limit the 4-CBA incorporation into the crude crystals by running the oxidation reactor to high conversions with forcing conditions. This requires a long residence time with a large and expensive, titanium lined reactor.

This constraint can (in theory) be overcome by employing a solution process and such a process has been described in a patent.¹³ This describes a process in which a large inventory of acetic acid/water is employed to keep the TA below its solubility limit and thus in solution throughout the reaction. Under these circumstances, 4-CBA is no longer trapped in crystals and can be driven to low levels at much reduced reactor residence times and reactor volumes. The high reactivity of 4-CBA to oxidation compared to *p*-toluic acid helps this and the 4-CBA rapidly reacts away. This technology has not, to date, been commercialised at industrial scale.

1.3.7 Final Comments on the Chemistry

The preceding sections have reviewed the chemistry of the autoxidation of *pX* in a predominantly acetic acid solvent and the industrial process by which it is practiced. It has considered a major draw-back of this process, namely the use of large and expensive reactors and considered a (seemingly unsuccessful) attempt to solve this by use of an acetic acid based solution process.

A further solution based *pX* oxidation chemistry has been described in the literature that uses high temperature water as the solvent. The assessment of this chemistry as a potential industrial process for production of TA is the subject of

this PhD study. It is time to introduce the autoxidation of *p*X in high temperature water.

1.4 Introduction to *p*-Xylene Oxidation in High Temperature Water

An alternative solvent for a solution process is high temperature water, specifically near critical and supercritical water. The homogeneously catalysed oxidation of methylaromatics in HTW was first reported by Holliday.⁶ Due to its industrial importance, the selective oxidation of *p*X to TA in HTW has been extensively studied *e.g.* by the University of Nottingham⁹⁸⁻¹⁰⁴ and by other groups.¹⁰⁵⁻¹¹³ The industrial application of this alternative solution process forms the subject matter for this PhD study and the concept is introduced in the following sections.

1.4.1 The Properties of Near Critical and Supercritical Water

The properties of high temperature water (near and supercritical water) have been extensively reviewed *e.g.* by Weingartner and Franck.⁸⁴ The variation in selected properties from ambient temperatures to supercritical conditions are summarised in Figure 1-11(a)–(d).

The critical point of water occurs at a temperature and pressure of 374.15 °C and 221.2 bar_a respectively. Above this temperature and pressure, water is ‘supercritical’ and cannot be liquefied by increasing pressure; it often has a much lower density than in the liquid phase except at very high pressures. On the approach to the supercritical region, from the liquid phase, water is in the near critical region. At these elevated temperatures, the hydrogen bonding networks that characterise aqueous water are progressively disrupted and water becomes more organic like in its solvent properties. Thus, whilst the dielectric constant (ϵ) of water at 20 °C is 80.4, as temperature rises the dielectric constant falls to become like methanol (ϵ 32.7), then like acetone (ϵ 20.9), dichloromethane (ϵ 9.1), acetic acid (ϵ 6.2) and finally (in the supercritical region) like benzene (ϵ 2.3) then hexane (ϵ 1.9), (all ϵ quoted are the values at 20 °C to 1 decimal place).

The ionic product, K_w of water increases in the near critical region particularly at lower pressures and then falls precipitously at the critical point. This makes NCW corrosive above $\sim 300^\circ\text{C}$, because of its high acidity, and this has held back the commercial application of N/SCW particularly where feedstocks have highly variable compositions.

1.4.2 Chemistry in Near Critical and Supercritical Water

Research activity of chemistries in high-temperature water chemistry has been growing for more than 30 years. SCWO has been established as a technology for total oxidation and destruction of toxic wastes.^{105, 114-118} Also, a wide range of chemical reactions have been studied where supercritical water plays the role of a solvent and/or reactant and/or catalyst.^{115, 119-123} These technologies are more fully considered in Chapter 2.

There are several factors that make NCW and SCW advantageous for certain types of chemistry. The increase in the ionic product in NCW as the concentration of both H^+ and OH^- ions increases in the near critical region enhancing both acid and base catalysed reactions. The progressive drop in the dielectric constant makes a wide range of solvent properties available.

It is thus perhaps not surprising that autooxidations, for which acetic acid/water mixtures are generally excellent solvents, can be undertaken in high temperature water. Under these conditions, oxygen⁸⁴, $p\text{X}$ ^{124, 125} and TA all have high solubility, reaction kinetics are fast, and as the produced TA remains in solution, 4-CBA does not become trapped in crystals and can be reacted away to low levels. However, keeping TA in solution leaves it vulnerable to undesirable decarboxylation and cross coupling side reactions.

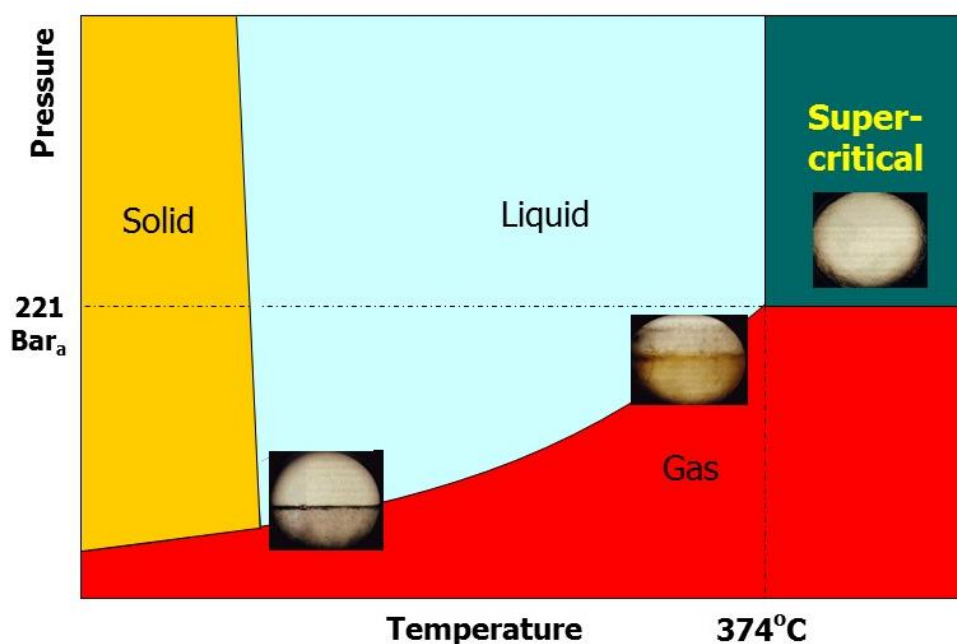


Figure 1-11(a). The phase diagram of water. The supercritical region occurs at temperatures and pressures above the critical point (shown by the dotted lines). The near critical region is in the liquid phase on the approach to the supercritical temperature. The phase photos show how the liquid/gas phase boundary blurs in the near critical region and disappears in the supercritical region. Source: Figures 1-11(a)-(d) are adapted from material from the UoN ¹²⁶ and other sources.¹²⁷⁻¹²⁹

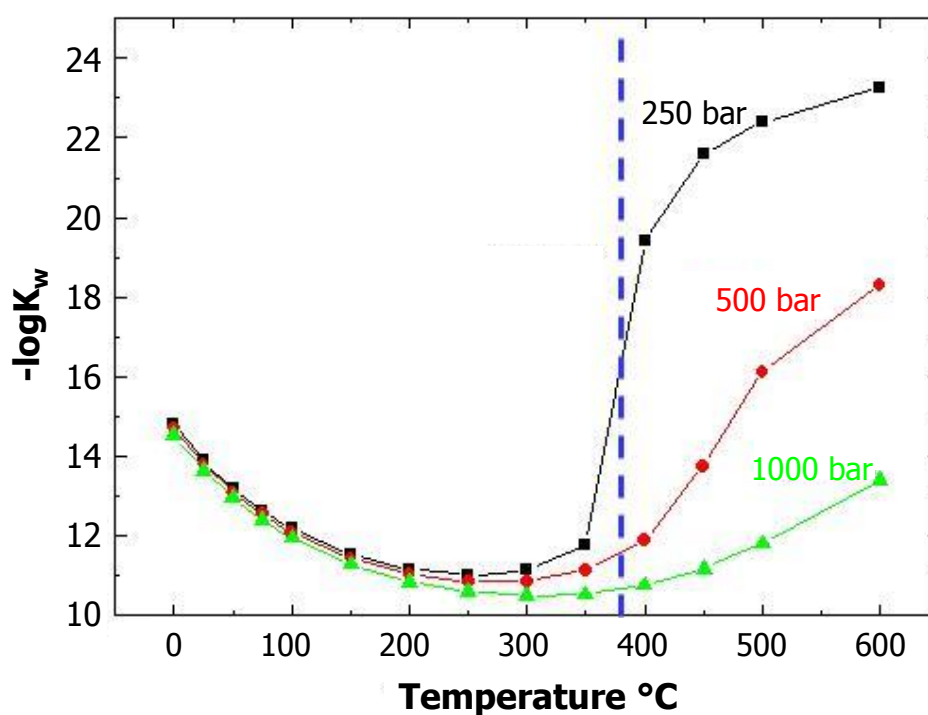


Figure 1-11(b). The variation of the ionic product of water, $K_w = [H^+][HO^-]$ with temperature. Note the increase in acidity in the near critical region and then the large drop in acidity around the critical temperature (shown by the dashed line).

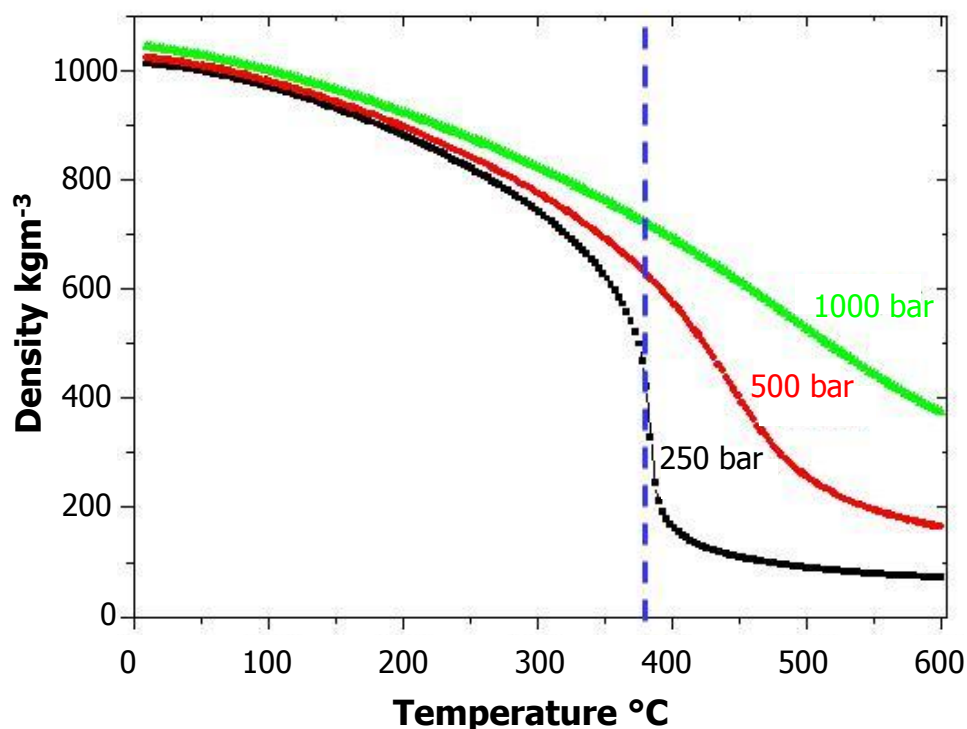


Figure 1-11(c). The variation of the density of water with temperature. Note the large changes in density that occur on the approach to the critical temperature (shown by the dashed line) particularly at lower supercritical pressures.

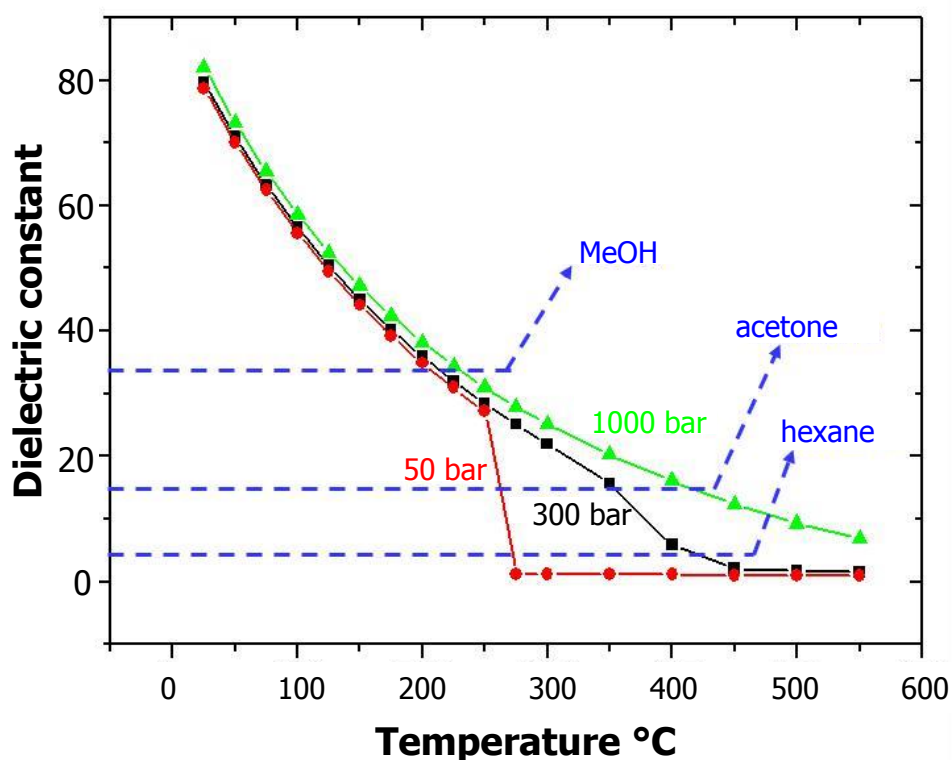


Figure 1-11(d). The progressive drop in the dielectric constant of water with increasing temperature. Dashed lines give the ambient values for methanol, acetone and hexane showing how water becomes progressively less polar with increasing temperature.

Thus, the broad objectives of this project are to quantify the yield of TA that can be obtained from *p*X oxidation in HTW, assess the extent of the undesirable side reactions and determine whether such a process could compete with the established acetic acid based industrial process. Detailed objectives will be considered in Section 1.7 but first we consider the challenges in introducing new process technology into a mature commodity chemical market such as PTA.

1.5 Challenges in the Introduction of New Process Technology

The aim of this project is to establish if *p*X N/SCWO could substitute the established industrial process for PTA. However, there are huge challenges in substituting an established major process technology with an alternative.

The chemical industry is highly capital intensive, for example a modern, world scale TA plant costs of the order of \$300M. Construction or commissioning delays and operation below the design capacity are very damaging to project economics. Thus, the industry is risk adverse and strongly favours incremental improvement of proven technology over transformational technology.

The situation is particularly challenging for the current TA technology because of its uniquely high overall process efficiency of ~97 %. It is also, in some respects, quite a Green Process, as defined by the principles of Green Chemistry.^{130, 131} If it were not for its huge scale and high market growth rates then it is unlikely that the industrial and scientific community would be attempting to find alternatives to the established technology.

It is instructive to review some recent attempts to develop alternatives to the established TA technology. This gives some perspective on the challenge faced by the *p*X N/SCWO technology.

Two examples are therefore considered:

- Bio-derived TA.
- Spray reactor technology.

1.5.1 Bio-Derived Terephthalic Acid

To understand the drive for bio-derived TA, it is helpful to appreciate the cost basis of soft drinks. Consider a 2 litre bottle of cola in the U.K. An unbranded cola can be purchased for around 30p and a branded cola for around 80p to £1. The cost of a PET bottle is $\sim 1 - 2\text{p}$ ¹³² so the cost of the sugary water content is probably $\sim 10 - 20\text{p}$. For a branded cola, the remaining margin of around 60 - 80p is the value of the brand. The low relative cost of a PET bottle means that this cost can double or treble or more without undermining the economics of the product.

PET polymer is made from two raw materials mono ethylene glycol (MEG) and TA. PET bottles have been made which are partially bio-derived where only the MEG component is bio-sourced or are fully bio-derived where both components are bio-sourced. Using bio-derived materials gives no significant change in bottle appearance or functionality and a comparison of bottles is shown in Figure 1-12.

The Coca-Cola Company have commercialised PlantBottle™ which contains up to 30 % bio-based material based on bio-derived MEG though this is currently a niche product targeted at environmentally concerned consumers.

Bio-derived routes to TA have been recently reviewed¹³³ and the main routes currently under investigation are summarised in Figure 1-13 produced from that review.

Some of these technologies have reached pilot plant scale though none have yet been commercialised. TA is a commodity material and it is unlikely that these technologies will significantly substitute fossil derived feedstock routes until the cost economics are favourable. Such cost information is commercial sensitive and not generally available and it is thus difficult to judge how close these technologies are to commercialisation. However, the low intensity of fermentation based technology and the current low price of oil provide significant head winds to commercialisation and it seems unlikely that there will be significant substitution of the fossil feedstock route to TA in the near term.



Figure 1-12. A 100 % bio-derived (left) and a fossil derived (right) PET water bottle. There is no loss of bottle quality or functionality in switching from fossil to bio-based feedstocks. The bottles were photographed by the author at the UoN.

Summary of the Key Technology Pathways to Bio-based PTA					
Bio-based Starting Material	Intermediate Materials	No. of key Process Steps from Starting Material to PTA	Production of Hydrocarbon as an Intermediate?	Theoretical Weight Yield from Starting Material to PTA	Key Industrial Technology Developer
Sugar	Oxygenated materials, <i>pX</i>	4	Yes	41 % (26 % to <i>pX</i>)	Virent
	<i>i</i> -BuOH, isobutylene, diisobutylene, <i>pX</i>	5	Yes	46 % (29 % to <i>pX</i>)	Gevo
	HMF, DMF, Diels-Alder, bicyclic ether, <i>pX</i>	5	Yes	61 % (92 % if ethylene is fossil-based)	Toray, UOP, Micromidas
	HMF, FDCA, Diels-Alder, bicyclic ether	4	No	61 % (92 % if ethylene is fossil-based)	BP
	Cis, cis-MA; cis, trans MA; trans, trans MA, Diels-Alder intermediate	5	No	61 % (92 % if ethylene is fossil-based)	Amyris/Draths
Limonene	<i>p</i> -Cymene	3	Yes	122 %	Sabir
Lignin	Various	3	Yes	16 % (assuming 10 % <i>pX</i> yield)	M&G

Figure 1-13. Current bio-based routes to bio-derived TA.¹³³ HMF is hydroxymethyl furfural, DMF is dimethyl furfural, FDCA is furan dicarboxylic acid, MA is muconic acid.

1.5.2 *p*-Xylene Spray Process

A significant technical innovation in TA process technology is a spray process for oxidising *p*X to TA. This concept has been developed by Subramaniam's group at the Center for Environmentally Beneficial Catalysis (CEBC) at the University of Kansas. The concept has been described¹³⁴ and the process economics considered¹³⁵; the process is also patented.¹³⁶

In this process, a solution comprising *p*X, acetic acid and soluble Co/Mn/Br catalyst components is pumped through a spray head to produce ~50 µ droplets in a vessel containing an oxygen and inert gas (either CO₂ or N₂) atmosphere. The *p*X reacts to produce intermediates and then TA and the heat produced evaporates (a proportion of) the acetic acid. The droplets and the TA particles produced descend under gravity and are collected in a slurry pool through which fresh oxygen and inert gas are being sparged. The process is claimed to produce TA containing a low level (< 25 ppm) of the intermediate 4-CBA which is thus suitable for PET production without the need for further purification. The process is also claimed to only oxidise (to CO₂ and CO) ~25 % of the acetic acid that is oxidised in the conventional process. The elimination of the purification plant and the reduced acetic acid oxidation are the major factors in claimed reductions of capital and variable costs of 55 % and 16 % respectively. The process is also claimed to have reduced environmental impact.

For a highly mature chemical commodity these claims represent very significant reductions and one would perhaps have expected the industry to have embraced the technology. However, at the time of writing, there has been no public announcement of any licensing of the technology within the industry.

This case study illustrates the challenge and difficulties in introducing a major, novel process technology into a mature commodity chemical market.

Building a large petrochemical plant involves the deployment of a large amount of capital (of the order of \$300M for a TA plant). Commissioning delays are hugely damaging to project economics and there is therefore a strong desire for proven technology that minimises technology risks. There therefore needs to be very large

potential benefits for companies to consider taking the risk. In TA, the main risk that companies have been prepared to take has been scale up, with plant capacities having increased from ~400k te/yr to ~2M te/yr over the last 20 years.

The capital benefit for the spray reactor arises from the elimination of the purification plant. As discussed in Section 1.2, current technologies with no purification plant produce medium grade terephthalic acid (MTA). These do not meet the pure grade specification of PTA and are generally used captively by the producer on their own in-house PET polymer plants. MTA processes, lacking a purification plant, tend to suffer from minor component impurity issues as discussed in Section 1.3.3. It has not yet been demonstrated that the spray technology can reduce the formation of these components and overcome such issues.

The existing TA process is in some respects a very good industrial process because it has such a high process yield of ~97 %. This limits the scope for improved yield, which is often a major driver of process improvement or substitution, and makes the current process very tough to beat. It is only the large industry size and relatively high growth rate that provides incentive to develop new technologies.

These case studies demonstrate the considerable challenges in introducing a major new process technology into the TA industry. The major benefit of *pX N/SCWO* is that it enables the recovery of the heat from the large reaction exotherm at a higher temperature compared to the conventional process. This makes the energy more thermodynamically valuable and produces a higher grade of steam. The economics of this are considered in more detail in Chapter 8 of this thesis. It also illustrates the difficulties in attempting to save capital cost by eliminating the purification plant and having a single stage process. Such an approach is only likely to achieve merchant market acceptance if it produces a PTA quality material. The insolubility of TA and its propensity to co-crystallise with intermediates and by-products of the process makes this a very difficult technical target.

1.6 Structure of the Project

This PhD project is linked to an industrial scale process development and is thus larger in scope than many PhD projects. The author undertook the rig and reactor

development and design, the experimental designs, the experimental supervision and the results interpretation. The experimental work was undertaken by a laboratory team. Also, there was consultancy with UoN supervisors and several post-doctoral students, with industrial colleagues and with Dr. Walt Partenheimer as an external consultant. The individuals involved are credited in the acknowledgements section.

The advantage of these arrangements was the large resources of people, of experimental facilities and of finance available. The author was therefore able to design and oversee a much larger number of experiments than in a more typical PhD. However, this also meant that the author did not personally perform all the experiments and analyses presented in this thesis.

1.7 Aims of the Project

This section introduces the broad aims of this PhD study.

The fundamental question to be addressed in this study is whether *pX* N/SCWO to produce PTA is economically viable when compared to the conventional acetic acid based process currently in use in the industry.

To make the N/SCWO process economic and commercially viable (against conventional technology) it is important to meet several criteria:

- The yield of TA must be comparable to that achieved with conventional technology of ~97 %.
- The TA material produced must meet with existing and long-established product specifications.
 - The level of residual reaction intermediates in the TA product must be low. For the PET polymerisation process, reaction intermediates act as polymer chain stoppers and limit the molecular weight that can be achieved.
 - The production of by-products (some of which are highly coloured) must be low as these impart undesirable colour to the polymer and are expensive to remove from the TA.
- The process flow sheet and plant design must:

- Have a lower cost than conventional technology. The cost needs to be lower than conventional to justify the risk of switching from an established and proven technology.
- Have a robust basis of safety.
- Have suitable (process side) materials of construction which can withstand the aggressive conditions of HTW for extended periods of years to decades.

The requirements around chemical yield and the residual concentrations of chemical intermediates and by-products can be influenced by different factors:

- The chemistry. This is impacted by process conditions, chosen reagents, catalysts employed, concentrations *etc.*
- The thermodynamics and physical properties.
- The hydrodynamics, particularly the choice of reactor design employed. The mixing and residence time distribution are important parameters.

These process requirements span multiple disciplines of process technology including chemistry, process engineering, reactor design and mixing, metallurgy and corrosion science, costing and economic analysis and hazard analysis.

This PhD aims to review and address (to an extent) all the issues posed in the above analysis. However, the issues raised above are extensive and some prioritisation will be necessary. In considering a new process technology from an industrial perspective, the key consideration is the chemical yield of the desired product. This is because without sufficient yield, there is no scope for an economic process, and all other considerations become irrelevant. For this reason, the primary focus of the study will be on the factors that influence chemical yield particularly the chemistry and the reactor design.

The next chapter reviews and extensively critiques the state of the art of *pX* N/SCWO at the commencement of this project. It then revisits the aims set out in this section and details specific issues and tasks to be addressed.

1.8 Structure of the Thesis

The structure of this PhD thesis is illustrated in Figure 1-14 and is described in the caption. This provides a valuable roadmap for navigating this thesis.

The Structure of the PhD Thesis

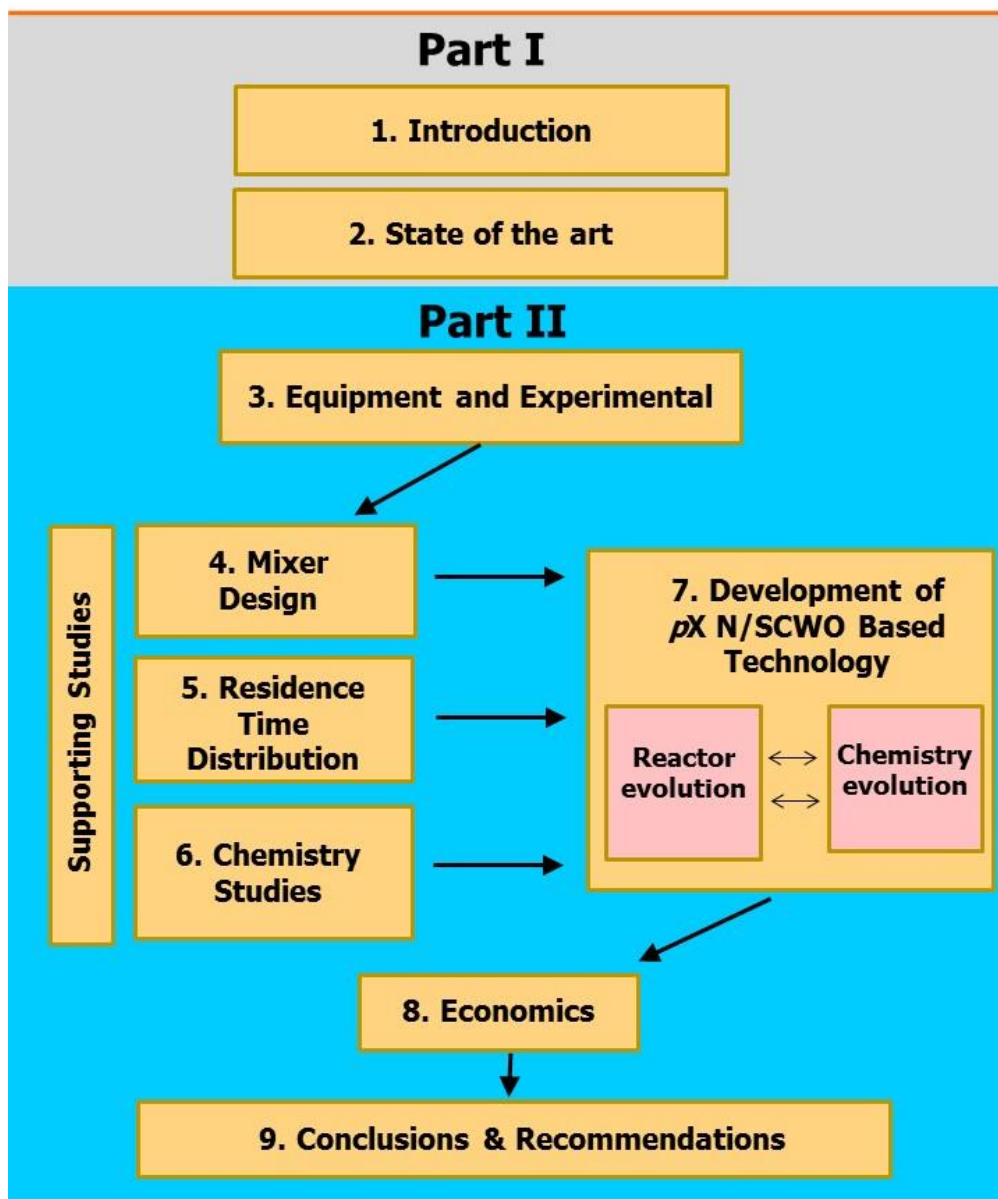


Figure 1-14. The structure of this PhD thesis. Part I contains two introductory chapters. Chapter 1 introduces *pX* oxidation and N/SCWO and describes the broad aims of the project. Chapter 2 describes and critiques the state of the art of *pX* N/SCWO at the commencement of this PhD project and uses this to provide more detailed aims and tasks. Part II contains the write up of the studies that have been undertaken for this PhD and comprises seven chapters. Chapter 3 gives the detail of the equipment and experimental procedures. Chapter 7 describes the development of the *pX* N/SCWO technology comprising both reactor and chemistry aspects. This development was facilitated by several supporting studies that are described in Chapters 4 – 6. Chapter 8 assesses the industrial economics of the technology. Finally, Chapter 9 concludes the thesis; it assesses the extent to which the aims articulated in Chapters 1 and 2 were addressed, draws conclusions about the industrial viability of the technology and makes recommendations for future studies.

1.9 References

1. M. Cesar, *SRI Report No. 9F, Terephthalic Acid*, SRI Consulting, Menlo Park, CA, 2005.
2. *Terephthalic Acid 05/06 - 6 PERP Report.*, Nexant Chem Systems, White Plains, NY, 2006.
3. *IHS Chemical World Analysis, PTA/DMT*, IHS Chemical Consulting, London, 2015.
4. E. O. C. Greiner, *PET Polymer*, SRI Consulting, Menlo Park, CA, 2009.
5. C. Lo, *Polyethylene Terephthalate (PET) PERP 2012-6*, Nexant Chem Systems, White Plains, NY, 2013.
6. R. L. Holliday, B. Y. M. Jong and J. W. Kolis, Organic synthesis in subcritical water - Oxidation of alkyl aromatics, *J. Supercrit. Fluids*, 1998, **12**, 255-260.
7. M. Numata, T. Isogai and T. Ogata, Process for producing terephthalic acid, CN Pat., 100 383 105, 2003.
8. J. Windle, Dimethyl terephthalate manufacturing process, US Pat., 3 839 414, 1970.
9. T. Fujii, S. Takeda, S. Takahashi and K. Namie, Process for the preparation of dimethyl terephthalate, US Pat., 4 096 340, 1975.
10. *Medium Quality Terephthalic Acid. PERP Report. 03/04S6, 2004*, Nexant Chem Systems, White Plains, NY, 2004.
11. A. G. Wonders, G. G. Lavoie, C. E. Sumner, B. W. Davenport, M. de Vreede and B. A. Tennant, Optimised liquid-phase oxidation, US Pat., 7 608 732, 2005.
12. W. Partenheimer, Methodology and scope of metal bromide autoxidation of hydrocarbons, *Catal. Today*, 1995, **23**, 69-158.
13. J. A. Turner, D. J. Royall, D. S. Hugall, G. H. Jones and D. C. Woodcock, Production of Terephthalic Acid, US Pat., 6 307 099, 2001.
14. S. D. Housley and J. A. Turner, Method for increasing oxidation reactor production capacity, US Pat., 7 060 853, 2006.
15. W. Partenheimer, The effect of zirconium in metal/bromide catalysts during the autoxidation of *p*-xylene - Part I. Activation and changes in benzaldehyde intermediate formation, *J. Mol. Catal. A: Chem.*, 2003, **206**, 105-119.
16. Q. B. Wang, X. Li, L. J. Wang, Y. W. Cheng and G. Xie, Kinetics of *p*-xylene liquid-phase catalytic oxidation to terephthalic acid, *Ind. Eng. Chem. Res.*, 2005, **44**, 261-266.
17. *SRI Report 9E. Terephthalic acid and dimethyl terephthalate*, SRI Consulting, Menlo Park, CA, 1997.
18. M. Feld and G. Zoche, Method for the recovery and reuse of cobalt and/or manganese components of catalysts (solubilizing salt by joint action of hydrogen bromide, acetic anhydride and acetyl bromide), US Pat., 4,490,297, 1981.
19. R. E. Michel, M. R. Kegelman and F. J. Sebelist, Catalyst Recovery, US Pat., 4 910 175, 1990.
20. A. L. Hensley, Catalyst recovery by residue incineration process, US Pat., 3 341 470, 1984.
21. S. S. Lande and J. K. Kochi, Formation and oxidation of alkyl radicals by cobalt (III) complexes, *J. Am. Chem. Soc.*, 1968, **90**, 5196-5207.

22. R. M. Dessau, E. I. Heiba and W. J. Koehl, Oxidation by metal salts. V. Cobaltic acetate oxidation of alkylbenzenes, *J. Am. Chem. Soc.*, 1969, **91**, 6830-6837.
23. E. I. Heiba, R. M. Dessau and W. J. Koehl, Oxidation by metal salts .3. Reaction of manganic acetate with aromatic hydrocarbons and reactivity of carboxymethyl radical, *J. Am. Chem. Soc.*, 1969, **91**, 138-145.
24. E. J. Y. Scott, Kinetics of reactions of cobalt(II) and cobalt(III) acetates with benzyl hydroperoxide in acetic acid at 25 degrees, *J. Phys. Chem.*, 1970, **74**, 1174-1182.
25. H. D. Holtz, Use of cobalt(II) ion and hydrochloric acid as catalyst for liquid-phase oxidation of alkylbenzenes, *J. Chem. Soc. D*, 1971, **0**, 1166-1166.
26. G. H. Jones, *p*-Xylene autoxidation studies - oxidation of cobalt(II) and manganese(II) acetates by peracids, *J. Chem. Soc., Chem. Commun.*, 1979, **0**, 536-537.
27. W. Partenheimer, A Chemical Model for the Amoco "MC" Oxygenation Process to Produce Terephthalic acid, in *Catalysis of Organic Reactions*, ed. D. W. Blackburn, Marcel Dekker Inc., New York, 1990, ch. 20, pp. 321-346.
28. W. Partenheimer, Characterisation of the reaction of cobalt(II) acetate, dioxygen and acetic acid, and its significance in autoxidation reactions, *J. Mol. Catal.*, 1991, **67**, 35-46.
29. W. Partenheimer, The redox and coordination chemistry of Co(OAc)₂, Mn(OAc)₂, and hydrogen bromide with *m*-chloroperbenzoic acid in acetic acid, *Abstr. Pap., Am. Chem. Soc.*, 1992, **204**, 19.
30. W. Partenheimer, presented in part at the Activation of Dioxygen and Homogeneous Catalytic Oxidation. [5th Proc. Int. Symp.] Plenum, New York, March, 1993.
31. J. Malyszko, S. Michalkiewicz, D. Goral and M. Scendo, Electrochemical characteristics of the Mn(III)/Mn(II) and Co(III)/Co(II) systems at platinum in anhydrous acetic acid solutions, *J. Appl. Electrochem.*, 1998, **28**, 107-113.
32. W. Partenheimer, Novel catalytic characteristics of the Co/Mn/Cl/Br liquid phase oxidation catalyst (1), in *Catalysis of Organic Reactions*, ed. F. E. Herkes, CRC Press, Florida, 1998, vol. 75, pp. 357-368.
33. W. Partenheimer, Function of metals and halides to control activity and selectivity in autoxidation reactions, *Abstr. Pap., Am. Chem. Soc.*, 2000, **220**, 503.
34. X. D. Jiao, P. D. Metelski and J. H. Espenson, Equilibrium and kinetics studies of reactions of manganese acetate, cobalt acetate, and bromide salts in acetic acid solutions, *Inorg. Chem.*, 2001, **40**, 3228-3233.
35. W. Partenheimer, The structure of metal/bromide catalysts in acetic acid/water mixtures and its significance in autoxidation, *J. Mol. Catal. A: Chem.*, 2001, **174**, 29-33.
36. W. Partenheimer, Comments on the paper "Low-bromide containing MC catalyst for the autoxidation of *para*-xylene" by B. Saha and J.H. Espenson [J. Mol. Catal. A 271 (2007) 1-5], *J. Mol. Catal. A: Chem.*, 2007, **275**, 240-240.
37. N. M. Emanuel, E. T. Denisov and Z. K. Maizus, in *Liquid Phase Oxidation of Hydrocarbons*, ed. B. J. Hazzard, Plenum Press, New York, 1967, vol. 158, p. 248.

38. M. Hronec and J. Ilavsky, Oxidation of polyalkylaromatic hydrocarbons. 12. Technological aspects of *p*-xylene oxidation to terephthalic acid in water, *Ind. Eng. Chem. Prod. Res. Dev.*, 1982, **21**, 455-460.
39. M. Hronec, Z. Cvengrosova and J. Ilavsky, Kinetics and mechanism of cobalt-catalysed oxidation of *p*-xylene in the presence of water, *Ind. Eng. Chem. Process Des. Dev.*, 1985, **24**, 787-794.
40. M. Hronec and Z. Hrabec, Liquid-phase oxidation of *p*-xylene catalyzed by metal-oxides, *Ind. Eng. Chem. Prod. Res. Dev.*, 1986, **25**, 257-261.
41. M. Haruštiak, M. Hronec and J. Ilavsky, Kinetics and mechanism of cobalt bromide catalyzed oxidation of *p*-xylene in the presence of phase transfer catalysts, *J. Mol. Catal.*, 1989, **53**, 209-217.
42. M. Haruštiak, M. Hronec and J. Ilavský, Kinetics and mechanism of phase-transfer catalyzed oxidation of *p*-xylene by molecular oxygen, *J. Mol. Catal.*, 1988, **48**, 335-342.
43. Z. Cvengrosova, M. Hronec, J. Kizlink, T. Pasternakova, S. Holotik and J. Ilavsky, Study of *p*-xylene reaction with Co-Br-pyridine catalyst .1. Reaction in acetic-acid, *J. Mol. Catal.*, 1986, **37**, 349-358.
44. Z. Cvengrosova, M. Hronec, J. Kizlink, L. Malik and J. Ilavsky, Study of *p*-xylene reaction with Co-Br-pyridine catalyst .2. Reaction in aqueous system, *J. Mol. Catal.*, 1987, **40**, 235-242.
45. A. Kaszonyi, M. Hronec, L. Lauko and J. Ilavsky, Study of the activity of Co-Br-py catalysts during oxidation of *p*-xylene in acetic-acid, *J. Mol. Catal.*, 1989, **57**, 105-112.
46. W. Partenheimer and R. K. Gipe, Catalytic Selective Oxidation, eds. S. T. Oyama and J. W. Hightower, American Chemical Society, Washington DC, 1993, vol. 523, ch. 7, pp. 81-88.
47. Y. Kamiya, Catalysis by cobalt and bromide ions in the autoxidation of alkylbenzenes in acetic acid, *J. Catal.*, 1974, **33**, 480-485.
48. Y. Kamiya, The autoxidation of tetralin catalysed by cobalt salt and sodium bromide in acetic acid, *Tetrahedron*, 1966, **22**, 2029-2038.
49. Y. Kamiya, T. Nakajima and K. Sakoda, Autoxidation of *p*-xylene catalyzed with cobalt monobromide in acetic acid, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 2211-2215.
50. K. Sakoda, Y. Kamiya and N. Ohta, Autoxidation of toluene catalyzed with cobalt monobromide in acetic acid, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 641-646.
51. Y. Kamiya and T. Ushiba, Autoxidation of toluic acids catalyzed by cobalt and bromide ions in acetic-acid, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 1563-1566.
52. Y. Kamiya, The oxidation of toluene by cobalt-copper-bromide system. A side-chain acetoxylation., *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3321-3325.
53. G. H. Jones, A mechanistic study of the origins of synergy and antagonism in the Co(OAc)Br-catalysed and Mn(OAc)Br-catalyzed autoxidation of *p*-xylene, *J. Chem. Res., Synop.*, 1982, 207-207.
54. G. H. Jones, A kinetic and mechanistic study of the redox chemistry of cobalt acetate in aqueous acetic-acid, *J. Chem. Res. (M)*, 1981, 2801-2867.
55. G. H. Jones, A kinetic and mechanistic study of the redox chemistry of cobalt acetate in aqueous acetic-acid, *J. Chem. Res., Synop.*, 1981, 228-229.
56. C. E. H. Bawn and T. K. Wright, Autoxidation of *p*-toluic acid catalyzed by cobalt bromide, *Discuss. Faraday Soc.*, 1968, 164-172.

57. D. A. S. Ravens, The kinetics and mechanism of the auto-oxidation of *p*-toluic acid in acetic acid solution catalyzed by cobalt and manganese bromides, *Trans. Faraday Soc.*, 1959, **55**, 1768-1776.
58. A. S. Hay and H. S. Blanchard, Autoxidation reactions catalyzed by cobalt acetate bromide, *Can. J. Chem.*, 1965, **43**, 1306-1317.
59. V. N. Aleksandrov, Mechanism of *p*-xylene oxidation in acetic-acid solution with cobalt-manganese-bromide catalyst, *Zh. Org. Khim.*, 1978, **14**, 1517-1522.
60. C. F. Hendriks, H. C. A. Vanbeek and P. M. Heertjes, Reactions of some peracids and hydroperoxides with cobalt(II) and cobalt(III) acetate in acetic-acid solution, *Ind. Eng. Chem. Prod. Res. Dev.*, 1979, **18**, 38-43.
61. P. Roffia, P. Calini, L. Motta and S. Tonti, By-product identification in the terephthalic acid production process and possible mechanisms of their formation, *Ind. Eng. Chem. Prod. Res. Dev.*, 1984, **23**, 629-634.
62. W. Partenheimer, Chemistry of the oxidation of acetic acid during the homogeneous metal-catalysed aerobic oxidation of alkylaromatic compounds, *Appl. Catal.*, A, 2011, **409-410**, 48-54.
63. W. Partenheimer, The effect of zirconium in metal/bromide catalysts on the autoxidation of *p*-xylene - Part II. Alternative metals to zirconium and the effect of zirconium on manganese(IV) dioxide formation and precipitation with pyromellitic acid, *J. Mol. Catal. A: Chem.*, 2003, **206**, 131-144.
64. W. Partenheimer, The complex synergy of water in metal/bromide autoxidations. Part II. Effect of water and catalyst on the aerobic oxidation of benzaldehydes and the effect of water on the elementary catalytic pathways, *Adv. Synth. Catal.*, 2005, **347**, 580-590.
65. G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals ($\cdot\text{OH}/\cdot\text{O}$) in aqueous-solution, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513-886.
66. I. M. Godfrey and M. V. Sargent, Preparation of methoxyphenols by Baeyer-Villiger oxidation of methoxybenzaldehydes, *J. Chem. Soc., Perkin Trans. 1*, 1974, DOI: 10.1039/p19740001353, 1353-1354.
67. L. N. Mander and C. M. Williams, Oxidative degradation of benzene rings, *Tetrahedron*, 2003, **59**, 1105-1136.
68. J. B. Dunn, M. L. Burns, S. E. Hunter and P. E. Savage, Hydrothermal stability of aromatic carboxylic acids, *J. Supercrit. Fluids*, 2003, **27**, 263-274.
69. J. Dermietzel, C. Wienhold, H. Grundmann, A. Staschok, J. Koch and E. Bordes, Tracer studies on carbon-monoxide and carbon-dioxide formation at liquid-phase oxidation of *p*-xylene, *Chem. Tech.*, 1983, **35**, 29-32.
70. N. S. Allen, M. Edge, J. Daniels and D. Royall, Spectroscopic analysis of organic contaminants in terephthalic acid: colour implications in poly(ethylene terephthalate) manufacture, *Polym. Degrad. Stab.*, 1998, **62**, 373-383.
71. P. Roffia, P. Calini and S. Tonti, Methyl acetate - by-product in the terephthalic acid production process - mechanisms and rates of formation and decomposition in oxidation, *Ind. Eng. Chem. Res.*, 1988, **27**, 765-770.
72. O. W. Kolling and J. L. Lambert, Dissociation of metal acetates in anhydrous acetic acid, *Inorg. Chem.*, 1964, **3**, 202-205.

73. A. I. Popov, in *The Chemistry of Non Aqueous Solvents. Volume III: Aprotic and Acidic Solvents*, ed. J. J. Lagowski, Elsevier Inc, New York, 1970, vol. III, ch. 5, p. 214.
74. P. J. Proll and L. H. Sutcliffe, Dissociation constants of some inorganic acetates in anhydrous acetic acid, *Trans. Faraday Soc.*, 1961, **57**, 1078-1087.
75. J. M. Vanniekerk and F. R. L. Schoening, The crystal structures of nickel acetate, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and cobalt acetate, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, *Acta Crystallogr.*, 1953, **6**, 609-612.
76. E. F. Bertaut, T. Q. Duc, P. Burlet, M. Thomas and J. M. Moreau, Crystal-structure of manganese acetate tetrahydrate, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1974, **30**, 2234-2236.
77. C. F. Hendriks, H. C. A. Vanbeek and P. M. Heertjes, Structure of cobalt(II) acetate and cobalt(III) acetate in acetic-acid solution, *Ind. Eng. Chem. Prod. Res. Dev.*, 1979, **18**, 43-46.
78. K. Sawada and M. Tanaka, Aquation of some transition-metal acetates in acetic-acid, *J. Inorg. Nucl. Chem.*, 1973, **35**, 2455-2464.
79. A. W. Davidson and W. Chappell, Further Studies on Acetic Acid - Acetate Solutions, *J. Chem. Soc.*, 1933, **55**, 3531-3537.
80. P. J. Proll, J. Walkley and L. H. Sutcliffe, Species of cobalt(II) in acetic acid .1. cobaltous acetate in presence of water and of sodium acetate, *J. Phys. Chem.*, 1961, **65**, 455-460.
81. W. P. Tappmeyer and A. W. Davidson, Cobalt and nickel acetates in anhydrous acetic acid, *Inorg. Chem.*, 1963, **2**, 823-825.
82. K. Sawada, K. Agata and M. Tanaka, Aquation of 1st row transition-metal perchlorates in acetic-acid, *Inorg. Chim. Acta*, 1978, **30**, 127-130.
83. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley - Interscience, New York, 2007.
84. H. Weingartner and E. U. Franck, Supercritical water as a solvent, *Angew. Chem., Int. Ed.*, 2005, **44**, 2672-2692.
85. V. N. Aleksandrov, Influence of water on the catalytic-oxidation of certain methylaromatic hydrocarbons in acetic-acid at increased temperatures, *Kinet. Catal.*, 1979, **20**, 288-292.
86. H. Bartnicka, I. Bojanowska and M. K. Kalinowski, Solvent effect on the dissociation-constants of aliphatic carboxylic-acids, *Aust. J. Chem.*, 1991, **44**, 1077-1084.
87. H. Bartnicka, I. Bojanowska and M. K. Kalinowski, Solvent effect on the Hammett reaction constant of substituted benzoic-acids, *Aust. J. Chem.*, 1993, **46**, 31-36.
88. J. K. Kochi and J. D. Bacha, Solvent effects on the oxidation of alkyl radicals by lead(IV) and copper(II) complexes, *J. Org. Chem.*, 1968, **33**, 2746-2754.
89. W. Partenheimer, The complex synergy of water in the metal/bromide autoxidation of hydrocarbons caused by benzylic bromide formation, *Adv. Synth. Catal.*, 2004, **346**, 297-306.
90. Q. B. Wang, X. Li, L. J. Wang, Y. W. Cheng and G. Xie, Effect of water content on the kinetics of *p*-xylene liquid-phase catalytic oxidation to terephthalic acid, *Ind. Eng. Chem. Res.*, 2005, **44**, 4518-4522.
91. A. Hioki, S. Funahashi, M. Ishii and M. Tanaka, Metal-complexes in acetic-acid .8. O-17 nuclear-magnetic-resonance studies on the acetic-acid exchange of manganese(II), iron(II), cobalt(II), nickel(II), and copper(II) perchlorates in acetic-acid, *Inorg. Chem.*, 1986, **25**, 1360-1364.

92. A. Hioki, S. Funahashi and M. Tanaka, Metal-complexes in acetic-acid .5. Proton magnetic-resonance studies on acetic-acid exchange at the 1st coordination sphere of manganese(II), *Inorg. Chem.*, 1983, **22**, 749-752.
93. A. Hioki, S. Funahashi and M. Tanaka, Metal-complexes in acetic-acid .7. O-17 and proton nuclear magnetic-resonance studies on acetic-acid exchange processes of the chloride, nitrate, and acetate of nickel(II) in acetic-acid, *J. Phys. Chem.*, 1985, **89**, 5057-5061.
94. A. Hioki, S. Funahashi and M. Tanaka, Metal-complexes in acetic-acid .9. Kinetic-study of acetic-acid exchange on manganese(II), cobalt(II), and copper(II) acetates in acetic-acid by O-17 nuclear-magnetic-resonance, *Inorg. Chem.*, 1986, **25**, 2904-2907.
95. P. D. Metelski, V. A. Adamian and J. H. Espenson, Mechanistic role of benzylic bromides in the catalytic autoxidation of methylarenes, *Inorg. Chem.*, 2000, **39**, 2434-2439.
96. J. L. Broecker, W. Partenheimer and B. I. Rosen, Manufacture of aromatic carboxylic acids using cerium to facilitate a low bromine/metal ratio in the oxidation catalyst, US Pat., 5,453,538, 1995.
97. W. Partenheimer, The Aerobic Oxidative Cleavage of Lignin to Produce Hydroxyaromatic Benzaldehydes and Carboxylic Acids via Metal/Bromide Catalysts in Acetic Acid/Water Mixtures, *Adv. Synth. Catal.*, 2009, **351**, 456-466.
98. P. J. Hamley, T. Ilkenhans, J. M. Webster, E. Garcia-Verdugo, E. Venardou, M. J. Clarke, R. Auerbach, W. B. Thomas, K. Whiston and M. Poliakoff, Selective partial oxidation in supercritical water: the continuous generation of terephthalic acid from *para*-xylene in high yield, *Green Chem.*, 2002, **4**, 235-238.
99. J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, E. M. Vaquero, L. M. Dudd, I. Pearson, D. Housley, W. Partenheimer, W. B. Thomas, K. Whiston and M. Poliakoff, Catalytic selective partial oxidations using O(2) in supercritical water: the continuous synthesis of carboxylic acids, *Green Chem.*, 2007, **9**, 1238-1245.
100. E. Garcia-Verdugo, E. Venardou, W. B. Thomas, K. Whiston, W. Partenheimer, P. A. Hamley and M. Poliakoff, Is it possible to achieve highly selective oxidations in supercritical water? Aerobic oxidation of methylaromatic compounds, *Adv. Synth. Catal.*, 2004, **346**, 307-316.
101. E. Garcia-Verdugo, J. Fraga-Dubreuil, P. A. Hamley, W. B. Thomas, K. Whiston and M. Poliakoff, Simultaneous continuous partial oxidation of mixed xylenes in supercritical water, *Green Chem.*, 2005, **7**, 294-300.
102. J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, E. Perez, I. Pearson, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Prevention of Manganese Precipitation during the Continuous Selective Partial Oxidation of Methyl Aromatics with Molecular Oxygen in Supercritical Water, *Adv. Synth. Catal.*, 2009, **351**, 1866-1876.
103. E. Perez, J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 1. Comparison with *ortho*-xylene and the role of the catalyst, *Green Chem.*, 2011, **13**, 2389-2396.
104. E. Perez, J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, M. L. Thomas, C. Yan, W. B. Thomas, D. Housley, W. Partenheimer and M.

- Poliakoff, Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 2. The discovery of better catalysts, *Green Chem.*, 2011, **13**, 2397-2407.
105. P. E. Savage, J. B. Dunn and J. L. Yu, Recent advances in catalytic oxidation in supercritical water, *Combust. Sci. Technol.*, 2006, **178**, 443-465.
 106. J. B. Dunn and P. E. Savage, High-temperature liquid water: A viable medium for terephthalic acid synthesis, *Environ. Sci. Technol.*, 2005, **39**, 5427-5435.
 107. J. B. Dunn and P. E. Savage, Terephthalic acid synthesis in high-temperature liquid water, *Ind. Eng. Chem. Res.*, 2002, **41**, 4460-4465.
 108. J. B. Dunn, D. I. Urquhart and P. E. Savage, Terephthalic acid synthesis in supercritical water, *Adv. Synth. Catal.*, 2002, **344**, 385-392.
 109. Y. L. Kim, S. J. Chung, J. D. Kim, J. S. Lim, Y. W. Lee and S. C. Yi, Uncatalyzed partial oxidation of *p*-xylene in sub- and supercritical water, *React. Kinet. Catal. Lett.*, 2002, **77**, 35-42.
 110. Y. L. Kim, J. D. Kim, J. S. Lim, Y. W. Lee and S. C. Yi, Reaction pathway and kinetics for uncatalyzed partial oxidation of *p*-xylene in sub- and supercritical water, *Ind. Eng. Chem. Res.*, 2002, **41**, 5576-5583.
 111. M. Osada and P. E. Savage, Terephthalic Acid Synthesis at Higher Concentrations in High-Temperature Liquid Water. 1. Effect of Oxygen Feed Method, *AIChE J.*, 2009, **55**, 710-716.
 112. M. Osada and P. E. Savage, Terephthalic Acid Synthesis at Higher Concentrations in High-Temperature Liquid Water. 2. Eliminating Undesired Byproducts, *AIChE J.*, 2009, **55**, 1530-1537.
 113. J. B. Dunn and P. E. Savage, Economic and environmental assessment of high-temperature water as a medium for terephthalic acid synthesis, *Green Chem.*, 2003, **5**, 649-655.
 114. Z. Y. Ding, M. A. Frisch, L. Li and E. F. Gloyna, Catalytic Oxidation in Supercritical Water, *Ind. Eng. Chem. Res.*, 1996, **35**, 3257-3279.
 115. P. E. Savage, Organic chemical reactions in supercritical water, *Chem. Rev.*, 1999, **99**, 603-621.
 116. P. E. Savage, A perspective on catalysis in sub- and supercritical water, *J. Supercrit. Fluids*, 2009, **47**, 407-414.
 117. M. B. García-Jarana, I. Kings, J. Sánchez-Oneto, J. R. Portela and B. Al-Duri, Supercritical water oxidation of nitrogen compounds with multi-injection of oxygen, *J. Supercrit. Fluids*, 2013, **80**, 23-29.
 118. B. Al-Duri, F. Alsoqyani and I. Kings, Supercritical water oxidation for the destruction of hazardous waste: better than incineration, *Philos. Trans. R. Soc., A*, 2015, **373** 20150013
 119. A. Kruse and E. Dinjus, Hot compressed water as reaction medium and reactant - 2. Degradation reactions, *J. Supercrit. Fluids*, 2007, **41**, 361-379.
 120. A. Kruse and E. Dinjus, Hot compressed water as reaction medium and reactant - Properties and synthesis reactions, *J. Supercrit. Fluids*, 2007, **39**, 362-380.
 121. J. Fraga-Dubreuil and M. Poliakoff, Organic reactions in high-temperature and supercritical water, *Pure Appl. Chem.*, 2006, **78**, 1971-1982.
 122. D. Broll, C. Kaul, A. Kramer, P. Krammer, T. Richter, M. Jung, H. Vogel and P. Zehner, Chemistry in supercritical water, *Angew. Chem., Int. Ed.*, 1999, **38**, 2999-3014.

123. M. D. Bermejo and M. J. Cocero, Supercritical water oxidation: A technical review., *AIChE J.*, 2006, **52**, 3933-3951.
124. J. F. Connolly, Solubility of Hydrocarbons in Water Near the Critical Solution Temperatures, *J. Chem. Eng. Data*, 1966, **11**, 13-16.
125. K. G. Knauss and S. A. Copenhaver, The solubility of *p*-xylene in water as a function of temperature and pressure and calculated thermodynamic quantities, *Geochim. Cosmochim. Acta*, 1995, **59**, 2443-2448.
126. E. Venardou, PhD thesis, University of Nottingham, 2004.
127. NIST - Physical properties of water, <http://webbook.nist.gov/chemistry>, Accessed September, 2017.
128. K. Heger, M. Uematsu and E. U. Franck, The Static Dielectric Constant of Water at High Pressures and Temperatures to 500 MPa and 550°C, *Ber. Bunsenges. Phys. Chem.*, 1980, **84**, 758-762.
129. W. L. Marshall and E. U. Franck, Ion product of water substance, 0--1000 °C, 1--10,000 bars New International Formulation and its background, *J. Phys. Chem. Ref. Data*, 1981, 295-304.
130. P. T. Anastas and J. C. Warner, *Green chemistry: theory and practice*, Oxford University Press, 2000.
131. P. Anastas and N. Eghbali, Green chemistry: principles and practice, *Chem. Soc. Rev.*, 2010, **39**, 301-312.
132. The price of making a plastic bottle, *The Economist*, Nov. 2014.
133. D. I. Collias, A. M. Harris, V. Nagpal, I. W. Cottrell and M. W. Schultheis, Biobased Terephthalic Acid Technologies: A Literature Review, *Ind. Biotechnol.*, 2014, **10**, 91-105.
134. M. Li, F. Niu, X. Zuo, P. D. Metelski, D. H. Busch and B. Subramaniam, A spray reactor concept for catalytic oxidation of *p*-xylene to produce high-purity terephthalic acid, *Chem. Eng. Sci.*, 2013, **104**, 93-102.
135. M. Li, T. Ruddy, D. Fahey, D. H. Busch and B. Subramaniam, Terephthalic Acid Production via Greener Spray Process: Comparative Economic and Environmental Impact Assessments with Mid-Century Process, *ACS Sustainable Chem. Eng.*, 2014, **2**, 823-835.
136. B. Subramaniam, D. H. Busch and F. Niu, Spray process for selective oxidation., US Pat., 9 238 608, 2010.

2 *p*-Xylene Near/Supercritical Water Oxidation; The State of the Art

2.1 Overview

This thesis explores the use of near critical and supercritical water as a medium for the industrial synthesis of TA from *pX* feedstock. This chapter briefly reviews literature on the full range of synthetic reactions performed in this media then considers oxidation reactions (and specifically xylene and *pX* oxidations) and reactors. The author then describes the N/SCWO rigs available at the start of this PhD project and considers the oxidation formulations and experimental and analytical techniques available. These designs, formulations, analytical and experimental techniques are extensively critiqued and this provides the starting basis for the programme of rig design, experimental improvements and chemistry development described in the later chapters.

2.2 Literature Review of Near/Supercritical Water Chemistry

2.2.1 Related Applications of SCW

An early application of SCWO, was for the total oxidative destruction of industrial wastes into small inorganic molecules such as CO₂ and H₂O. Early work was often uncatalysed but the use of homo and heterogeneous catalysts has increased with time. Reviews include Savage *et al.*,¹⁻⁴ Schneider *et al.*,⁵ Kritzer *et al.*⁶ and Marrone.⁷ Al-Duri *et al.*^{8,9} consider SCWO with hetero atoms. Corrosion aspects are considered by Kritzer *et al.*¹⁰ and the precipitation of salts by Marrone *et al.*^{11,12} Maharrey *et al.*^{13,14} considers mechanistic aspects and Dagaut *et al.*¹⁵ and Koda *et al.*¹⁶ consider kinetics. Applications include destruction of military waste¹⁷ and chemical weapons.¹⁸

SCW has been used as a medium to convert biomass to liquid or gaseous fuel as reviewed by Matsumura *et al.*¹⁹ and Vogel *et al.*²⁰ Selecting suitable materials of construction to avoid corrosion and the precipitation of salts can be problematic especially in the presence of sulfur, nitrogen and halides. However, with a well-defined feedstock, such difficulties can be usually overcome.

2.2.2 Chemical Synthesis in N/SCW

There is increasing interest and activity in chemical synthesis in N/SCWO. There are many publications that review work in this area.^{2, 3, 5, 21-33}

Table 2-1 summarises and references the main types of chemistries relevant to industrial commodities that have been reported.

2.2.3 Xylene N/SCWO Chemistry

Five academic groups have been active in the field of *pX* N/SCWO. The first publication was in 1998 by Holliday at the US Agricultural Research Service together with Clemson University. In 2002, there were publications by three additional groups, Kim at the Korea Institute of Science and Technology (with co-workers from the University of Hanyang), Savage at the University of Michigan and Poliakoff at the University of Nottingham. Holliday and Kim produced no further publications, Savage continued to publish experimental papers until 2009 and Poliakoff's latest experimental publications have been in 2016. The range of conditions employed by these groups for NCWO and SCWO are in Tables 2-2(a) and (b) respectively and the conditions for maximum yields of TA in Tables 2-2(c) and (d).

The various groups present their data in different ways and here, the data has been reworked and tabulated chronologically on a basis consistent with the reporting conventions to be employed in this thesis, as defined in Section 3.10.6.

The papers contain considerable variations in approach which make these comparisons difficult to construct. The data in the tables should be treated as indicative and reference made to the original papers for full details.

Table 2-1. The main types of N/SCW chemistry relevant to industrial commodities currently reported in the literature. This field is extensive and growing and the reader is referred to the referenced literature for a fuller analysis.

Reaction type	Reactant	Catalysts	Products	References
Oxidation				
	<i>p</i> -Xylene	MnBr ₂	Terephthalic acid	See Section 2.2.3
	Ethanol		Formaldehyde	34
	Methane		Methanol, formaldehyde	35
	Cyclohexane		Cyclohexene, cyclohexanone, cyclohexanol <i>etc.</i>	36
	<i>i</i> -Butene		<i>i</i> -Butyraldehyde, <i>i</i> -butanol	37
	Propane	MnO ₂ , Co ₂ O ₃	Methanol, acetic acid, acetone	38
	Methanol	Ag/Cu	Formaldehyde	39
Hydrolysis				
	Esters		Alcohols & organic acids	22, 40
	Nitriles		Amides, Carboxylic acids	22, 41, 42
	Amides		Carboxylic acids	22
Dehydration	1,4-Butanediol		Tetrahydrofuran	43, 44
Rearrangement (Beckman)	Cyclohexanone oxime		ϵ -caprolactam	45-48
Alkylation	Phenol		Alkylphenols	49
Coupling (Heck)	Iodobenzene, Styrene	Base	<i>Trans</i> - & <i>cis</i> -stilbene	50, 51
Decarboxylation	Acetic acid	Zirconia	Acetone/CO ₂	52
		KOH	Acetone/CH ₄ /CO ₂	
Hydration	Propylene	MoO ₃ /Al ₂ O ₃	2-propanol	53

Table 2-2(a). The range of *p*X NCWO conditions reported in the literature.

Author Lead/First	Date	Reactor type	Residence time mins	Temperature °C	Pressure bar	[<i>p</i> -Xylene] %	Catalyst(s)	[Catalyst] M	<i>p</i> X: Metal Ratio	Oxidant	Oxidant Stoich-ometry wrt TA	TA yield %	<i>p</i> -toluic acid yield %	BA yield %	CO yield %	CO ₂ yield %	C mass account-ability %
Holliday	Jan-98	Batch	25-40	375	241.4	9.72	MnBr ₂	0.0474	19.2	O ₂	1.00-1.33	0 - 64	14 - 24	NR	NR	NR	NR
Savage / Dunn	Jan-02	Batch	60	250-350	NR	0.85-2.55	Mn, Co, Ni, Zr, Hf, (OAc)/Br	0.0089	3.0-9.0	H ₂ O ₂	0.67-2.29	0 - 49	0.3-2.5	1-2	NR	NR	97
Kim	Apr-02	Batch	30 - 360	240 - 374	220-300	0.085 - 1.58	None	0	NA	O ₂	0.27 - 1.47	0 - 24.9	0.06-57.2	NR	Neg	Neg	0.04-116.7
Poliakoff / Hamley	Apr-02	Batch	10	308	NR	NR	None	0	NR	O ₂	12.0	44	NR	NR	NR	NR	NR
Poliakoff / Hamley	Apr-02	Batch	10	315	156	NR	MnBr ₂	0.0063	NR	O ₂	12.0	70	NR	NR	NR	NR	NR
Poliakoff / Hamley	Apr-02	Flow	2.08-12.8	200-350	240-280	0.58-0.7	MnBr ₂	0.0034-0.0102	6.5-16.1	O ₂	0.45-1.78	0 - 66	0 - 64	0 - 5.8	NR	NR	0 - 98
Kim	Oct-02	Batch	15 - 20	240-374	220-300	0.47-4.17	None	0	NA	O ₂	0.21-1.0	1 - 29	6 - 20	NR	Neg	Neg	93 - 100
Savage / Dunn	Oct-05	Batch	85	250	NR	0.32	MnBr ₂	0.007 - 0.012	1.7 - 2.9	O ₂	1.16 - 3.67	35	3 - 25	NR	2	6	90
Savage / Dunn	Oct-05	Batch	10.2	300	NR	0.32	Mn, Co, Zr, (OAc)/Br	0.002 - 0.012	2.5 - 15.0	O ₂	1.16 - 3.67	41	35 (max)	2-4	1 - 3	2 - 16	90
Savage / Osada	Feb-09	Batch	50 - 150	300	70 - 170	3.19	MnBr ₂	0.014 - 0.028	7.1 - 14.3	O ₂	2.0 - 3.0	80 - 90	0.2 - 4.3	1.4-2.5	NR	NR	75 - 97
Savage / Osada	May-09	Batch	90 - 190	300	NR	6.38	MnBr ₂	0.007 - 0.028	21.5 - 85.8	O ₂	1.33 - 2.0	18.7 - 70.9	0 - 41	ND	NR	NR	29 - 80
Poliakoff / Perez	May-11	Flow	0.32	330	230	0.43	Cu/Co/NH ₄ /Br	0.0015	26.8	O ₂	1.61	64.9 - 70.5	NR	2.8 - 3.2	NR	17.0 - 17.8	84.7 - 91.5

Notes, applicable to Tables 2-2 (a) - (d)

Entries listed chronologically.

Date is when the paper first entered the public domain (including on-line publishing).

NR: Not reported. NR-sig: Not reported but text notes that was significant. NA: Not applicable. Neg: Negligible.

Tables cover a wide range of conditions; refer to the original papers for full details.

Tables cover papers that report new data and so exclude review papers.

Table 2-2(b). The range of *p*X SCWO conditions reported in the literature.

Author Lead/First	Date	Reactor type	Residence time mins	Temperature °C	Pressure bar	[<i>p</i> -Xylene] %	Catalyst(s)	[Catalyst] M	<i>p</i> X: Metal Ratio	Oxidant	Oxidant Stoichiometry wrt TA	TA yield %	<i>p</i> -toluic acid yield %	BA yield %	CO yield %	CO ₂ yield %	C mass accountability %
Savage / Dunn	Jan-02	Batch	7.5-15	380	237-415	0.32-1.38	MnBr ₂	0.00385-0.0116	6.67-20	H ₂ O ₂	0.67-2.0	20 - 57	0 - 3	2 - 16	NR	NR	<80
Kim	Apr-02	Batch	30	450	220-260	3.82 - 8.36	None	0	NA	O ₂	0.15 - 1.0	0 - 0.003	0.02 - 1.1	NR	NR-sig	NR-sig	0.06-1.2
Poliakoff / Hamley	Apr-02	Flow	0.15-2.17	400	240-280	0.58-2.0	MnBr ₂	0.0102	5.3-18.5	O ₂	0.87-1.8	2 - 90	1 - 10	1 - 6	NR	NR	13 - 100
Kim	Oct-02	Batch	14	400	220-300	0.47-4.17	None	0	NA	O ₂	0.21-1.0	3	29	NR	NR-sig	NR-sig	93 - 100
Poliakoff / Verdugo	Feb-04	Flow	0.083	380	230	0.428	MnBr ₂	0.0103	3.93	O ₂	1.65	~85	<0.1	4.5	NR	NR	90
Poliakoff / Verdugo	Apr-05	Flow	0.32	380	230	0.428	MnBr ₂	0.0106	3.79	O ₂	1.65	~62	NR	3	NR	NR	NR
Poliakoff / Perez	May-11	Flow	0.097	380	230	0.428	None	0	NA	O ₂	1.61	0.6	5	0.14	NR	14.3	21
Poliakoff / Perez	May-11	Flow	0.097	380	230	0.428	HBr	0.00257-0.0205	NA	O ₂	1.61	3.7 - 19.1	5.9 - 13.6	1.1 - 2.6	NR	26.6 - 33.7	46 - 61
Poliakoff / Perez	May-11	Flow	0.097	380	230	0.428	Mn, Co, HBr/Br, BA	0.0026	15.7	O ₂	1.61	6.3 - 36.1	18.3 - 26.5	0.9 - 4.6	NR	14.3 - 18.4	47 - 91
Poliakoff / Perez	May-11	Flow	0.10	380	230	0.428	~22 metals, 3 halides	0.0026	15.7	O ₂	1.61	1.9 - 66.8	0 - 24.6	0.1 - 8.2	NR	10.7 - 27.1	12.6 - 86.6

See Table 2-2(a) for notes.

Table 2-2(c). The *p*X NCWO conditions for maximum TA yields as reported in the literature.

Author Lead/First	Date	Reactor type	Residence time mins	Temperature °C	Pressure bar	[<i>p</i> -Xylene] %	Catalyst(s)	[Catalyst] M	<i>p</i> X: Metal Ratio	Turnover frequency /s	Oxidant	Oxidant Stoichiometry wrt TA	TA yield %	<i>p</i> -toluic acid yield %	BA yield %	CO yield %	CO ₂ yield %	C mass accountability %
Holliday	Jan-98	Batch	40	375	241.4	9.72	MnBr ₂	0.047	19.2	0.023	O ₂	1.33	64	14	NR	NR	NR	NR
Savage / Dunn	Jan-02	Batch	60	300	NR	0.85	MnBr ₂	0.0089	9.0	0.005	H ₂ O ₂	2.29	49	2	1	NR	NR	97
Kim	Apr-02	Batch	30	240	260	0.46	None	0	NA	NA	O ₂	1	24.9	23.5	NR	Neg	Neg	116.7
Poliakoff / Hamley	Apr-02	Batch	10	308	NR	NR	None	0	NR	NA	O ₂	12	44	NR	NR	NR	NR	NR
Poliakoff / Hamley	Apr-02	Batch	10	315	156	NR	MnBr ₂	0.0063	NR	NA	O ₂	12	70	NR	NR	NR	NR	NR
Poliakoff / Hamley	Apr-02	Flow	2.43	300	250	0.58	MnBr ₂	0.0102	5.35	0.10	O ₂	1.78	66	ND	5.8	NR	NR	81
Kim	Oct-02	Batch	20	300	220	NR	None	0	NA	NA	O ₂	0.50	29	5.5	NR	Neg	Neg	93 - 100
Savage / Dunn	Oct-05	Batch	5.5	300	NR	0.32	MnBr ₂	0.007	4.29	0.05	O ₂	1.11	94	ND	NR	< 2	< 2	90
Savage / Osada	Feb-09	Batch	130	300	70 - 130	3.19	MnBr ₂	0.014	21.5	0.01	O ₂	3.00	90	0.1	1.9	NR	NR	92.8
Savage / Osada	May-09	Batch	160	300	NR	6.38	MnBr ₂	0.007	85.8	0.03	O ₂	2.33	70.9	5.7	ND	NR	NR	80.1
Poliakoff / Perez	May-11	Flow	0.320	330	230	0.43	Cu/Co/NH ₄ /Br	0.0015	26.8	3.9	O ₂	1.61	70.5	2	3.2	NR	17.8	91.5

See Table 2-2(a) for notes.

Table 2-2(d). The *p*X SCWO conditions for maximum TA yields as reported in the literature.

Author Lead/First	Date	Reactor type	Residence time mins	Temperature °C	Pressure bar	[<i>p</i> -Xylene] %	Catalyst(s)	[Catalyst] M	<i>p</i> X: Metal Ratio	Turnover frequency /s	Oxidant	Oxidant Stoichiometry wrt TA	TA yield %	<i>p</i> -toluic acid yield %	BA yield %	CO yield %	CO ₂ yield %	C mass accountability %
Savage / Dunn	Jan-02	Batch	7.5	380	242	0.743	MnBr ₂	0.0077	9.09	0.05	H ₂ O ₂	1.38	57	8	3	NR	NR	<80
Kim	Apr-02	Batch	30.0	450	220	4.555	None	0	NA	NA	O ₂	0.15	0.003	1.1	NR	NR-sig	NR-sig	1.2
Poliakoff / Hamley	Apr-02	Flow	0.30	400	250	0.580	MnBr ₂	0.0103	5.32	1.1	O ₂	1.20	~90	ND	6 - 8	NR	NR	72 - 100
Kim	Oct-02	Batch	14.0	400	220	NR	None	0	NA	NA	O ₂	0.50	3	29	NR	NR-sig	NR-sig	93 - 100
Poliakoff / Verdugo	Feb-04	Flow	0.083	380	230	0.428	MnBr ₂	0.0103	3.93	2.7	O ₂	1.65	~85	<0.1	4.5	NR	NR	90
Poliakoff / Verdugo	Apr-05	Flow	0.32	380	230	0.428	MnBr ₂	0.0106	3.8	0.5	O ₂	1.65	~62	NR	3	NR	NR	NR
Poliakoff / Perez	May-11	Flow	0.10	380	230	0.428	MnBr ₂	0.0026	15.7	5.2	O ₂	1.61	36.1	24.6	4.2	NR	18.4	88.7
Poliakoff / Perez	May-11	Flow	0.10	380	230	0.428	Cu/Co/NH ₄ /Br	0.0026	15.7	7.2	O ₂	1.61	66.8	NR	5.0	NR	17.9	89.7

See Table 2-2(a) for notes.

Holliday *et al.*⁵⁴ oxidised a number of different alkyl aromatics including *p*X using a small batch reactor with long residence times. They noted the importance of having both bromide and a transition metal in the catalyst system and suggested the likelihood of a free radical mechanism.⁵⁵ They tried many first row metals as catalysts and found Mn(II) the best. They reported CuBr as a superior catalyst for toluene to BA oxidation. They noted that Hastelloy C276 was a superior material of construction to stainless 316L for this application. They suggested that a flow reactor may be better for these reactions but did not try this.

In 2002 Kim *et al.*^{56, 57} published two papers on uncatalysed *p*X N/SCWO. They used a larger Hastelloy C276 batch reactor, with long residence times. They measured CO₂ and CO by GC and reported them to be negligently small at subcritical conditions but more significant when supercritical but they did not give numbers. The maximum yield was 28.9 % TA at 300 °C with lower yields at supercritical conditions. They saw typical intermediate, under conversion products and very variable and sometimes very high levels of toluene (up to ~65 %). They reported kinetic rate constants and activation energies.

The first publication by Poliakoff's group at the UoN on *p*X SCWO was by Hamley *et al.*⁵⁸ They noted a 'Green' context (with reference to Anastas' ⁵⁹⁻⁶² Twelve Principles of Green Chemistry) and the potential for increase in energy efficiency in a higher temperature process. They reported the use of continuous flow reactors with short residence times and commented on the importance of early mixing of the *p*X to avoid corrosion and yield loss.

Garcia-Verdugo *et al.*⁶³ (2004) compared the dicarboxylic acid yields from SCWO of *ortho*, *meta* and *para*-xylenes at the optimised conditions for *p*X SCWO reported by Hamley.⁵⁸ The work was subsequently extended to mixtures of xylenes.⁶⁴

Fraga-Dubreuil *et al.*⁶⁵ (2006), ⁶⁶ (2007) extended the SCWO of methyl aromatics to a wider array of feedstocks including toluene, cumene, dimethyl naphthalene, dimethoxytoluene and methyl pyridines.

Fraga-Dubreuil *et al.*⁶⁷ (2009) addressed the problem of manganese catalyst precipitation and fouling in SCWO. They undertook *o*X SCWO and assessed the extent of Mn catalyst recovery. They added aromatic acids or mineral acids to the

catalyst formulation to increase the manganese recovery. The best formulations added 27.3 mM of BA to the catalyst feed which increased Mn recovery from 76 % to 97 %.

The following two papers arose in part from work in this thesis and are available in Appendix 1.

Pérez *et al.*⁶⁸ (2011) compared the SCWO of *o*X and *p*X but with unsaturated catalyst that produced under conversion products and lower yields of the dicarboxylic acids. This paper introduced a new CO₂ titration method that enabled an estimate of over oxidation. *o*PA was consistently obtained at higher yield than TA and with lower over oxidation; this was attributed to the ability of the *o*X to *o*PA system to pass through the phthalide intermediate *via* an intra molecular cyclisation.

Pérez *et al.*⁶⁹ (2011) made a systematic study of possible catalysts for *p*X N/SCWO. The study used unsaturated catalysts and this made it possible to see differences in catalytic activity between formulations. They demonstrated that MnBr₂, FeBr₃ and CuBr₂ had high catalytic activity with CuBr₂ being the most active. They demonstrated synergistic effects between metals and between metals and ammonium bromide; Cu with Co, Ni, La, Eu or NH₄ showed the strongest synergy.

At the University of Michigan, Savage *et al.*^{70 71} (2002) undertook preliminary investigations of *p*X NCWO and SCWO. They used small stainless steel batch reactors with long residence times.

Savage *et al.*⁷² (2003) investigated the thermal stability of six aromatic carboxylic acids (TA, *i*PA, *o*PA, TM anhydride, BA and 2,6-naphthalene dicarboxylic acid) at 250 - 410 °C for times up to 240 minutes. TA was stable for 1 hour at 300 °C and formed 10 - 15 % BA at 350 °C.

Savage *et al.*⁷³ (2005) undertook further *p*X N/SCWO to TA optimisation. They used a larger scale batch autoclave than previously and introduced analysis for CO and CO₂ using GC. They reported that the staging of catalyst addition was not beneficial compared to a single shot.

Osada & Savage ^{74 75} (2009) reported TA synthesis at higher *pX* concentrations. Multiple shots of O₂ feed were found to be superior to single shot or to a continuous O₂ feed.

There are other publications which, while not directly concerned with xylene N/SCWO, are of some relevance to this topic. Saha, Deka ⁷⁶ (2013) used CeO₂ catalyst for *pX* oxidation in water at 70 °C. The National Chemical Laboratory ⁷⁷ (of the Indian Government in Pune, India) used transition metal (Co/Mn/Cu) substituted polyoxometalates to effect a bromine free *pX* oxidation to mostly *p*-toluic acid with minor amounts of TA in water at 180 °C with air as the oxidant. Partenheimer and Fulton ^{78, 79} reported the use of the X-ray absorption techniques XANES and EXAFS to probe MnBr₂ structures in N/SCW. In the near edge region, the transmitted X-ray intensity drops when its energy matches the binding energy of an electron in an atom and the absorption is sensitive to the oxidation state and coordination of the element. At higher energies, photoelectrons are ejected and produce interference patterns with forward-propagating waves that are sensitive to coordination structure. Results showed a transition from octahedral to tetrahedral coordination for MnBr₂ solutions over the NCW to the SCW region.

2.2.4 Reactors and Mixing in N/SCW Systems

There are a-number-of challenges when attempting to mix SCW, NCW and ambient temperature streams in small scale equipment:

- Length scales are short and flows are often laminar or at best transitional (to turbulent) in nature.
- There are appreciable thermal gradients and density differences between SCW and subcritical water streams.

Hessel ⁸⁰ summarises the mixing principles that have been developed for micro-mixing at small scale. Small reactors tend to have low Reynolds numbers and so turbulent diffusion is not available as a mixing mechanism. In such flow, mixing is achieved by reducing the diffusion length between reactants by splitting reactant fluids into small fluid segments to enhance mixing performance.

Some of the simplest mixing arrangements are tee-pieces and the mixing efficiency of these have been extensively studied, as in Chilton and Genereaux,⁸¹ Ger and Holley,⁸² Forney and Kwon,⁸³ Reed and Narayan,⁸⁴ Maruyama, Suzuki and Mizushina,⁸⁵ Forney and Lee,⁸⁶ O’Leary and Forney,⁸⁷ Tosun,⁸⁸ Cozewith and Busko.⁸⁹ Forney, Lee, Cozewith and Busko provide good summaries of the works prior to their publications.

In these studies, a variety of parameters were used to characterise the efficiency and extent of the mixing. These were generally expressed in dimensionless form and can be characterised as those describing the effect of turbulence such as jet and pipe Reynolds numbers, those related to the relative momenta of the streams such as velocity ratio, diameter ratio, flow rate ratio and those describing the relative buoyancy of the streams such as densimetric Froude number and density ratio.

A SCW/NCW mixing application that has received considerable attention is the production of nano-particles. In this application, a sub-critical water stream containing dissolved metal salt(s) is contacted with a SCW stream. The metal ions rapidly hydrolyse to form insoluble metal oxide particles that nucleate and precipitate as nano-particles. This clearly has close parallels with the mixing requirements of N/SCWO.

Wakashima⁹⁰ considers the characteristics and mechanisms for nano-particle synthesis and establishes the following criteria for mixer design:

- The attachment of reacting metal salt solution, which contains hydrosols and metal oxide nuclei, to the channel wall should be prevented.
- The instantaneous and uniform mixing of SCW with the metal salt solution is desirable for smaller particle sizes and sharp size distribution.
- A smooth and quick discharge after mixing without stagnant or circulating zones at arbitrary mixing flow rates of the two streams, along with a short average residence time and a narrow residence time distribution, is desirable.
- Minimal heat conduction through the mixer body material from the SCW to the ambient temperature metal salt solution in-order-to minimise

temperature change prior to mixing and to prevent unwanted nucleation and precipitation upstream of the mixer.

It is likely that these principles would also be beneficial for *pX* N/SCWO.

The literature describes numerous mixing arrangements for producing nanoparticles. Adschiri ⁹¹⁻⁹³ employed tee-piece mixers, Wakashima ^{90, 94} describes swirl type mixers and Mae ⁹⁵ describes a mixer employing a movable needle. At the University of Nottingham, Blood, ^{96, 97} Denyer ^{98, 99} and Lester ¹⁰⁰⁻¹⁰² developed a visual technique to simulate the mixing point of a reactor where a dense aqueous solution is mixed with a less dense organic stream. This work led to the invention of a 'buoyancy reactor' in which the lighter stream was injected downwards, in a narrow diameter pipe, into an up flow of the heavier stream in a wider pipe. The arrangement exploited the buoyancy of the lighter fluid to aid mixing in the annular gap between the two pipes. This mixing arrangement was subsequently applied to *pX* N/SCWO by Li ¹⁰³ and Pérez *et al.* ¹⁰⁴ and is described in Section 2.3.1.

Housley *et al.* ¹⁰⁵ (the author of this thesis) used dimensionless groups to analyse competing effects in tee-pieces and buoyancy mixers and consider their use at industrial scale. Vogel *et al.* ¹⁰⁶⁻¹⁰⁸ and Adschiri *et al.* ¹⁰⁹ have applied neutron radiography to directly image NCW and SCW mixing. Sierra-Pallares *et al.* ¹¹⁰ used computational fluid dynamics (CFD) to assess the competing effects of forced and natural convection and applied this to tee-pieces and buoyancy mixers. Tighe *et al.* ¹¹¹ considered counter flow mixers under supercritical conditions and considered limitations in the visualisation method of Blood *et al.* regarding gradients in transport properties at and around the critical point; they reviewed previous studies on density differences and considered their relevance to this type of mixing; they concluded that a study of hydrothermal vents ¹¹² was the most relevant.

2.2.5 *p*-Xylene N/SCWO Process Synthesis

Savage *et al.* ¹¹³ undertook an initial economic assessment of *pX* NCWO and SCWO. They showed ~10 % higher capital investment and ~10 % lower energy

intensity for these technologies, both within the 20 % uncertainty quoted. Further analysis of this aspect can be found in Chapter 8 of this thesis.

2.3 N/SCWO Experimental Facilities

This section describes the experimental facilities available at the start of this PhD project.

2.3.1 The University of Nottingham N/SCWO Rigs

At the start of this PhD project, the UoN School of Chemistry had two SCW rigs (known as Rig 22 and Rig 23) that had been applied to a variety of feed stocks and chemical transformations including *ortho* and *para*-xylene oxidation.^{58, 63-69, 104} In addition the School of Chemical and Environmental Engineering had developed reactors suitable for the production of metal oxide nano-particles in SCW.¹⁰⁰⁻¹⁰²

Rig 22 as configured for xylene SCWO is shown in Figures 2-1 and 2-2. Rig 23 was of a similar construction. A brief description of the rig is given here and more detail can be found in references.^{58, 63}

For xylene oxidation work, three feeds (water/hydrogen peroxide, catalyst solution and the organic reagent) are pumped into the rig at the desired pressure and flow rate using HPLC pumps. The high pressure water/hydrogen peroxide stream passes through an electrically heated pre-heater and warms to a temperature sufficient for the decomposition of the peroxide to a solution of oxygen in supercritical water.¹¹⁴⁻

116

The three streams are contacted in a tubular reactor whose design is shown in Figure 2-3. The reaction is potentially dangerous; if oxygen and *pX* contact without sufficient dilution with water vapour then, under this condition, the *pX* can spontaneously detonate. This could occur in a cool spot in the reactor where phase separation of oxygen from the water is possible. The reactor and rig are therefore enclosed behind acrylic sheeting screens as can be seen in Figure 2-2. The aftermath of such an explosive event is shown in Figure 2-4.

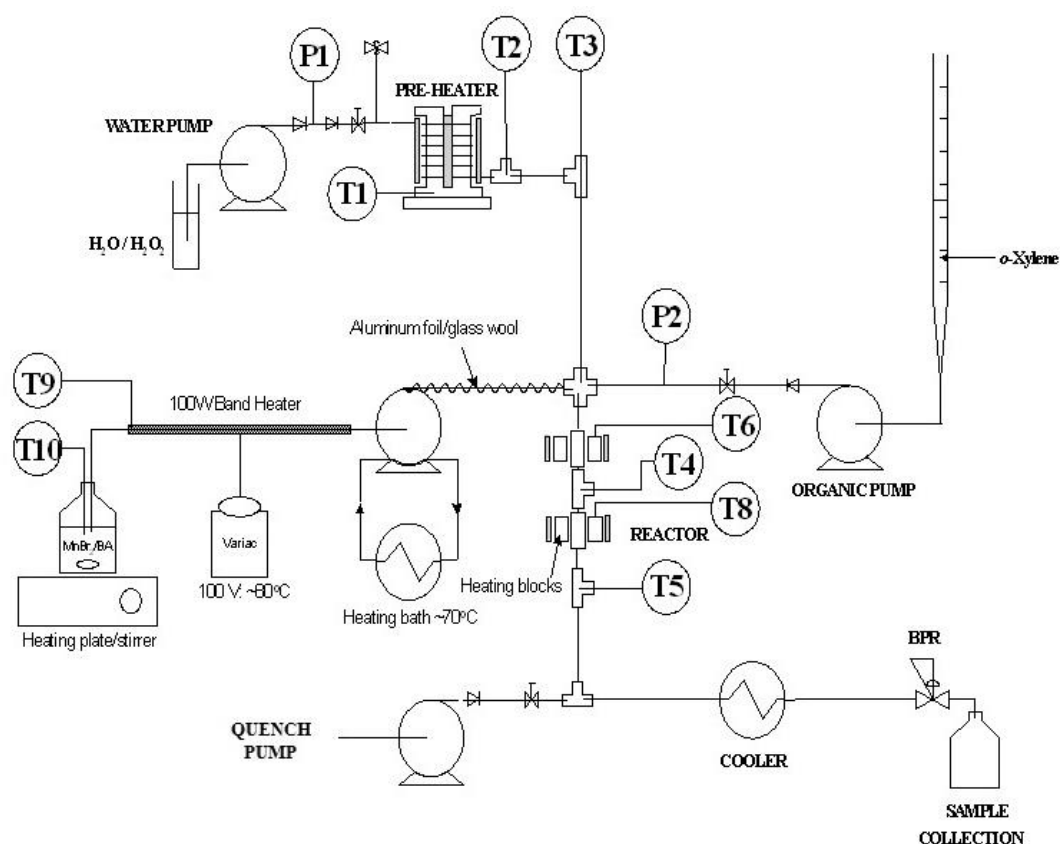


Figure 2-1. Line diagram of the University of Nottingham xylene N/SCWO rig 22. Hydrogen peroxide solution is pumped to an electrically heated, pre-heater coil where it is decomposed to oxygen and water. Either *para* or *ortho*-xylene (from a burette) and metal salt catalyst solution are pumped to a mixing cross and into a reactor. There is facility to warm the catalyst feed, feed lines and pump head to enable additional additives (of limited solubility) to be fed. The three feed streams are mixed in a mixing cross piece and flow into an electrically heated tubular reactor. At the reactor exit, the reaction is quenched with water or a sodium hydroxide solution and the products are cooled. Pressure is reduced and controlled by a back-pressure regulator (BPR) which drops the pressure of the products to atmospheric pressure and they are then collected. P are pressure transducers and T are thermocouples. Adapted from UoN references.^{58, 63, 67}



Figure 2-2. Photo of the University of Nottingham xylene N/SCWO rig 22. The heater controllers (a) are top left back, the HPLC feed pumps (b) are top and bottom left, the hot catalyst feed system (c) is top centre left, the *pX* burette (d) is top left, the peroxide feed vessel (e) is bottom left, the preheater (f) is bottom centre, the mixer, reactor and quench assembly is to the right (g) (wrapped in lagging and within an additional safety cabinet) and the BPR (h) is bottom centre left. Quench feed and the collection vessel are at the bottom out of shot. The rig is screened with acrylic sheeting (i).

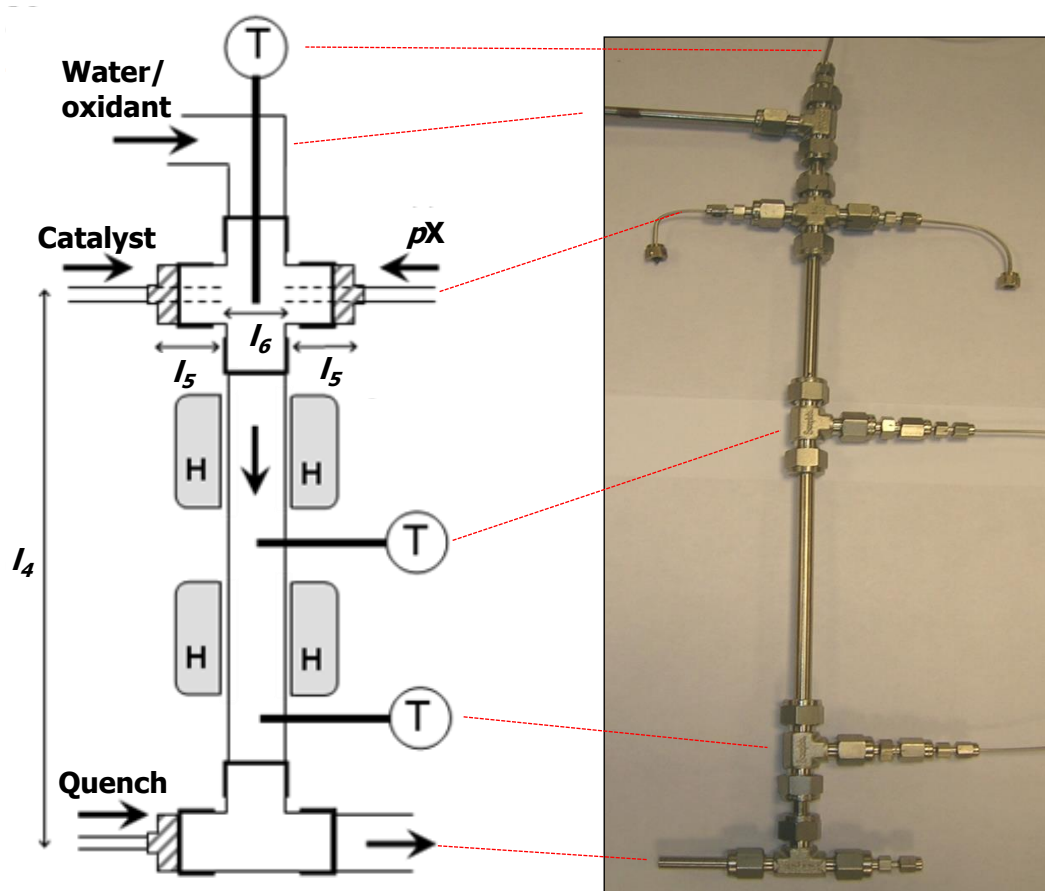


Figure 2-3. The down flow Tubular (TB) reactor construction in use on the University of Nottingham N/SCWO rigs. The three feed streams are mixed in the mixing cross piece at the top. The quench is injected at the tee-piece at the bottom. H are electrical heating blocks (not in photograph) and T are thermocouples. Tubing sizes were $\frac{1}{4}$ " O.D. for the main reactor and $\frac{1}{16}$ " O.D. for the catalyst and xylene feed lines. Fittings were $\frac{1}{4}$ " Swagelok. Dimensions $l_4 = 34$ cm, $l_5 = 3$ cm, $l_6 = 1$ cm. The extent of the feed line penetration into the mixing cross was varied (shown dotted). The volume of the reactor is ~ 5.7 mL. Source: UoN.¹⁰⁴



Figure 2-4. A ¼" O.D. pipe after rupture by a *pX* detonation with O₂ under NCWO conditions. The shredded ribbon structure is typical of a pipe rupture by a detonation event. Note the manganese oxide fouling evident on the interior surface of the pipe which is typical in N/SCWO using manganese based catalysts.

At the outlet of the reactor, the product was cooled by either indirect cooling, using a double pipe heat exchanger or by a combination of quenching followed by indirect cooling. Quenching (*i.e.* adding a flow of cool water or other solution) was used in-order-to avoid the formation of solids. Water was used as quench when oxidising *oX* because *o*-phthalic acid is water soluble (to 0.6 % w/w at ambient temperature). Sodium hydroxide solution was used when oxidising *pX* because TA is highly insoluble but can be kept in solution as its sodium salt. Pressure in the unit was controlled using a back-pressure regulator. Liquid was collected for GC and HPLC analysis. There was no provision for gas capture and analysis.

The School of Chemical Engineering at the UoN had developed reactors suitable for the production of metal oxide nano-particles in SCW.¹⁰⁰⁻¹⁰² These made use of mixers that enhanced mixing by introducing a buoyant stream of SCW into an up flow of denser NCW with buoyancy aided mixing occurring in an up flow annulus. The concept was adapted for *pX* N/SCWO as illustrated in Figure 2-5. This reactor concept could be substituted for the other reactor in the rig.

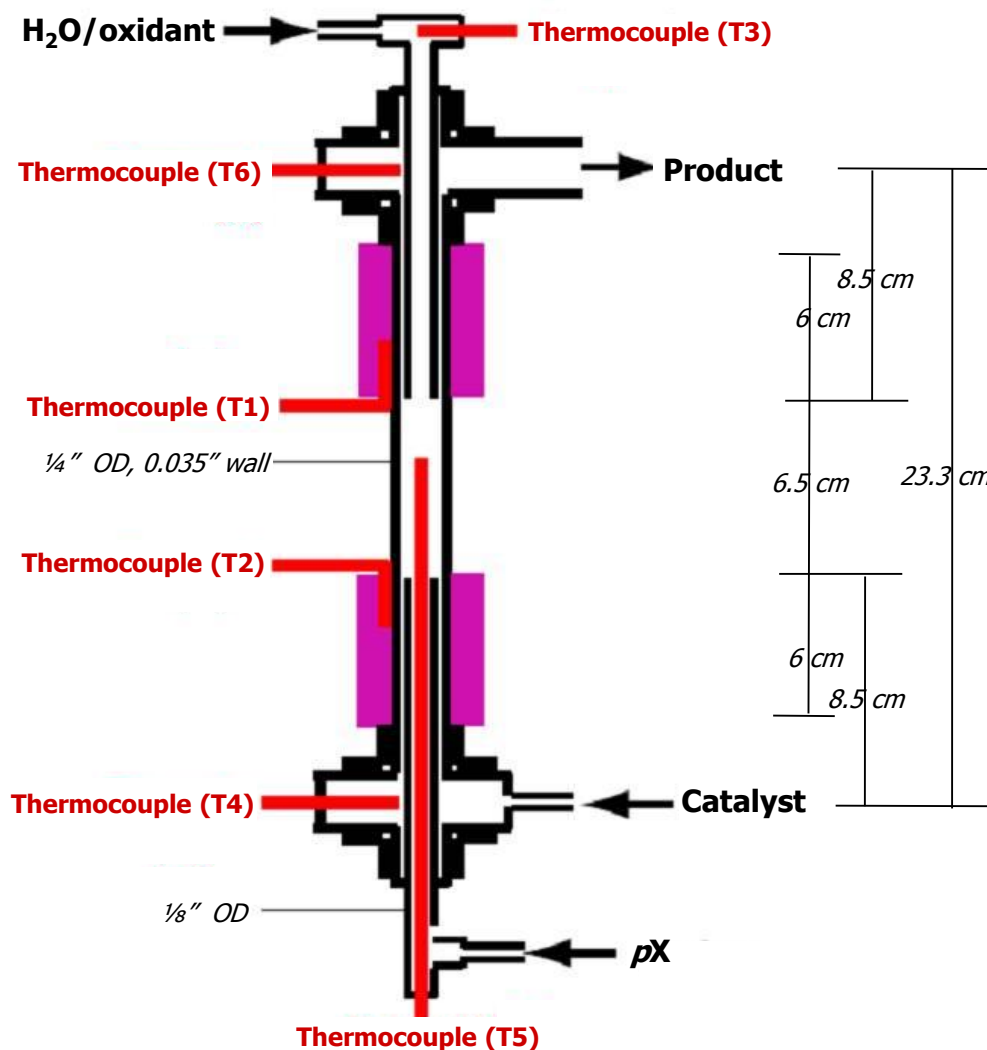


Figure 2-5. A buoyancy mixer adapted as a reactor for pX N/SCWO. A down flowing SCW/O₂ stream is introduced into an up flowing NCW stream containing catalyst (e.g. MnBr₂) and pX . The combined streams flow up an annulus with mixing enhanced by the buoyancy of the lighter SCW. Source: UoN.¹⁰³

2.3.2 The IP1 and K5 N/SCWO Rigs

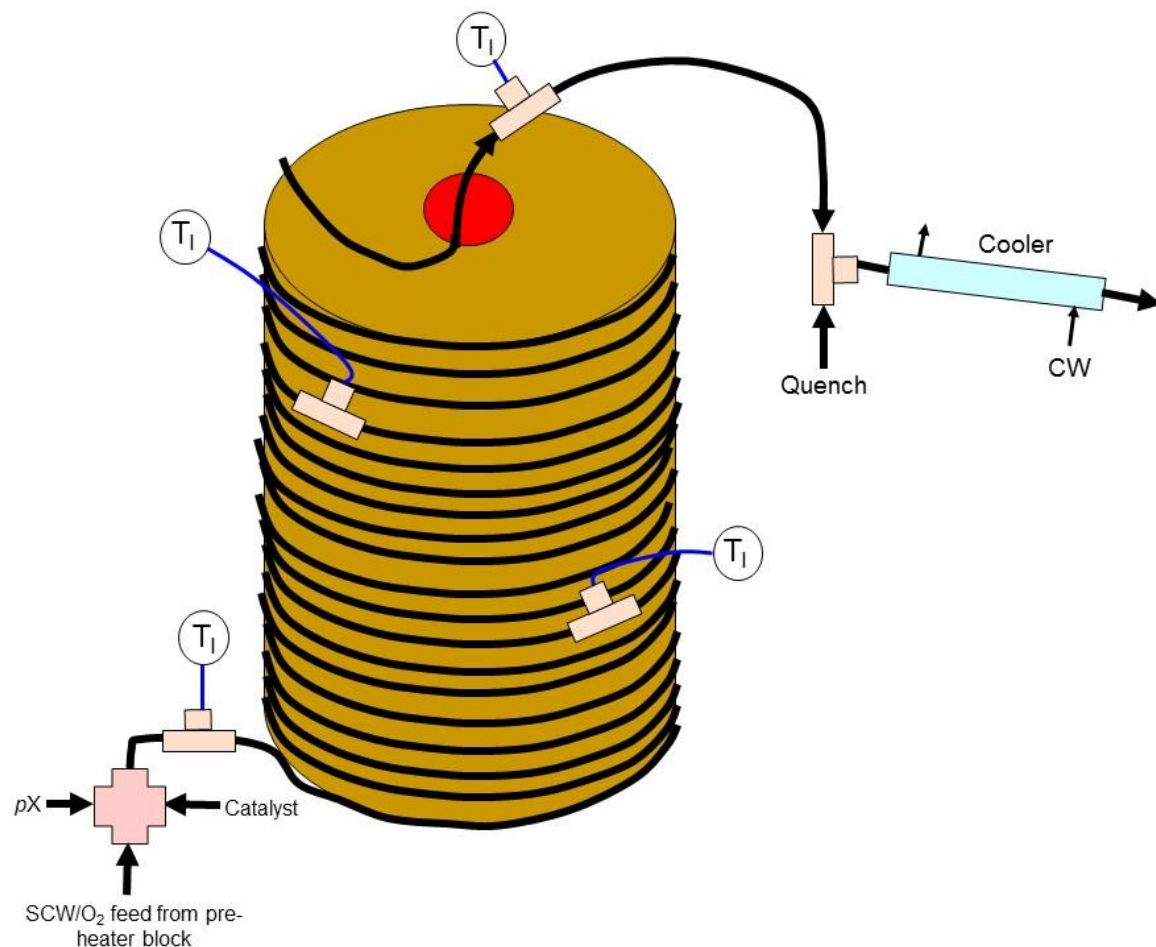
This *pX* N/SCWO project had conceived of two N/SCWO rigs, one suitable for initial scouting studies and the other to produce data (of a higher precision) suitable for kinetics determination and process design. These rigs were known as IP1 and K5. The design criteria (*i.e.* the material balances that need to be achieved for these concepts) are considered more fully in Section 2.5.1 below. The designs of these rigs, at the commencement of this PhD thesis, are set out in the next sections.

The IP1 Rig

A rig was available that had been designed to the standard needed for initial scouting in the field of SCWO and was known as the IP1 rig. This rig followed many of the concepts of the UoN rigs 22 and 23 but differed in its detailed design and had been applied to reactions of several (non-xylene) feed stocks in N/SCW. This rig became available to the author and his co-workers at the commencement of this PhD project.

The rig comprised of similar components as the UoN rigs 22 and 23 as described in the previous Section 2.3.1. *e.g.* feed systems, reactor, quench, cooler, BPR, product collection *etc.* These components are described in detail in Chapter 3 on experimental and equipment. However, the reactor design differed from those used on rigs 22 and 23 and is described and critiqued in this Chapter. This reactor is illustrated schematically in Figure 2-6.

Figure 2-6. Schematic of the mixer and reactor design initially employed on the IP1 SCWO rig. SCW/O₂, organic and catalyst streams enter a ¼" Swagelok compression fitting mixing cross through ⅛" O.D. pipes. A photo of the arrangement can be seen in Figure 3-5. The mixed streams exit from the top of the cross in ⅛" O.D. tubing and flow into a tee-piece into which a thermocouple for temperature indication (T_i) is inserted. The flow then enters the reactor which is ⅛" O.D. 0.028" wall thickness tubing, wrapped around a 140 mm long, 75 mm diameter cylindrical brass block heated with a 1 kW electrical cartridge heater inserted into a 15 mm drilled hole on the centre line of the block axis (illustrated as a red circle). The total length of the reactor coil was initially 6.1 m though this was subsequently varied and details can be found in Chapter 3. At a third and two thirds of the reactor length, thermocouples were inserted into the process flow using ⅛" Swagelok tee-pieces pressed against the block to maintain temperature. At the exit of the reactor, a further thermocouple was inserted in-line using a similar tee-piece arrangement. The reactor pipe then leaves the block, passes through a high point and enters a tee-piece orientated so the process flow enters from above and a quench fluid enters from below. The quenched stream exits from the side and enters a pipe in pipe cold water cooler. A photo of the arrangement (but from a later stage of the project) can be seen in Figure 7-1.



The reactor block was orientated so that the flow in the reactor was upwards throughout to avoid locations where gas pockets could accumulate. Such accumulation of gas is hazardous but can only occur under sub-critical conditions; this could be a cool spot in a supercritical system. At the end of the reactor block, the flow went through a high point and quench was introduced immediately after this – this was to try to avoid back flow of quench fluid into the reactor. Photos of the rig can be found in Section 3.3.

The Kinetics (K5) Rig

The IP1 rig was designed for initial scouting studies on SCW processes. It was recognised that this rig would not generate data of sufficient precision for detailed pilot plant design and the assessment of process economics. This requires detailed data on reaction kinetics obtained with high material balance; there is a fuller discussion of this aspect in Section 2.5.1.

At the start of this PhD project, a rig capable of generating such ‘kinetics quality’ data for *pX* SCWO had been designed and was under construction. This was known as the K5 rig; K designated ‘kinetics’ data capability and 5 was because it was to be the fifth rig; however, rigs 2 through 4 were never built. The author of this thesis was not involved in this design, but took the rig over during its commissioning; however, a description of the initial design and the philosophies behind it are provided here.

The requirements for ‘kinetics quality’ data were identified as:

- Accurate control of the *pX* flow into the rig. This flow was at a low feed rate.
- Good control of reactor temperature with an isothermal temperature profile.
- The ability to handle solid TA in the product work up section without the need to use a sodium hydroxide quench. It was unclear whether the sodium hydroxide affected the chemistry during cooling and this quench also prevented the collection of solid TA for characterisation.

The approach to achieving these requirements are discussed in the following paragraphs.

The K5 rig as originally installed is shown in Figure 2-7.

The *pX* was fed by a motorised, twin barrel syringe pump, manufactured by ISCO (model 260D). The syringe is driven by a stepper motor which should give a more continuous and more accurate feed profile than the reciprocating piston stroke of a HPLC pump. Twin syringes enable a switch to the second barrel while the first is reloading after discharge. The catalyst, oxygen/water and quench feeds were fed by Jasco HPLC pumps.

The heating, cooling and temperature control of the reactor was undertaken using a sand bath. This comprised an electrically heated element and a cooling coil around which sand is fluidised by blowing air. The reactor is placed within this fluidised, hot sand. This provides a high heat transfer coefficient and an even temperature distribution within the sand.

The reactor employed is illustrated schematically in Figure 2-8.

The pressure control was by a Thar back pressure regulator. This BPR design incorporates an oscillating needle at the small diameter orifice where the pressure drop occurs. Such a design is claimed to be suitable for handling the let-down of solid slurries as the needle is designed to dislodge solid particles which build up around the orifice. The effectiveness of this design for the *pX* N/SCWO duty is reviewed in Chapter 3.

Gas-liquid separation was affected in a pressurised separator vessel. This had a level control system that used liquid sensing switches to affect a discharge between two levels. The gas discharge from the GLS passed through an on-line gas analyser which quantified CO, CO₂ and O₂ levels.

Fuller details of the equipment deployed can be found in Chapter 3.



Figure 2-7. The K5 kinetics rig as originally installed. The secondary containment cabinet is constructed of (blue painted) steel with polycarbonate sheeting and has extraction visible at the top (a). Hinged doors to enable cabinet closure can be seen to the left and centre (b). The feed vessels are mounted on a rack to the left of the camera position and are out of shot. The ISCO twin syringe pump for pX can be seen in the top left cabinet (c) and three Jasco HPLC pumps (d), for catalyst solution, peroxide solution and quench solution, are in the bottom left cabinet. The reactor cabinet is top right and a description of its contents follows. The pre-heater coil (e) is contained in the metal enclosing casing in the top left. The sand bath (f) is the large blue container at bottom left and the reactor is inside this. The quench point (g) is to the right and slightly above the sand bath and the cooler is the coil (h) above that. The back-pressure regulator (i) is inside the grey housing labelled ‘Thar’. The gas/liquid separator (j) is the flanged vessel at bottom right and extends down into the sampling area in the lower right cabinet. The sampling area is not enclosed (as it is at low pressure) and it is banded (k). Plastic collection containers (l) are visible. There is a Julabo temperature controlled bath (m) in the left of the sampling area that can pump cold fluid around the sand bath cooling coil. The Rosemount gas analysis unit is mounted to the right of the camera position and is out of shot.

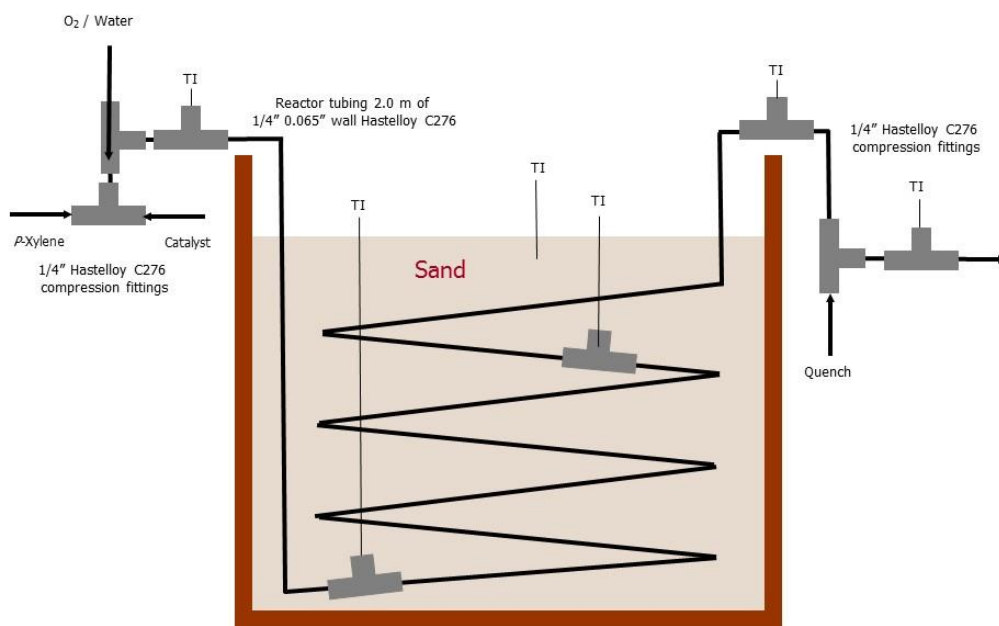


Figure 2-8. The reactor initially deployed on the K5 rig with a sand filled 'fluidised bed' heating bath. The reactor was constructed using 2 m of 1/4" O.D. Hastelloy C276 tubing with 0.065" wall thickness and compression fittings of the same material. The mixing of the SCW and oxygen, catalyst and *p*X streams was affected using a buoyancy mixer. All feed inlet pipes were 1/4" O.D. except SCW/O₂ which was 1/8" O.D. The mixer was constructed using two 1/4" Hastelloy tee-pieces and the downflow 1/8" SCW/O₂ feed pipe extended into the opposite arm of the tee-piece as illustrated; this mixer arrangement was located outside of the sand bath. The reactor tubing entered the sand whose temperature was measured with a thermocouple. In process reactor temperature measurement was made at the start, one third, two thirds and end points of the reactor length using thermocouples inserted into 1/4" tee-pieces. Quench occurred outside the sand bath in a tee-piece with down flow process fluid and up flow quench fluid. Further process temperature measurement was made following the quench.

2.4 Xylene SCWO Chemistry

This section describes the formulations and reactor performance and the product work up and analysis techniques that were available at the UoN at the start of this PhD project.

2.4.1 Formulations and Reaction Performance

At the project outset, the IP1 rig had only been used for non-oxidative SCW reactions and had not been used for xylene SCWO. The UoN rigs had been used for a wide variety of reactions including the oxidation of methyl aromatics and both *o*X and *p*X N/SCWO.⁶⁵

A typical UoN xylene N/SCWO formulation for reactors such as those in Figure 2-3 was as follows.

Three feed streams comprised:

- 4 mL/min of aqueous catalyst solution, containing ~1700 ppm Mn and ~5000 ppm Br added as 0.031 M Mn(OAc)₂ and 0.062 M HBr solution or as 0.031 M MnBr₂ solution.
- 8 mL/min of 1.8 % v/v hydrogen peroxide solution made by diluting 30 % v/v.
- 0.07 mL/min (~0.06 g/min) of *o*X or *p*X to give 0.5 % w/w concentration in the reactor.

The quench stream comprised:

- Quench with 3.5 mL/min of water or 1.0 M, 4 % w/w sodium hydroxide solution for *o*X, *p*X respectively.

All the chemicals were purchased from Sigma Aldrich and used without further purification.

The reactor was operated at 230 bar and 380 °C.

This gave the following formulation metrics:

- The in-process catalyst concentrations were approximately one third of the concentrations in the catalyst feed stream.
- A liquid residence time of ~6 s.
- A substrate:catalyst metal ratio of ~2:1.

- An oxygen stoichiometry of 150 % of that necessary to fully oxidise the xylene to its corresponding dicarboxylic acid.
- ~4 x sodium hydroxide excess necessary to solublise the TA assuming stoichiometric conversion of the *pX*.

However, there was considerable variation of formulations and their effectiveness as reported in the UoN School of Chemistry publications. In 2002, Hamley *et al.*⁵⁸ reported oxidising *pX* at temperatures between 200 °C and 400 °C using MnBr₂ catalyst and claimed TA yields up to ~90 % achieved at 400 °C with 120 % of stoichiometric oxygen and a residence time of ~9 -18 s. In 2004, Garcia-Verdugo *et al.*⁶³ reported oxidising *ortho*, *meta* and *para*-xylene at these optimum conditions and claimed dicarboxylic acid yields of 46 %, 66 % and 90 % respectively. In 2007, Fraga-Dubreuil *et al.*⁶⁶ reported 75 %, 66 % and 70 % yields for SCWO of the three xylene isomers at 380 °C. In 2009, Fraga-Dubreuil *et al.*⁶⁷ reported up to 78 % yield of *oPA* for SCWO of *oX* at 380 °C using MnBr₂ catalysts that had been stabilised by the addition of soluble aromatic carboxylic acids. Such formulations could improve Mn recovery from 76 % to up to 99 % for MnBr₂ based catalysts.

2.4.2 Product Work Up and Analysis Techniques

This section summarises the product work up and analysis techniques in place at the project inception as developed at the UoN. The detail of the methods can be found in the relevant UoN publications.^{58, 63, 66, 67}

When performing *pX* N/SCWO, it is necessary to quench with sodium hydroxide solution in-order-to keep the TA that has been formed in solution as its soluble sodium salt. When using *oX*, it is possible to not use sodium hydroxide quench and to quench with water for *oPA* concentrations of up to the solubility limit of ~0.5 %.

After quench, the flow passes into a cooler (which is a water-cooled heat exchanger), in which the process fluid is cooled and then the flow passes through a filter and a back-pressure regulator. The liquor is collected for subsequent analysis. There was provision for gas capture and analysis by GC.

For *pX* N/SCWO, the quenched liquors were analysed by HPLC for the intermediates *p*-tolualdehyde, *p*-toluic acid and 4-CBA, for the product TA and for the by-product BA. For *oX* oxidations, the analysis was for the equivalent *ortho* isomers. In addition, because *oX* oxidation could be quenched by water, the manganese catalyst remained in solution and the Mn^{2+} concentration could be measured by atomic absorption spectroscopy.

The degree of manganese recovery in the liquor is important because the homogeneous manganese catalyst in solution tends to precipitate from the reaction mixture as black manganese oxides which contribute to fouling. For *pX* SCWO, this measurement is not currently possible because the sodium hydroxide quench precipitates the manganese as a gelatinous hydroxide, which cannot be easily filtered and quantified.

2.5 Critique of the State of the Art

The aim of this PhD is to assess the practical and economic suitability of N/SCWO for oxidising *pX* to TA at an industrial scale. This section critiques the chemical formulations and experimental facilities available at the outset of the project (in January 2010), that have been described in the preceding sections, from this perspective.

This critique forms the basis for many of the rig and reactor design improvements and chemistry improvements described in Chapters 3 to 6 of this thesis.

2.5.1 Material Balance and Analysis

One cannot over-state the importance of obtaining a good material balance when undertaking an industrial process development. Sir John Cornforth¹¹⁷ puts it thus:

“Anyone who has helped to plan an industrial synthesis tends to pity the poverty of the criteria that academic synthesis must meet.”

Variable cost considerations tend to trump capital cost issues in large scale commodity industrial processes. Thus, a high and well quantified yield of the

desired product is of great importance. In addition, by-products often cause process difficulties and can be expensive to remove. It's therefore vitally important to know the fate of the *pX*, preferably to > 99 % if not > 99.9 % material balance.

Experiments that achieve material balances in the range ~20 % - 95 % are often suitable for initial scouting studies. Experiments that yield the quality of data suitable to design an industrial process require material balances of ~99 % (± 1 %) or even 99.9 % (± 0.1 %) and can be described as of 'kinetics quality'. Academic synthesis is typically of initial scouting quality and rarely achieves kinetics quality.

Tables 2.2(a) – (d) that summarise the published literature on *pX* N/SCWO show that all the published literature is of IP quality. For example, an early paper from Poliakoff's group⁵⁸ reports a 90 % yield of TA, however later papers report a variable and lower yield TA at the same conditions.

A factor in this variable (and often poor) material balance is the lack of (systematic) analysis for volatile components, especially unreacted *pX*. The early work from University of Nottingham and University of Michigan also lacked CO_x analysis though both groups added this later, but with differing approaches. The work at KIST was uncatalysed, and produced a lot of toluene; this is not reported by the other groups that used catalysed reactions; this could be a feature of uncatalysed reactions and the toluene could be a precursor for benzoic acid.

This lack of 'kinetics quality' data is a serious knowledge gap for the industrial assessment of this technology and the provision of such data is an important aim of this PhD project. Clearly full analysis of volatiles and off-gases is important aspect of this.

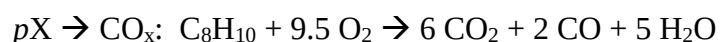
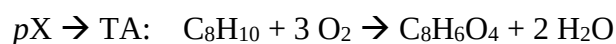
One can breakdown the overall material balance into individual component material balances. These include:

- Aromatic material balance or carbon material balance. This considers the fate of the *pX* feedstock to unreacted xylene, intermediates, TA product and by-products such as benzoic acid, binuclears, trimellitic acid, CO₂ and CO.

- Oxygen balance considers the fate of the hydrogen peroxide fed to oxygenated organics, excess oxygen and undecomposed, unreacted peroxide.
- Metals' balance considers the fate of the soluble catalyst metals to recovered metal in solution and precipitated metal oxides and hydroxides.
- Bromine balance considers the fate of the soluble catalyst bromide to recovered bromide in solution, organic bromides and gaseous forms of bromine such as bromine or hydrogen bromide.
- Additives balance considers the fate of any additional additives in the feed streams *e.g.* benzoic acid added as a catalyst stabiliser. This can interact with the aromatics balance as benzoic acid is also produced as a by-product.
- Water balance considers water fed, water produced from the decomposition of hydrogen peroxide, water produced by hydrocarbon oxidations and quench water.
- Sodium hydroxide balance considers the fate of the sodium hydroxide quench to produce sodium salts of acids such as sodium terephthalate, to produce carbonates by reaction with carbon dioxide or to be in excess.

The carbon material balance is the most important accountability because of its importance in assessing process variable cost and viability. The carbon balance being achieved in the UoN *pX* N/SCWO oxidations at the start of this project were variable and typically around 60-90 %. The most serious omissions from the analysis were the lack of analysis for unreacted *pX* and the lack of routine analysis of CO₂ and CO. There was also no analysis for minor by-products though this omission is of more importance to product quality considerations and is of less importance to the material balance because the components are only present in small quantities. The yield of TA achieved was of the order of 60-90 %. It was noted in Chapter 1 that the current, acetic acid based process achieves ~99 % (chemical) yield of TA which is exceptionally high for an industrial process. The relative economics of the acetic and N/SCWO processes are considered in Chapter 8. This analysis shows that there is an economic trade-off between TA yield and the enhanced energy recovery achievable in N/SCWO; thus, a lower chemical yield of ~95 % to TA is economically viable for the N/SCWO process.

The UoN base case formulation uses an oxygen excess of 20-60 % above the stoichiometric amount needed for full conversion of the fed *p*X to TA. An excess is needed for two reasons, firstly to enable the reaction to proceed to completion without the need for excessive residence time and secondly because full oxidation to CO₂ and CO uses much more oxygen than the partial oxidation to TA:



the latter giving a CO₂:CO ratio of 3:1 which is a typical ratio in the acetic acid based process.

It is possible that excess oxygen causes increased over oxidation thus forming a vicious circle where increased oxygen causes more oxidation that requires yet more oxygen. This is clearly a very important aspect for study.

The catalyst metals balance has only been measured for *o*X oxidation where *o*PA is soluble (at ambient temperatures at low substrate concentrations) and so water based quench can be used. This enables the manganese to be kept in solution. The manganese recovery ⁶⁷ has been found to be ~76 % without and ~97 % with stabilising additives.

Measurement of the soluble bromide in the quenched liquor shows that the bromine recovery is ~60-80 %. In the acetic based process, the purged bromide is not recovered and bromide recovery is not critical to the process economics. It is thought that a small amount of aromatic ring bromination occurs but this had not been quantified at the project inception.

In N/SCWO, water is used as the solvent and is also produced by the oxidation reactions occurring. Water is not destroyed in the reaction (to any significant extent) and this is a big advantage compared to the acetic acid solvent based process where acetic loss is a significant factor in the variable cost. The water balance is therefore easily calculable and is not of much experimental interest and has not been measured.

A gas liquid separator is used to separate out residual gas for subsequent GC analysis. On the University of Nottingham rig the gas liquid separator is a glass vessel. The gas separated by the gas/liquid separator potentially comprises the following components:

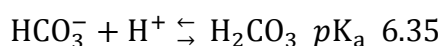
- Oxygen – this is any excess from the oxygen added (originally as hydrogen peroxide).
- Carbon dioxide – this is produced by the decarboxylation of aromatic acids and the total destructive oxidation of aromatics. These processes are described in Section 1.3 of this thesis. The carbon dioxide is not obtained quantitatively if using sodium hydroxide solution as a quench because it can be captured in solution as sodium carbonate.
- Carbon monoxide – this is produced by the decarbonylation of aromatic aldehydes and the total destructive oxidation of aromatics. In the latter, the aromatic ring is split open and the oxidation then becomes an aliphatic process. Thus, aliphatic aldehydes and acids are formed and these can decarbonylate and decarboxylate to carbon monoxide and carbon dioxide respectively. Aliphatic decarbonylation has a lower activation energy than aromatic decarbonylation because in the latter the aldehyde is stabilised by the aromatic π orbitals. Thus, it is likely that the-majority-of the carbon monoxide derives from the total oxidation route rather than from decarbonylation of aroyl radicals. The CO is not seen when using sodium hydroxide solution as a quench and it is not known what form the CO takes; possibly it is captured as sodium formate.

This GC analysis was not routine and had only been undertaken for a small number of cases.

In the acetic acid based process, additional minor gases are seen including methane and methyl bromide. It is currently not known if these are produced in the N/SCWO process though, if present, they would likely be at much lower levels because their major formation routes are from acetic acid.

Sodium hydroxide is used at an excess of around 20 – 30 % with respect to full neutralisation of all the acidic species present. Excess sodium hydroxide will

neutralise TA, other organic acids such as the intermediates *p*-toluic acid and 4-CBA and by-product benzoic acid. It can also capture carbon dioxide as carbonate and may capture carbon monoxide as formate. The strengths of acidic species can be measured by pK_a . Such values are determined at ambient conditions and will be different at N/SCW conditions. However, the ambient values provide some guidance to the relative acidity of the various species present:



The pK_a of water (whose conjugate base is the hydroxide ion) is 15.74. Thus, the HBr will tend to be neutralised by the quench sodium hydroxide first, followed by the aromatic acids (two neutralisations will overlap slightly with the extent of the overlap depending on the proximity of their respective pK_a values). Any excess sodium hydroxide will then neutralise the carbonic acid to initially form bicarbonate and then carbonate. This could form the basis for an alternative method to measure over oxidation if the bicarbonate, carbonate and formate could be quantified by titration; this possibility will be investigated during this project.

The HPLC analysis had been used to measure intermediates, product TA and by-product BA. It had not been used to measure the formation rate of minor by-products; this is probably not of great importance to the material balance but is of concern regarding product quality. The formation rates of these minors will therefore be measured during this project.

The importance of measuring material balance and of accurately quantifying over oxidation was discussed at the start of this section. On the UoN rig, off-gas analysis

has been undertaken using a micro GC but only on an intermittent basis. Gas is separated from liquid in a glass separation vessel and then passed to the GC to measure O₂, CO₂ and CO. The efficiency of the gas stripping is unknown. Also, as discussed above, the quench sodium hydroxide may capture the CO as formate while any excess sodium hydroxide (beyond that necessary to neutralise the organic acids) will progressively capture the CO₂ as bicarbonate and carbonate. Once captured in these ways, the CO₂ cannot be stripped from the liquid without re-lowering the pH and this would not decompose any formate. The UoN work has made no attempt to quantify these effects and so can only be regarded as indicative of the minimum CO₂ and CO levels and not as quantitative. These issues will be addressed during this PhD project.

2.5.2 Rig Design

This section considers the capability of the current rig designs for achieving the overall aims of the project and considers improvements that could or should be made. This section excludes the reactor design which is covered in detail in the subsequent Sections 2.5.3 to 2.5.5.

Scale of the Rigs

The first consideration is whether the scale of the rigs is suitable. Important considerations are safety, cost, reactor flow regime, material balance capability and heat losses.

The current rigs are quite small scale and this is a major advantage for safety as it limits hazardous inventories. The *pX* N/SCWO process has several hazards including high pressure, substrate flammability and explosive decomposition. The latter occurs when *pX* contacts oxygen at pressure in the absence of water; such a mixture will detonate with no source of ignition required. A major cause of these conditions is a cool spot (< ~280 °C) where *pX* could phase separate from water in the liquid phase.^{118, 119} The use of small scale equipment clearly gives safety advantages and is also advantageous for cost.

The next consideration is reactor flow regime. The length scales in small scale equipment are short and this often leads to laminar or transitional flows, even in low viscosity systems, while the equivalent full-scale equipment would have fully turbulent flow. This aspect is considered in detail in the next Section 2.5.3.

High material balance (of at least 95 % and preferably > 99 %) are of great importance in the development of new commodity chemical processes because reaction selectivity and variable cost tends to dominate the process economics. It is often difficult to achieve good material balance in small scale equipment. However, this problem has improved over the last 20 years with improved analytical techniques and process instrumentation *e.g.* modern thermal mass flow meters are accurate to 1 % (of their range) or better even at very low flows. Therefore, it should be possible to achieve a good material balance even with small scale equipment. However, this is an important issue for this project and a critical success factor and this aspect is given more consideration in Section 2.5.1.

Chemical oxidations are exothermic and produce heat. That heat can stay in the process phase and cause the phase temperature to increase, known as adiabatic operation, or be removed from the phase to give constant temperature, known as isothermal operation. Operation can also be intermediate between these with partial heat removal. The heat loss from a system increases with higher temperatures because of higher thermal driving force and at smaller scale because of a higher surface area to volume ratio. Thus, small scale SCWO experiments are prone to high heat losses and temperatures tend to fall quickly unless considerable support heating and lagging is applied. It is therefore difficult to undertake adiabatic operation at small scales but isothermal operation is easier. At large plant scale, heat removal is more difficult and adiabatic operation (or at least partial adiabatic) is often preferred. An important aspect of small scale pilot work is to collect chemical kinetic data and such kinetics are usually highly activated with temperature. Chemical activation energies are typically in the range of ~60 - 140 kJ/mol; for comparison activation energies for diffusion processes are typically ~15 - 25 kJ/mol. Thus, kinetic data collected at several temperatures under isothermal conditions is usually more useful and once collected, the kinetics of adiabatic operation can be predicted. This aspect therefore favours small scale operation

with the proviso that sufficient support heating can be applied to keep the rig isothermal.

In summary, the relatively low costs and safety advantages of small scale equipment are well worth retaining. However, this presents several challenges for the project:

- To understand the effect of turbulence on process performance so that results from small scale rigs can be used to predict full scale plant performance.
- To obtain a good material balance (> 99 %) with small scale equipment.
- To obtain isothermal rig operation.

Feed Systems and Source of Oxygen

The feed systems use HPLC pumps and rely on pump rate calibrations and measurements of volume and time to assess feed rates. Modern thermal mass flow meters have high accuracy even at low flow rates, provide a continuous flow rate measurement and are relatively cheap (against the equipment budget available). They should be trialled on at least the *pX* feed. The catalyst feed may be more challenging because of the bromide content which may necessitate a high grade of material such as titanium. Such meters may be unsuitable for hydrogen peroxide solutions because of the tendency for the peroxide to gas off, particularly when in contact with metal components.

The melting point of *pX* is ~13 °C and increases with pressure. *pX* is thus prone to freezing when pumped at high pressures at ambient temperatures. This is a problem on the rig, particularly in winter, and the *pX* line should be trace heated to enable year-round operation.

Manganese based catalysts are prone to hydrolysis under N/SCWO conditions and produce insoluble mixtures of manganese oxides which are quite fouling in the reactor. Work at the UoN⁶⁷ has shown that Mn based catalysts can be stabilised by the addition of aromatic carboxylic acids (such as benzoic acid, oPA or TMA) to the catalyst feed but these have limited solubility and require a warm feed system (*i.e.* reservoir, feed lines and pump head) to attain the required additive levels. This

is operationally difficult at small scale due to high heat losses. It would be advantageous to develop catalyst formulations that are less prone to hydrolysis and that do not require sparingly soluble additives.

Another aspect of the current rig design is the use of hydrogen peroxide as the source of oxygen. The alternative would be to feed and meter oxygen gas and water in separate feed streams. The UoN have practiced this historically but found it difficult to control and produced mixtures of both under and over oxidised products. However, the author suspects that this was related to the use of an old O₂ flow control device and that better results could be obtained with a modern thermal mass flow meter and control valve. The use of peroxide has advantages and disadvantages.

The advantages are:

- It provides a cheap and convenient source of oxygen in laboratory rig scale operations.
- Its use places a lower limit on the ratio of oxygen to water that can be fed to the rig. This is an important safety feature as it eliminates the possibility of feeding a water-lean reaction mix leading to a decomposition of *pX* in oxygen. This aspect forms part of the basis of safety for the IP1 rig.

The disadvantages are:

- Its cost would preclude its use in full scale, commercial operations where oxygen gas would be used.
- While there is literature¹¹⁴⁻¹¹⁶ that suggests that quantitative decomposition of the peroxide can be achieved, the author has concerns that residual (*i.e.* ppm level) peroxide could provide a source of hydroxyl radicals¹²⁰ leading to increased *pX* oxidation to CO₂.
- The tendency for peroxide to decompose prematurely (*i.e.* before reaching the preheater), particularly if contacting metal. This is problematic if it occurs on the suction side of the feed pump as it can cause gas locking and reduced flow.

- The use of peroxide limits the $O_2:pX$ ratio that can be achieved to below that which would likely be used in a commercial process. This could be overcome (to an extent) by using 50 % peroxide solution.

The safety considerations and convenience make the continued use of peroxide preferable. However, it will be important to address the concerns raised during this PhD project.

Quenching and Cooling

The quenching and cooling system on the UoN rig works well and rarely gives problems.

Filtering and Back Pressure Regulators

The purpose of the filters immediately upstream of the back-pressure regulator is to prevent particles of precipitated catalyst oxides from entering the BPR and blocking the small orifices over which the pressure is dropped. However, there are two possible philosophies that can be adopted for the choice of filter mesh size:

- Use a very fine mesh size (of ~ 0.5 microns) that removes all but colloidal particles.
- Use a larger mesh size (perhaps of $\sim 20 - 100$ microns) that removes larger particles but allows through smaller ones that would not block or damage the BPR.

Use of the former strategy causes the pressure drop across the filter to rise as it blinds with fine particles. The BPR must be continuously adjusted to keep the pressure in the reactor constant. Eventually the BPR is fully opened and all the pressure drop is occurring across the filter. The pressure then starts to rise and the unit must be shutdown. Workers at the UoN have generally adopted this strategy and run times are typically $\sim 1-2$ hours before it is necessary to shut down. Residence times in the rig are typically up to a few tens of seconds so this is adequate time to achieve equilibrium (requiring $5 - 10$ residence times) and take multiple samples for one condition.

Use of the latter strategy could enable samples for several conditions to be taken during one run, which would raise productivity, with the proviso that the smaller particles passed do not lead to premature failure of the BPR. There could be an optimum filter size that maximises the unit's productivity but this aspect has not been investigated.

The BPR is a critical piece of equipment that contains small orifices that can become blocked. There are commercially available devices that incorporate a needle that continuously oscillates into and out of the orifice and dislodges particulate build up. These devices are claimed to be more resilient to particulates and should be trialled in this application.

Gas/Liquid Separation

The stream exiting the BPR is expected to contain both liquid and gas. The gas components could potentially include oxygen, carbon dioxide and carbon monoxide. The oxygen is unused excess and the CO₂ and CO are from over oxidation and decarboxylation and decarbonylation reactions as discussed in Section 1.3.

The UoN rigs, as configured during the project, did not have routine provision for gas collection and analysis and this is clearly a serious omission. There are several ideas for gas collection systems:

- Gas/liquid separator vessel.
- Gas syringe.
- Chemical capture of gas.

A gas/liquid separator would be a vessel into which the discharge of the BPR would be fed. The gas would disengage and be taken off the top while the liquid would be taken off the bottom. The gas stream could be fed to a GC or IR gas analyser to provide continuous gas monitoring. It would be necessary to implement level control within the separator and it would probably be necessary to provide stripping nitrogen to ensure that dissolved gases were removed from the liquid. It is likely that the vessel would work better if it were under a positive pressure of 2 – 3 bar,

to aid the discharge of the liquid stream. It would also require pressure relief to protect against a BPR failure that allowed high pressure in the vessel.

Another concept is to attach a gas tight syringe onto the discharge of the BPR and allow the flow to push the plunger out. The two-phase mixture would phase separate and the liquid phase could be expelled leaving the gas that could be injected to a GC. Possible issues could be:

- The need for protection against overpressure on the syringe. This may preclude the use of glass.
- Inability to provide stripping nitrogen to the liquid phase.
- Limited ability to clean up the gas stream thus requiring injection of a dirty sample in to the GC.
- Only batch sampling and thus intermittent and labour intensive if multiple analyses are required.

The third concept is to inject excess quench sodium hydroxide so that in addition to keeping the TA in solution (as its sodium salt), the CO₂ is captured as sodium carbonate and is also retained in solution. The oxygen would be unaffected. It is less clear what would happen to the CO, it might be captured as sodium formate. Options to analyse the solution for carbonate and formate are considered in Section 2.5.1 on analytical procedures.

2.5.3 Reactor Flow Regime

Flow regimes can be characterised by their degree of turbulence. Reynolds number is a measure of the balance of inertial and viscous forces and indicates whether a flow is laminar or turbulent in nature. Laminar flow occurs when viscous forces are dominant and this occurs in (pipe) flows with Reynolds numbers of less than about 2200. As inertial forces become more important and Reynolds number increases above 2200, flows become increasingly turbulent in nature and turbulent eddies appear; such flows are termed ‘transitional’. Full turbulence occurs when inertial forces dominate and this occurs at Reynolds numbers above $\sim 10^6$. The degree of turbulence at transitional Reynolds numbers determines the degree of ‘axial dispersion’¹²¹⁻¹²³ that occurs for flow along a pipe as illustrated in Figure 2-

9 reproduced from Levenspiel.^{124, 125} In laminar flow there is a linear gradient of axial flow velocity across the radius of a pipe with zero axial velocity at the wall and maximum axial velocity at the pipe centre. Thus, a pulse of material introduced evenly into a laminar pipe flow will become axially dispersed as material at the centre of the pipe moves at a higher axial velocity than material at or near the wall.

The degree of dispersion will increase linearly as the velocity increases and will be greater at higher Schmidt number and is thus greater in liquids than gases. As axial velocity increases further, inertia begins to overcome viscosity and turbulent eddies appear in the flow. These eddies break down the radial gradient of axial flow velocities such that a more constant flow rate occurs across most of the radius of the pipe but with near zero flow at the walls. This enables a reasonable approximation to 'plug flow' of material with low levels of axial dispersion. Thus, the degree of axial dispersion drops rapidly at Reynolds numbers above 2200 and is very low with fully turbulent flow.

A typical UoN formulation for the ¼" O.D. reactor has a total pump rate of ~12 mL/min. Figure 2-10 shows hydrodynamic analysis for this reactor size. The UoN reactor uses ¼" tubing with 0.035" wall thickness and the Reynolds number at this condition is ~1800 at supercritical conditions (380 °C, 230 bar) and drops to ~700 at sub critical conditions (330 °C, 230 bar), see case references 11 and 12 in the figure. The turbulence is less at subcritical conditions because the density and viscosity are higher. These Reynolds numbers can be increased by using smaller internal diameter tubing (*i.e.* thicker walled tubing), to ~1000 and ~2700 for subcritical and supercritical flow as shown in case references 3 and 5.

Copyrighted material removed.

Figure 2-9. The degree of axial dispersion in pipe flow. Laminar flow occurs at Reynolds numbers of less than ~ 2200 . In this region, maximum flow velocity occurs at the pipe centre and there is a gradient of velocity to the pipe wall. Axial dispersion thus increases with velocity and Re. It is higher in liquids which have higher Schmidt number (due to lower diffusivity). Axial dispersion decreases progressively as turbulence develops at Reynolds numbers > 2200 . The flow is fully turbulent at $Re \sim 10^6$. The figure is reproduced from Levenspiel.^{124, 125} D = dispersion or axial dispersion coefficient m^2s^{-1} , u = fluid velocity ms^{-1} , d_t = tube diameter m. The dimensionless group (D/ud_t) is the dispersion number and is the parameter which measures the extent of axial dispersion. Sc = Schmidt number, $\mathcal{D}$ = diffusivity m^2s^{-1} , μ = viscosity Nsm^{-2} , ρ = density kgm^{-3} .

The IP1 rig reactor differs from the UoN reactor in that it uses $\frac{1}{8}$ " O.D. tubing. It has pumps capable of delivering ambient flows rates of ~ 24 mL/min. Although this tubing size had not been used to perform a xylene SCWO prior to the commencement of this PhD study, the conditions that could be achieved in this reactor are shown in Figure 2-11. This shows that this reactor is (just) capable of operating in the turbulent regime in both the supercritical and sub-critical conditions achieving Reynolds numbers of ~ 3640 and ~ 9465 respectively. A comparison of the conditions achievable with this reactor and the UoN reactor can be seen by comparing Figure 2-10 and Figure 2-11 (compare case references 3 and 13 for subcritical conditions and case refs 5 and 16 for supercritical conditions).

Chapter 1 reviewed the chemistry of the *p*X oxidation process. The main reaction pathway proceeds *via* a series of sequential reactions and intermediates as described in Section 1.3.1. Further, there are several side reactions that include over oxidation of *p*X and oxidation of acetic acid to CO₂ and CO and the production of coupled aromatics by-products as described in Sections 1.3.2, 1.3.4 and 1.3.3 respectively. Furthermore, in near critical and supercritical water, metal salt catalysts will (to some degree) hydrolyse and precipitate insoluble metal oxides which may be fouling. This tendency to fouling can produce blockages in process equipment, particularly if it contains narrow dimensions.

Important questions that this project will seek to address are what is the effect of residence time distribution (RTD) on both the main reaction sequence and on the side reactions and how can the RTD be optimised?

The two most studied idealised reactor residence time distributions are plug flow and back mixed. There are numerous texts describing the characteristics of these distributions, a well-known one being Levenspiel.¹²⁴ In plug flow, all elements of the fluid have an identical residence time while in back mixed, there is a distribution of residence times. Other RTDs can be characterised as combinations of plug flow and back mixed reactors deployed in series and/or in parallel. Plug flow can be modelled by multiple back mixed zones in series (typically ~ 5 are required to achieve an approximation to plug flow). Thus, the equivalent number of back mixed zones provides a measure of the degree of plug flow. This is an alternative (measure of the degree of plug flow) to the degree of axial dispersion,

that was discussed and illustrated in Figure 2-9. The optimisation of RTD for this system is discussed further in Chapter 5.

Plug flow is often difficult to achieve in small scale equipment because length scales are small leading to low Reynolds numbers and thus a tendency towards laminar flow with high axial dispersion. Maximising Reynolds number requires high flow velocities in narrow tubing but this can lead to problems with high pressure drops and tube blockage from fouling.

It was therefore decided to test a reactor using narrower tubing than the ¼" O.D., 0.035" wall tubing used in the UoN tubular reactor. Commercially available Hastelloy tubing sizes are shown in Table 2-3. The Table also shows the Reynolds numbers that can be achieved at near and supercritical conditions and an estimate of the order of magnitude of the pressure drop obtained using standard chemical engineering pipe flow correlations.

Table 2-3. Commercially available Hastelloy tubing with estimates of Reynolds numbers and Pressure Drops when using the standard University of Nottingham *pX N/SCWO* formulation. Conditions: near critical 330 °C/230 bar, supercritical 380 °C/230 bar, pump rate 12 mL/min at ambient, reactor volume 5.73 mL, reactor residence time subcritical 19.3 s, supercritical 6.0 s. Physical properties obtained from NIST.¹²⁶

Tube Outer Diameter (")	Tube Wall Thickness (")	Internal Diameter (mm)	Reynolds number		Estimated pressure drop ^a (bar)	
			Near critical	Super critical	Near critical	Super critical
¼	0.035	4.57	700	1815	7.7x10 ⁻⁶	9.6x10 ⁻⁶
¼	0.065	3.05	1050	2720	8.8x10 ⁻⁵	1.1x10 ⁻⁴
⅛	0.028	1.75	1820	4730	2.4x10 ⁻³	8.5x10 ⁻³
⅛	0.035	1.40	2280	5940	0.02	0.04
1/16	0.020	0.57	5580	14510	6.4	16.4

a. Pressure drop (bar) = $2f\rho v^2 l / (10^5 d)$ where Friction factor (laminar flow) $f = 16\nu / (1000v\rho d)$, Friction factor (turbulent flow, smooth wall) $f = 0.079 / Re^{0.25}$, ρ = density (kg/m³), v = velocity (m/s), l = reactor length (m), d = reactor diameter (m), ν = dynamic viscosity (cP), Re = Reynolds Number and assuming turbulent at $Re > 2200$.

Case	1/4" rx, NCW, Varying Temperature				1/4" rx, SCW, Varying Temperature		1/4" rx, NCW, Varying Flow				1/4" UoN, 0.035" wall thickness	
Case reference	1	2	3	4	5	6	7	8	9	10	11	12
Pipe diameter (O.D.) "	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Pipe diameter (O.D.) m	6.35E-03	6.35E-03	6.35E-03	6.35E-03	6.35E-03	6.35E-03	6.35E-03	6.35E-03	6.35E-03	6.35E-03	6.35E-03	6.35E-03
Wall thickness "	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.035	0.035
Pipe internal diameter (I.D.) "	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.18	0.18
Pipe internal diameter (I.D.) m	3.05E-03	3.05E-03	3.05E-03	3.05E-03	3.05E-03	3.05E-03	3.05E-03	3.05E-03	3.05E-03	3.05E-03	4.57E-03	4.57E-03
Cross sectional area m2	7.30E-06	7.30E-06	7.30E-06	7.30E-06	7.30E-06	7.30E-06	7.30E-06	7.30E-06	7.30E-06	7.30E-06	1.64E-05	1.64E-05
Reactor length m	0.785	0.785	0.785	0.785	0.785	0.785	0.785	0.785	0.785	0.785	0.349	0.349
Reactor volume ml	5.73	5.73	5.73	5.73	5.73	5.73	5.73	5.73	5.73	5.73	5.73	5.73
Ambient flow rate ml/min	12.0	12.0	12.0	12.0	12.0	12.0	12.0	24.0	60.0	124.0	12.0	12.0
Mass flow rate kg/s	2.00E-04	2.00E-04	2.00E-04	2.00E-04	2.00E-04	2.00E-04	2.00E-04	4.00E-04	1.00E-03	2.07E-03	2.00E-04	2.00E-04
Temperature C	280	300	330	360	380	400	330	330	330	330	330	380
Pressure bara	230	230	230	230	230	230	230	230	230	230	230	230
Phase	liquid	liquid	liquid	liquid	supercritical	supercritical	liquid	liquid	liquid	liquid	liquid	supercritical
Dynamic viscosity cP	9.86E-02	9.10E-02	7.99E-02	6.63E-02	3.07E-02	2.74E-02	7.99E-02	7.99E-02	7.99E-02	7.99E-02	7.99E-02	3.07E-02
Kinematic viscosity m2/s	1.27E-07	1.23E-07	1.18E-07	1.15E-07	1.47E-07	2.05E-07	1.18E-07	1.18E-07	1.18E-07	1.18E-07	1.18E-07	1.47E-07
Density kg/m3	774.5	739.8	675.4	576.0	208.7	133.7	675.4	675.4	675.4	675.4	675.4	208.7
Flow rate at T&P ml/min	15.5	16.2	17.8	20.8	57.5	89.7	17.8	35.5	88.8	183.6	17.8	57.5
Flow velocity at T&P m/s	0.035	0.037	0.041	0.048	0.131	0.205	0.041	0.081	0.203	0.419	0.018	0.058
Reynolds Number	848	918	1046	1259	2721	3044	1046	2092	5230	10808	697	1814
Residence time s	22.2	21.2	19.4	16.5	6.0	3.8	19.4	9.7	3.9	1.9	19.3	6.0

Figure 2-10. Typical hydrodynamic conditions for ¼" O.D. N/SCWO reactors. The first (horizontal) block gives pipe geometry data and the second gives process conditions. The third block gives physical property data (obtained from NIST) and the final block gives calculated hydrodynamic parameters including the Reynolds number (highlighted in brown) and residence time (highlighted in green). Data in blue text are inputs to the spreadsheet and data in black are calculated or look ups. Cases 1-4 are NCW conditions of increasing temperature of 280-360 °C at the normal operating flow rate, an ambient flow rate of 12 mL/min. The Reynolds number line shows values to ~1260 which are laminar flow. Cases 5 & 6 are SCW cases at 380-400 °C and the same ambient flow; Re are ~3000 which are transitional between laminar and turbulent flow. Cases 7-10 are NCW at 330 °C with increasing ambient flow rates from 12 – 124 mL/min. The HPLC pumps on the UoN rigs could only deliver up to 24 mL/min with Re ~2000 which is laminar flow but close to the initial onset of turbulence. Cases 9 & 10 show higher flows (which were not achievable with the equipment available) but illustrate the flows that would be needed for turbulent flows (*i.e.* for Re > 5000). Cases 11 & 12 show the conditions that could be achieved using thinner wall tubing as was in use on the UoN rig. Comparative cases (with thicker wall tubing) are cases 3 and 5 respectively; this shows that Re drops as pipe I.D. increases for a given flow rate.

Figure 2-11. Typical hydrodynamic conditions that can be achieved using the proposed 1/8" O.D. N/SCWO reactors. The data structure and colour coding is the same as that described in the caption to Figure 2-10 and the case numbers follow on from that figure. Cases 13 - 15 are NCW at 330 °C with increasing ambient flow rate from 12 – 30 mL/min. Cases 16 - 18 are SCW cases at 380 °C and at the same ambient flows (of 12 - 30 mL/min). The Reynolds number line (highlighted in brown) shows Re in the NCW regime of ~1800 – 4550 which span laminar, transitional and early turbulence and Re in the SCW regime of ~4700 – 11800 which are turbulent. The residence times (highlighted in green) show the mean residence times that can be achieved for the proposed reactor length (and volume) for the various cases.

Case	1/8" rx, NCW, base case	1/8" rx, NCW, 2x rate	1/8" rx, NCW, 2.5x rate		1/8" rx, SCW, base case	1/8" rx, SCW, 2x rate	1/8" rx, SCW, 2.5x rate
Case reference	13	14	15		16	17	18
Pipe diameter (O.D.) "	0.125	0.125	0.125		0.125	0.125	0.125
Pipe diameter m	3.18E-03	3.18E-03	3.18E-03		3.18E-03	3.18E-03	3.18E-03
Wall thickness "	0.028	0.028	0.028		0.028	0.028	0.028
Pipe internal diameter "	0.069	0.069	0.069		0.069	0.069	0.069
Pipe internal diameter (I.D.) m	1.75E-03	1.75E-03	1.75E-03		1.75E-03	1.75E-03	1.75E-03
Cross sectional area m2	2.41E-06	2.41E-06	2.41E-06		2.41E-06	2.41E-06	2.41E-06
Reactor length m	8.082	8.082	8.082		8.082	8.082	8.082
Reactor volume ml	19.50	19.50	19.50		19.50	19.50	19.50
Ambient flow rate ml/min	12.0	24.0	30.0		12.0	24.0	30.0
Mass flow rate kg/s	2.00E-04	4.00E-04	5.00E-04		2.00E-04	4.00E-04	5.00E-04
Temperature C	330	330	330		380	380	380
Pressure bara	230	230	230		230	230	230
Phase	liquid	liquid	liquid		supercritical	supercritical	supercritical
Dynamic viscosity cP	7.99E-02	7.99E-02	7.99E-02		3.07E-02	3.07E-02	3.07E-02
Kinematic viscosity m2/s	1.18E-07	1.18E-07	1.18E-07		1.47E-07	1.47E-07	1.47E-07
Density kg/m3	675.4	675.4	675.4		208.7	208.7	208.7
Flow rate at T&P ml/min	17.8	35.5	44.4		57.5	115.0	143.8
Velocity m/s	0.123	0.245	0.307		0.397	0.795	0.993
Reynolds Number	1819	3638	4548		4733	9465	11832
Residence time s	65.8	32.9	26.3		20.3	10.2	8.1

As tubing diameter (*i.e.* the length scale) is reduced, the velocity increases proportionately faster than the length scale reduces and so the Reynolds number rises. The Table shows that (at these flow rates) the pressure drops only become significant for 1/16" O.D. tubing and are not excessive. This analysis suggests that plug flow conditions can best be achieved using the smallest diameter tubing. However, the manganese based catalyst system is prone to fouling and thus there are doubts about the minimum diameter of tubing that can be practically employed without blockage occurring.

Thus, in the light of the preceding discussion, principles that can be used for the design of the flow regime for laboratory scale *pX* N/SCWO reactors are as follows:

- Employ reactors capable of operating over a range from laminar flow to the nearest approach to plug flow that it is practical to engineer.
- Therefore, use the smallest tube possible. Note that:
 - At the flow rates currently used, pressure drop is not a constraint.
 - Reactor fouling and blockage will probably be a constraint. However, the UoN reactor has successfully used 0.035" wall, 1/4" tubing for *pX* SCWO.

2.5.4 Reactor Residence Time

The mean residence time of a given reactor can be calculated as:

$$\tau = V_R/r$$

where τ is mean residence time (s), V_R is the reactor volume (mL) and r is the flow rate under reactor conditions (mL/s). The reactor volume can be calculated from a knowledge of pipe and fittings geometries (as defined in the Swagelok catalogue) and the flow rate is the ambient pump rate adjusted to reactor conditions using a water density obtained from NIST with the assumption that the feeds can be approximated to the same physical properties as pure water. Estimates of the residence time of the UoN N/SCWO reactor are given in Table 2-2.

For N/SCWO there are several ways to vary the mean residence time:

- Vary reactor volume.
- Vary flow rate in the reactor.
- Vary the reactor temperature.
- Vary the reactor pressure.

Reactor volume is not easy to vary on an experiment to experiment basis. This is because the reactors are built using Swagelok fittings. These are available in stainless steel and in Hastelloy; the latter are expensive so stainless fittings are preferred. However, in this process, both Hastelloy and stainless fittings are prone to some corrosion and once split apart and disassembled, they rarely reseal effectively and must be replaced. Thus, it is only realistic to vary reactor volume during periodic reactor rebuilds. It might be possible to design a reactor with a variable volume by using multiple inlets though this was not attempted.

Varying reactor residence time by varying the pump rates is quick and simple and can be achieved both between and within experiments if required. A downside is that the Reynolds number and degree of axial dispersion will vary at the same time, *e.g.* the UoN reactor would have Reynolds numbers of 700/1810 and 1400/3620 at NCW (330 °C)/SCW (380 °C) 230 bar conditions at 12 mL/min and 24 mL/min ambient flow rates respectively.

Reactor residence time varies with reactor temperature or pressure because of the strong variation of the density of water with temperature and pressure in the near critical and supercritical regions as is illustrated in Figure 1-11. Thus, the UoN 5.73 mL reactor would have a mean residence times of 21.2, 19.3, 16.5, 6.0, 3.8 s at 300, 330, 360, 380, 400 °C respectively with a 12 mL/min ambient pump rate at 230 bar. However, chemical reactions are generally strongly activated with temperature and reaction selectivity is often strongly influenced. In addition, the dielectric constant of water exhibits strong gradients in these regions and this could affect the solvation of transition state species and impact reaction outcomes. For these reasons, the variation of temperature or pressure are the least preferred methods of varying residence time for this chemistry.

As was discussed in Section 1.4, it is believed that the *pX* N/SCWO proceeds by a free radical chain mechanism. Such reactions depend on the balance of chain

propagation reaction steps over termination steps and achieving significant reaction rates depends on building up a concentration of propagating radicals. These types of reactions, when run in plug flow reactors, tend to show lags for initiation and long ‘tail-outs’ where the reaction slowly dies. Thus, considerable residence time is needed to drive the reactions to very high conversions. Initiation lags are not seen in CSTRs except in the start-up operations. It is difficult to achieve high conversions in CSTRs because some material always has a short residence time.

Another issue is that the feed substrates, intermediates and products are in contact with the catalyst, oxygen and propagating radicals, at the reaction temperature, throughout the reaction residence time and may be degraded to undesirable by-products.

It is therefore important to determine the effect of both residence time and of RTD on reaction outcome as measured by yield and selectivity of the main and side reactions and this will be a focus in these PhD studies.

2.5.5 Reactor Orientation and Mixer Design

In the *pX* N/SCWO system the reactors must mix a supercritical water, low density stream (containing oxygen) with a higher density, near critical water stream (containing catalyst salts and organic). The SCW and NCW streams have densities of ~130 - 200 and ~575 - 775 kgm⁻³ respectively. When mixing streams with significant density differences the reactor orientation becomes important.

The possible modes of poor mixing are follows:

- a) *pX* and SCW/oxygen are contacted with insufficient catalyst.
- b) Metal salt (*i.e.* catalyst) and SCW/oxygen are contacted with insufficient *pX*.
- c) *pX* and metal salt are contacted with insufficient SCW/oxygen.

Mode (a) leads to uncatalysed (or at least under catalysed) oxidation of *pX* that would be less selective than catalysed oxidation. Mode (b) is analogous to the process for producing nanoparticles and would thus lead to a degree of catalyst precipitation. It is currently unknown if the precipitated catalyst would have any

catalytic activity and this question will need be addressed within this project. Catalyst precipitation is likely to be undesirable because of the potential to give fouling and mixer blockage. Mode (c) is currently thought to be the most benign poor mixing mode though the pX and salt solution would be immiscible and so it would be important that any droplets of pX were effectively conveyed into and dispersed within regions containing the SCW and oxygen.

Buoyancy driven flows can be characterised by appropriate dimensionless numbers. The Grashof number is the ratio of buoyancy forces (driven by density difference) to viscous forces under natural convection. The transition from laminar to turbulent flow in the boundary layer (between phases of differing densities) occurs for $10^8 < Gr < 10^9$. The Grashof number is analogous to the Reynolds number which is the ratio of inertial forces to the viscous forces and governs the nature of the flow in forced convection. The Richardson number (Ri) is the ratio of Grashof number to the square of Reynolds number ($Ri = Gr/Re^2$) and gives the ratio of buoyancy and inertial forces. For $Ri > 10$ forced convection is negligible and the system will be prone to flow stratification, *i.e.* the separation of the flow into unmixed layers. For $Ri < 0.1$ natural convection is negligible.

The UoN reactor (illustrated in Figure 2-3) is down flow with the supercritical flow introduced downwards into the reactor and with the catalyst and pX streams introduced as side streams into this down flow. At the base case operating condition, the values of the hydrodynamic groups are $Re \sim 700$, $Gr \sim 10^7$ and $Ri \sim 66$. The Re and Gr shows that neither inertial nor buoyancy forces are sufficient to produce turbulence and that the flow is therefore laminar. The Ri shows inertia is negligible compared to buoyancy and that these systems will therefore be prone to flow stratification.

Thus, the UoN reactor is in the laminar regime with neither inertial or buoyancy forces able to provide sufficient energy to overcome the viscous forces. Mixing therefore must rely on the division of the flow field and molecular diffusion over small length scales. In this regard, the small diameter of the injection pipes is beneficial. Wakashima⁹⁰ advises avoiding attachment of the metal salt flow to the wall and the extension of the feed pipes into the centre of the flow is beneficial in this regard. He also advises the avoidance of recirculation zones and so the mixing

cross side arms could be undesirable. The system is prone to stratification and so the vertical reactor orientation is likely to be beneficial. The injected catalyst and substrate fluids will tend to sink due to their higher density but it is unclear how efficiently injected streams will mix with the main flow or with each other. The mixing arrangement does not exploit the buoyancy of the SCW stream in the way that Lester *et al.*¹⁰¹ advocate.

The injection of the (dense) quench stream at the low point of the system minimises the risk of backflow into the reaction zone. However, the horizontal orientation at the mixing point must give a high risk of flow stratification at this point and of inefficient mixing of the quench fluid.

If low temperature were to occur in the reactor leading to phase separation, the down-flow configuration gives no intrinsic tendency for the (oxygen containing gaseous) lighter phase to be swept out of the rig. This is a potential safety concern as contact of *pX* with this gaseous phase could lead to explosive mixtures.

The IP1 reactor had not been deployed for xylene N/SCWO at the start of this project. However, the rig and reactor were available and therefore some consideration was given to how suitable the design would be for this duty. This reactor (illustrated in Figure 2-6) introduces the SCW, NCW and organic streams into a mixing cross that is orientated horizontally. It uses lower diameter 1/8" O.D. tubing than the 1/4" O.D. used in the UoN reactor. The data in Table 2-3 show that this enables some turbulence to be achieved which would be beneficial for mixing. The other dimensionless numbers are the same as for the UoN reactor ($Gr \sim 10^7$ and $Ri \sim 66$) and therefore there is a risk of stratification. It is probable that this mixer design could be improved by the use of the principles advocated by Lester *et al.*¹⁰¹

The use of 1/8" tubing for *pX* N/SCWO is unproven and the tendency of the catalyst to oxidise, hydrolyse, precipitate and foul must be of concern in narrow bore tubing. The flow in the IP1 reactor is continuously rising. Such upward flow is desirable for safety in N/SCWO as it will tend to sweep out any phase separated material from the reactor.

The quench is injected just beyond the highpoint of the system as a down flow of sodium hydroxide solution into an angled down flow of the reactor stream. The

flows are just into the turbulent regime and length scales are low, so mixing is probably reasonably efficient. It is possible that some quench could get back over the highpoint and flow back into the reactor. There is no clear means of detecting whether this is happening though there might be some indication from the final thermocouple at the end of the reactor.

2.5.6 Chemistry Formulations and Analysis

This section reviews the approaches of three main groups (KIST and the Universities of Nottingham and Michigan) to investigating pX N/SCWO chemistry and the chemistry formulations available. It notes what information was available at the start of this PhD project, what became available during the project and how this new information influenced the direction.

Workers at KIST and Michigan used batch autoclaves while Nottingham used continuous flow rigs. The comparisons in Tables 2-2 (a)-(d) show that the batch experiments were using residence times an order of magnitude greater than the equivalent continuous experiments for similar process conditions and conversions. This suggests that the batch experiments either:

- were not kinetically limited but constrained by other factors such as mass transfer or mixing,
- had excessive residence time,

or both. Continuous work is more valuable from an industrial perspective as any process at this scale would need to be continuous and the data obtained are less kinetically constrained. However, the analysis in Section 2.5.3 has highlighted the need to increase turbulence to further improve mixing and ensure that kinetic limited data is being collected. The paper by Perez *et al.*⁶⁹ introduced the concept of investigating ‘unsaturated’ or ‘stressed’ catalysts (*i.e.* catalysts with insufficient concentration and time to produce full conversion) which is a valuable addition; this suggestion came from Partenheimer. Stressing the catalyst is particularly valuable in estimating the turnover frequency of the catalyst, under kinetically controlled conditions, and estimates are given in Tables 2-2(c) and (d); for these, each step in the reaction pathway given in Figure 1-2 is regarded as one catalytic

oxidation step. The frequency estimates were $\sim 4 \text{ s}^{-1}$ and $\sim 5 - 7 \text{ s}^{-1}$ for sub and supercritical oxidation respectively. These values were 2 – 3 orders of magnitude greater than in the work in batch reactors further suggesting that these experiments were not kinetically limited. For comparison, the overall frequency for the conventional acetic acid *pX* oxidation process is $\sim 0.1 \text{ s}^{-1}$ though the peak frequency for the rapid *pX* oxidation step is $\sim 7 \text{ s}^{-1}$. Thus, the catalysts in the two processes seem to be of similar activities although the temperatures are 100 – 180 °C apart. They are also mid-range for catalytic industrial processes which typically have turnover frequencies in the range 0.01 – 100 s^{-1} .

The mechanism of *pX* oxidation catalysis in the conventional acetic acid based process is discussed in Section 1.3.1 and Figure 1-5 shows the catalyst redox cascade that is believed to occur. The work by Holliday⁵⁴ and Savage's group^{70, 71} produced an initial assessment of various alternative *pX* N/SCWO catalysts while Poliakoff's group⁶⁹ undertook a thorough and systematic study which significantly advanced this area, particularly the discovery and application of copper-based catalysts. This work occurred concurrently with and was part of this PhD study; a copy of the resulting paper is available in Appendix 1. This work had a significant impact on the direction of this PhD and the paper is reviewed in Chapter 6.

Work by Fulton and Partenheimer *et al.*^{78, 79} probed catalytic structures (for manganese based catalysts) in N/SCW.

A further advantage of continuous work, as practiced at the UoN, is that it can provide good information on reactor fouling. The work of Fraga-Dubreuil *et al.*⁶⁷ on manganese oxide fouling in *oX* SCWO is particularly valuable. The work uses *oX* because the solubility of *oPA* allows the use of water quench thus allowing an assessment of catalyst recovery and hence stability. The solubilities of *oPA* and TA in water are 0.6 % and < 0.01 % w/w respectively at 20 °C and thus, the *oX* N/SCWO reaction can be quenched with water when working with substrate concentration of < 0.5 %. Fraga-Dubreuil's paper pre-dates this PhD and does not form part of this thesis even though the author was a co-author on the paper. However, the formulations presented were used during (the early stages) of this

PhD study. The copper based catalysts (mentioned above) were found to substantially reduce fouling and this aspect is reviewed in Chapter 6.

The approach of using *o*X as an analogue for *p*X was mentioned above as being advantageous for catalyst stability work. *o*X is also advantageous because *p*X is prone to freezing when pumped at pressure at ambient temperatures; this is especially problematic in winter months whereas *o*X does not freeze under these conditions. The suitability of *o*X as an analogue was further investigated by Perez *et al.*⁶⁸ in work inspired by Partenheimer. Again, this work occurred concurrently with this PhD study and the author was a co-author of the resulting paper, a copy of which is available in Appendix 1. The work shows that there are significant differences in outcome for the two feed stocks because the *ortho* position enables the formation of the cyclised intermediate phthalide and this influences the reaction outcomes. Because of this difference and because TA is a material of much greater industrial significance, the use of *o*X as a *p*X analogue was not pursued in this PhD project despite the operational advantages.

The UoN work was undertaken at low substrate concentrations, up to a maximum of 2 % w/w. The other groups went to higher concentrations with Holliday at 9.7 % being the highest; this difference probably mirrors the use of flow reactors at UoN and batch reactors at other groups. Industrial deployment would require high concentrations but engineering this in a flow reactor is challenging because of phase and heat transfer considerations; this aspect is discussed in detail in Section 5.9. Again, the provision of data for high substrate concentrations under flow conditions is an important target for this PhD study.

Savage *et al.*⁷² undertook an initial study of the stability of the aromatic acid products that included TA. This is clearly an important aspect which is pursued further in Chapter 5 in relation to residence time distribution and in Chapter 6 in relation to additional chemical effects such as the effect of oxygen.

There is very little in the literature on the level of production of by-products in *p*X N/SCWO. Limited data on CO_x and BA production is available as documented in Table 2-2(a)-(d) but no data on the colour species discussed in Section 1.3.3 and in the literature¹²⁷ is available. This is clearly a serious knowledge gap as these minor

components are critical to the acceptability of N/SCWO produced PTA in the market place. The provision of such data is key target for this PhD project.

2.5.7 Economic Issues

Savage *et al.*¹¹³ also produced a first attempt at a process synthesis and industrial costing. Such costings can be divided into variable and capital costs and these are vital aspects for this PhD project that are tackled in Chapter 8.

2.5.8 Materials Issues

The materials of construction in use on the UoN reactor at the project inception were as follows. Feed vessels were glass, suction side, low pressure feed lines were plastic (PVC or polypropylene) except for the *pX* line which was stainless steel as *pX* causes plastics to swell. Delivery side, high pressure feed lines were stainless steel. The reactor tubing was Hastelloy C276 and reactor fittings were stainless steel. Pipe work downstream of the reactor was stainless steel. The gas/liquid separator and product collection vessels were glass.

Corrosion occurred in the pre-heater and in the reactor and the pipework and fittings required replacement after a few months. The corrosion was both general corrosion and stress corrosion cracking; these corrosion patterns are illustrated in Figure 2-12. N/SCW is known to be corrosive due to its acidity^{10, 28} and this is at its maximum at ~300 °C as can be seen in Figure 1-11(b). The corrosion and cracking are made worse by the bromide in the reactor and by the high thermal gradients in small scale equipment at high temperatures. The corrosion rates had not been quantified.

Literature usually only documents the reactor materials employed. Holliday *et al.*⁵⁴ noted that Hastelloy C was a superior material of construction to stainless 316L. KIST used Hastelloy C while the University of Michigan initially used stainless steel 316L but switched to Hastelloy C. No author gives quantitative data on rates of corrosion for *pX* N/SCWO.

The cost of Hastelloy tubing and fittings is very high and there is thus an incentive to avoid their use where possible. The rate of corrosion should be quantified and the relative merits of using Hastelloy or stainless steel established. This is a target in this PhD project.

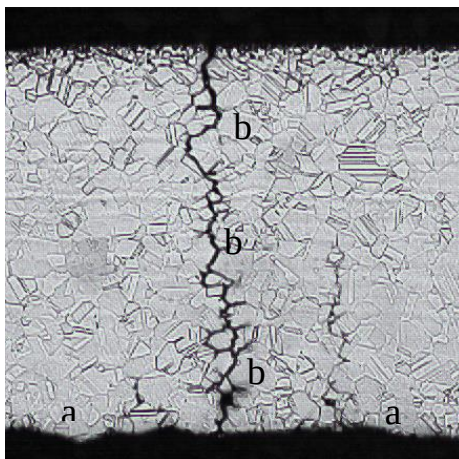


Figure 2-12. A micrograph of a sectioned wall of an 1/8" O.D. Hastelloy C276 preheater tube used in a SCW duty with the process contact wall at the bottom and the exterior (non-process contact) wall at the top. It shows (a) general corrosion and (b) stress corrosion cracking caused by exposure to the SCW. Note that general corrosion occurs over the whole contact surface - contrast the process contact wall to the exterior wall where no corrosion had occurred. Also, note that stress corrosion cracking occurs along the metal grain structure.

The use of a glass gas/liquid separator is questionable from a safety perspective as a failure of the BPR could lead to the full system pressure being applied causing the vessel to shatter. It would be safer if it were to be replaced by a metal vessel, though this would mean the interior would no longer be visible and it could be more difficult to control its internal liquid level.

2.5.9 Critique Summary

This section summarises the key issues that have been identified in this critique of the technology at the project inception.

The project should provide reaction data that are of a 'kinetics' quality. This requires a high material balance that is repeatable. It should include the main reactants, intermediates and required product and by-products that impact the variable cost. It should provide data at high substrate concentrations that would be

needed for industrial deployment. It should also include minor components that impact product quality including those that are not significant to the overall material balance.

It should provide an assessment of variable and capital costings and establish the yield of TA needed for an economic process.

It should identify suitable materials of construction, particularly for the oxidation reactor. It should determine the rates of corrosion for possible candidate materials.

It should identify suitable catalyst formulations and determine their activity and selectivity and whether these are fouling and the level of catalyst recovery achievable.

2.6 Detailed Aims and Tasks for this Project

This section revisits the broad aims of this project that were set out in Section 1.7 and uses the issues identified in the above critique to provide a more detailed set of aims and tasks to be addressed in this PhD project.

2.6.1 Reactor Design and Mixing Issues

Mixing is an important component of reactor design and has been identified as a major focus for this project. There are several major mixing issues:

- How should the component streams for this reaction system be mixed?
- What is the effect of residence time distribution (RTD) within the reactor on the course of the reaction?
- How should the reaction be quenched; how should any quench solution be mixed with the reaction liquor?

A thorough understanding of these issues is important for a further major reactor design issue:

- How should the reactor be scaled up?

Each of these questions can be broken down into additional smaller questions as considered in the following sections.

Component Stream Mixing Issues

Consider the mixing of component streams. There are three component streams for this reaction system comprising pX , aqueous catalyst and oxygen. In the laboratory, a highly practical way to generate an oxygen stream (in the presence of water) is by the thermal decomposition of aqueous hydrogen peroxide.¹¹⁴⁻¹¹⁶ The feeding of gaseous oxygen is also possible, particularly at larger scales.

Component mixing questions include. What order should the component streams be mixed in? What is the effect of excess oxygen on pX , catalyst and product stability? Is staging of oxygen/catalyst/ pX beneficial? What is the most effective method to mix streams with large density differences? What is the effect of pre-heating the catalyst stream prior to mixing and how much catalyst hydrolysis then occurs?

Residence Time Distribution Issues

RTD questions include the following. What is the effect of the idealised RTDs of plug flow and back mixed on reaction yield and selectivity? How do these affect the distribution of by-products? How can these RTDs be designed for pX SCWO at laboratory scale? What is the optimum RTD?

Quench Mixing Issues

Quench mixing questions include. How can quench solution be efficiently mixed with the process fluid? What is the best quench material to use? What is the effect of quenching on the reaction chemistry?

Scale Up Issues

Scale up questions include. How does mixing scale up to full plant scale? What would be a suitable reactor design for the larger scale? What are the major hazards of the process and what is the safe operating envelope? How could these hazards be mitigated for a full-scale process?

2.6.2 Chemistry Issues

Chemistry issues also are a major focus of this PhD project. From an industrial perspective, the most important chemistry question is:

- What is the optimised yield of TA for this chemistry and is this yield sufficient to enable an economic industrial process?

This question can be broken down into several smaller and more manageable questions:

What is the effect of phase? What are the chemistry effects of working in the supercritical, liquid and gas phases?

What are the effects of process conditions, specifically temperature, pressure, catalyst nature and concentration, substrate concentration *etc.* on the intermediates and product yields? What are the optimum conditions?

What by-products are produced? Do these differ (in nature and quantity) from those produced in the acetic acid process? What is the extent of over oxidation to CO₂ and CO? What are the production rates of these by-products? Can these be effectively separated from the desired product?

What catalyst components (*e.g.* metals) are effective? How can the catalyst be optimised? How can the catalyst be stabilised against hydrolysis and precipitation?

What is the role of the reaction quench and how does this affect the chemistry? What is the effect of the quench pH on the reaction course, *e.g.* does aromatic acid decarboxylation occur?

Does the use of hydrogen peroxide as the oxygen source affect or compromise the chemistry?

What are the reaction mechanisms? How do these differ from those observed in the acetic acid based process?

2.6.3 Reactor Materials Issues

Corrosion and materials issues are not a major focus of this PhD project. However, some consideration will be given to the measurement of in process corrosion rates and what would be suitable materials of construction for a *pX* N/SCWO reactor.

2.6.4 Process Integration and Economic Issues

Process integration assesses how individual unit operations can be integrated into an overall process that can then be economically assessed for their capital and variable costs. A detailed study of these aspects is a considerable undertaking that is beyond the scope of this PhD project. However, an initial assessment will be made of how the economics of a *pX* N/SCWO process would compare to the existing acetic acid based process.

2.7 References

1. P. E. Savage, A perspective on catalysis in sub- and supercritical water, *J. Supercrit. Fluids*, 2009, **47**, 407-414.
2. P. E. Savage, Organic chemical reactions in supercritical water, *Chem. Rev.*, 1999, **99**, 603-621.
3. P. E. Savage, S. Gopalan, T. I. Mizan, C. J. Martino and E. E. Brock, Reactions at supercritical conditions: Applications and fundamentals, *AIChE J.*, 1995, **41**, 1723-1778.
4. P. E. Savage, J. B. Dunn and J. L. Yu, Recent advances in catalytic oxidation in supercritical water, *Combust. Sci. Technol.*, 2006, **178**, 443-465.
5. H. Schmieder and J. Abeln, Supercritical Water Oxidation: State of the Art, *Chem. Eng. Technol.*, 1999, **22**, 903-908.
6. P. Kritzer and E. Dinjus, An assessment of supercritical water oxidation (SCWO): Existing problems, possible solutions and new reactor concepts, *Chem. Eng. J.*, 2001, **83**, 207-214.
7. P. A. Marrone, Supercritical water oxidation—Current status of full-scale commercial activity for waste destruction, *J. Supercrit. Fluids*, 2013, **79**, 283-288.
8. M. B. García-Jarana, I. Kings, J. Sánchez-Oneto, J. R. Portela and B. Al-Duri, Supercritical water oxidation of nitrogen compounds with multi-injection of oxygen, *J. Supercrit. Fluids*, 2013, **80**, 23-29.
9. B. Al-Duri, F. Alsoqyani and I. Kings, Supercritical water oxidation for the destruction of hazardous waste: better than incineration, *Philos. Trans. R. Soc., A*, 2015, **373** 20150013
10. P. Kritzer, Corrosion in high-temperature and supercritical water and aqueous solutions: a review, *J. Supercrit. Fluids*, 2004, **29**, 1-29.
11. M. Hodes, P. A. Marrone, G. T. Hong, K. A. Smith and J. W. Tester, Salt precipitation and scale control in supercritical water oxidation—Part A: fundamentals and research, *J. Supercrit. Fluids*, 2004, **29**, 265-288.
12. P. A. Marrone, M. Hodes, K. A. Smith and J. W. Tester, Salt precipitation and scale control in supercritical water oxidation—part B: commercial/full-scale applications, *J. Supercrit. Fluids*, 2004, **29**, 289-312.
13. S. P. Maharrey and D. R. Miller, Quartz capillary microreactor for studies of oxidation in supercritical water, *AIChE J.*, 2001, **47**, 1203-1211.
14. S. P. Maharrey and D. R. Miller, A Direct Sampling Mass Spectrometer Investigation of Oxidation Mechanisms for Acetic Acid in Supercritical Water, *J. Phys. Chem. A*, 2001, **105**, 5860-5867.
15. P. Dagaut, M. Cathonnet and J.-C. Boettner, Chemical kinetic modeling of the supercritical-water oxidation of methanol, *J. Supercrit. Fluids*, 1996, **9**, 33-42.
16. S. Koda, N. Kanno and H. Fujiwara, Kinetics of Supercritical Water Oxidation of Methanol Studied in a CSTR by Means of Raman Spectroscopy, *Ind. Eng. Chem. Res.*, 2001, **40**, 3861-3868.
17. L. S. Cohen, D. Jensen, G. Lee and D. W. Ordway, Hydrothermal oxidation of Navy excess hazardous materials, *Waste Manag.*, 1998, **18**, 539-546.

18. P. A. Marrone, S. D. Cantwell and D. W. Dalton, SCWO System Designs for Waste Treatment: Application to Chemical Weapons Destruction, *Ind. Eng. Chem. Res.*, 2005, **44**, 9030-9039.
19. Y. Matsumura, T. Minowa, B. Potic, S. R. A. Kersten, W. Prins, W. P. M. van Swaaij, B. van de Beld, D. C. Elliott, G. G. Neuenschwander, A. Kruse and M. Jerry Antal Jr, Biomass gasification in near- and super-critical water: Status and prospects, *Biomass Bioenergy*, 2005, **29**, 269-292.
20. A. A. Peterson, F. Vogel, R. P. Lachance, M. Froling, J. M. J. Antal and J. W. Tester, Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies, *Energy Environ. Sci.*, 2008, **1**, 32-65.
21. N. Akiya and P. E. Savage, Roles of water for chemical reactions in high-temperature water, *Chem. Rev.*, 2002, **102**, 2725-2750.
22. D. Broll, C. Kaul, A. Kramer, P. Krammer, T. Richter, M. Jung, H. Vogel and P. Zehner, Chemistry in supercritical water, *Angew. Chem., Int. Ed.*, 1999, **38**, 2999-3014.
23. Z. Y. Ding, M. A. Frisch, L. Li and E. F. Gloyna, Catalytic Oxidation in Supercritical Water, *Ind. Eng. Chem. Res.*, 1996, **35**, 3257-3279.
24. C. A. Eckert, C. L. Liotta, D. Bush, J. S. Brown and J. P. Hallett, Sustainable reactions in tunable solvents, *J. Phys. Chem. B*, 2004, **108**, 18108-18118.
25. A. Galkin and V. Lunin, Subcritical and supercritical water: a universal medium for chemical reactions, *Russ. Chem. Rev.*, 2005, **74**, 21-35.
26. A. R. Katritzky, S. M. Allin and M. Siskin, Aquathermolysis: Reactions of Organic Compounds with Superheated Water, *Acc. Chem. Res.*, 1996, **29**, 399-406.
27. A. R. Katritzky, D. A. Nichols, M. Siskin, R. Murugan and B. M. Subramanian, Reactions in high-temperature aqueous media, *Chem. Rev.*, 2001, **101**, 837-892.
28. A. Kruse and E. Dinjus, Hot compressed water as reaction medium and reactant - Properties and synthesis reactions, *J. Supercrit. Fluids*, 2007, **39**, 362-380.
29. R. Marr and T. Gamse, Use of supercritical fluids for different processes including new developments—a review, *Chem. Eng. Process.*, 2000, **39**, 19-28.
30. T. Punniyamurthy, S. Velusamy and J. Iqbal, Recent Advances in Transition Metal Catalyzed Oxidation of Organic Substrates with Molecular Oxygen, *Chem. Rev.*, 2005, **105**, 2329-2364.
31. M. Siskin and A. R. Katritzky, A review of the reactivity of organic compounds with oxygen-containing functionality in superheated water, *J. Anal. Appl. Pyrolysis*, 2000, **54**, 193-214.
32. M. Siskin and A. R. Katritzky, Reactivity of Organic Compounds in Superheated Water: General Background, *Chem. Rev.*, 2001, **101**, 825-836.
33. M. Watanabe, T. Sato, H. Inomata, R. L. Smith, K. Arai, A. Kruse and E. Dinjus, Chemical Reactions of C1 Compounds in Near-Critical and Supercritical Water, *Chem. Rev.*, 2004, **104**, 5803-5822.
34. C. H. Oh, R. J. Kochan, T. R. Charlton and A. L. Bourhis, Thermal-Hydraulic Modeling of Supercritical Water Oxidation of Ethanol, *Energy Fuels*, 1996, **10**, 326-332.

35. D. Bröll, A. Krämer and H. Vogel, Heterogeneously Catalyzed Partial Oxidation of Methane in Supercritical Water, *Chem. Eng. Technol.*, 2003, **26**, 733-737.
36. T. Richter and H. Vogel, The Partial Oxidation of Cyclohexane in Supercritical Water, *Chem. Eng. Technol.*, 2002, **25**, 265-268.
37. T. Richter and H. Vogel, The Partial Oxidation of Isobutene in Sub- and Supercritical Water, *Chem. Eng. Technol.*, 2003, **26**, 688-690.
38. U. Armbruster, A. Martin and A. Krepel, Partial oxidation of propane in sub- and supercritical water, *J. Supercrit. Fluids*, 2001, **21**, 233-243.
39. D. Broll, A. Kramer, H. Vogel, I. Lappas and H. Fuess, Heterogeneously catalyzed partial oxidation in supercritical water, *Chem. Eng. Technol.*, 2001, **24**, 142-146.
40. H. Oka, S. Yamago, J. Yoshida and O. Kajimoto, Evidence for a Hydroxide Ion Catalyzed Pathway in Ester Hydrolysis in Supercritical Water, *Angew. Chem., Int. Ed.*, 2002, **41**, 623-625.
41. A. Krämer, S. Mittelstädt and H. Vogel, Hydrolysis of Nitriles in Supercritical Water, *Chem. Eng. Technol.*, 1999, **22**, 494-500.
42. E. Venardou, E. Garcia-Verdugo, S. J. Barlow, Y. E. Gorbaty and M. Poliakoff, On-line monitoring of the hydrolysis of acetonitrile in near-critical water using Raman spectroscopy, *Vib. Spectrosc.*, 2004, **35**, 103-109.
43. T. Richter and H. Vogel, The dehydration of 1,4-butanediol to tetrahydrofuran in supercritical water, *Chem. Eng. Technol.*, 2001, **24**, 340-343.
44. T. Richter and H. Vogel, Dehydration of 1,4-butanediol to form tetrahydrofuran in supercritical water, *Chem. Ing. Tech.*, 2001, **73**, 90-93.
45. M. Boero, T. Ikeshoji, C. C. Liew, K. Terakura and M. Parrinello, Hydrogen Bond Driven Chemical Reactions: Beckmann Rearrangement of Cyclohexanone Oxime into ϵ -Caprolactam in Supercritical Water, *J. Am. Chem. Soc.*, 2004, **126**, 6280-6286.
46. Y. Ikushima, O. Sato, M. Sato, K. Hatakeda and M. Arai, Innovations in chemical reaction processes using supercritical water: an environmental application to the production of ϵ -caprolactam, *Chem. Eng. Sci.*, 2003, **58**, 935-941.
47. Y. Yamaguchi, N. Yasutake and M. Nagaoka, Ab initio study of noncatalytic Beckmann rearrangement and hydrolysis of cyclohexanone-oxime in subcritical and supercritical water using the polarizable continuum model, *J. Mol. Struct.: THEOCHEM*, 2003, **639**, 137-150.
48. C. Yan, J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, M. Poliakoff, I. Pearson and A. S. Coote, The continuous synthesis of ϵ -caprolactam from 6-aminocapronitrile in high-temperature water, *Green Chem.*, 2008, **10**, 98-103.
49. T. Sato, G. Sekiguchi, T. Adschiri and K. Arai, Non-catalytic and selective alkylation of phenol with propan-2-ol in supercritical water, *Chem. Commun.*, 2001, DOI: 10.1039/b104184n, 1566-1567.
50. R. Zhang, O. Sato, F. Zhao, M. Sato and Y. Ikushima, Heck Coupling Reaction of Iodobenzene and Styrene Using Supercritical Water in the Absence of a Catalyst, *Chem. - Eur. J.*, 2004, **10**, 1501-1506.

51. R. Zhang, F. Zhao, M. Sato and Y. Ikushima, Nuncatalytic Heck coupling reaction using supercritical water, *Chem. Commun.*, 2003, DOI: 10.1039/b302683c, 1548-1549.
52. M. Watanabe, H. Inomata, R. L. Smith Jr and K. Arai, Catalytic decarboxylation of acetic acid with zirconia catalyst in supercritical water, *Appl. Catal., A*, 2001, **219**, 149-156.
53. K. Tomita, S. Koda and Y. Oshima, Catalytic Hydration of Propylene with MoO₃/Al₂O₃ in Supercritical Water, *Ind. Eng. Chem. Res.*, 2002, **41**, 3341-3344.
54. R. L. Holliday, B. Y. M. Jong and J. W. Kolis, Organic synthesis in subcritical water - Oxidation of alkyl aromatics, *J. Supercrit. Fluids*, 1998, **12**, 255-260.
55. R. A. Sheldon and J. K. Kochi, *Metal Catalysed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
56. Y. L. Kim, S. J. Chung, J. D. Kim, J. S. Lim, Y. W. Lee and S. C. Yi, Uncatalyzed partial oxidation of *p*-xylene in sub- and supercritical water, *React. Kinet. Catal. Lett.*, 2002, **77**, 35-42.
57. Y. L. Kim, J. D. Kim, J. S. Lim, Y. W. Lee and S. C. Yi, Reaction pathway and kinetics for uncatalyzed partial oxidation of *p*-xylene in sub- and supercritical water, *Ind. Eng. Chem. Res.*, 2002, **41**, 5576-5583.
58. P. J. Hamley, T. Ilkenhans, J. M. Webster, E. Garcia-Verdugo, E. Venardou, M. J. Clarke, R. Auerbach, W. B. Thomas, K. Whiston and M. Poliakoff, Selective partial oxidation in supercritical water: the continuous generation of terephthalic acid from *para*-xylene in high yield, *Green Chem.*, 2002, **4**, 235-238.
59. P. Anastas and N. Eghbali, Green chemistry: principles and practice, *Chem. Soc. Rev.*, 2010, **39**, 301-312.
60. P. T. Anastas and M. M. Kirchhoff, Origins, current status, and future challenges of Green Chemistry, *Acc. Chem. Res.*, 2002, **35**, 686-694.
61. P. T. Anastas, M. M. Kirchhoff and T. C. Williamson, Catalysis as a foundational pillar of Green Chemistry, *Appl. Catal., A*, 2001, **221**, 3-13.
62. P. T. Anastas and J. C. Warner, *Green chemistry: theory and practice*, Oxford University Press, 2000.
63. E. Garcia-Verdugo, E. Venardou, W. B. Thomas, K. Whiston, W. Partenheimer, P. A. Hamley and M. Poliakoff, Is it possible to achieve highly selective oxidations in supercritical water? Aerobic oxidation of methylaromatic compounds, *Adv. Synth. Catal.*, 2004, **346**, 307-316.
64. E. Garcia-Verdugo, J. Fraga-Dubreuil, P. A. Hamley, W. B. Thomas, K. Whiston and M. Poliakoff, Simultaneous continuous partial oxidation of mixed xylenes in supercritical water, *Green Chem.*, 2005, **7**, 294-300.
65. J. Fraga-Dubreuil and M. Poliakoff, Organic reactions in high-temperature and supercritical water, *Pure Appl. Chem.*, 2006, **78**, 1971-1982.
66. J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, E. M. Vaquero, L. M. Dudd, I. Pearson, D. Housley, W. Partenheimer, W. B. Thomas, K. Whiston and M. Poliakoff, Catalytic selective partial oxidations using O(2) in supercritical water: the continuous synthesis of carboxylic acids, *Green Chem.*, 2007, **9**, 1238-1245.
67. J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, E. Perez, I. Pearson, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Prevention of Manganese Precipitation during the Continuous Selective Partial

- Oxidation of Methyl Aromatics with Molecular Oxygen in Supercritical Water, *Adv. Synth. Catal.*, 2009, **351**, 1866-1876.
68. E. Perez, J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 1. Comparison with *ortho*-xylene and the role of the catalyst, *Green Chem.*, 2011, **13**, 2389-2396.
 69. E. Perez, J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, M. L. Thomas, C. Yan, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 2. The discovery of better catalysts, *Green Chem.*, 2011, **13**, 2397-2407.
 70. J. B. Dunn and P. E. Savage, Terephthalic acid synthesis in high-temperature liquid water, *Ind. Eng. Chem. Res.*, 2002, **41**, 4460-4465.
 71. J. B. Dunn, D. I. Urquhart and P. E. Savage, Terephthalic acid synthesis in supercritical water, *Adv. Synth. Catal.*, 2002, **344**, 385-392.
 72. J. B. Dunn, M. L. Burns, S. E. Hunter and P. E. Savage, Hydrothermal stability of aromatic carboxylic acids, *J. Supercrit. Fluids*, 2003, **27**, 263-274.
 73. J. B. Dunn and P. E. Savage, High-temperature liquid water: A viable medium for terephthalic acid synthesis, *Environ. Sci. Technol.*, 2005, **39**, 5427-5435.
 74. M. Osada and P. E. Savage, Terephthalic Acid Synthesis at Higher Concentrations in High-Temperature Liquid Water. 2. Eliminating Undesired Byproducts, *AIChE J.*, 2009, **55**, 1530-1537.
 75. M. Osada and P. E. Savage, Terephthalic Acid Synthesis at Higher Concentrations in High-Temperature Liquid Water. 1. Effect of Oxygen Feed Method, *AIChE J.*, 2009, **55**, 710-716.
 76. K. Deori, D. Gupta, B. Saha, S. K. Awasthi and S. Deka, Introducing nanocrystalline CeO₂ as heterogeneous environmental friendly catalyst for the aerobic oxidation of *para*-xylene to terephthalic acid in water, *J. Mater. Chem. A*, 2013, **1**, 7091-7099.
 77. N. A. Alekar, S. Gopinathan and C. Gopinathan, Catalytic liquid phase oxidation of *p*-xylene using transition metal substituted polyoxometalates, *Indian J. Chem., Sect. A*, 2000, **39**, 439-441.
 78. Y. S. Chen, J. L. Fulton and W. Partenheimer, The structure of the homogeneous oxidation catalyst, Mn(II)(Br⁻¹)(x), in supercritical water: An X-ray absorption fine-structure study, *J. Am. Chem. Soc.*, 2005, **127**, 14085-14093.
 79. Y. S. Chen, J. L. Fulton and W. Partenheimer, A XANES and EXAFS study of hydration and ion pairing in ambient aqueous MnBr₂ solutions, *J. Solution Chem.*, 2005, **34**, 993-1007.
 80. V. Hessel, H. Lowe and F. Schonfeld, Micromixers - a review on passive and active mixing principles, *Chem. Eng. Sci.*, 2005, **60**, 2479-2501.
 81. T. H. Chilton and R. P. Genereaux, The mixing of gases for reaction, *Trans. Am. Inst. Chem. Eng.*, 1930, **25**, 102-122.
 82. A. M. Ger and E. R. Holley, Comparison of single-point injections in pipe-flow, *J. Hydraul. Div., Am. Soc. Civ. Eng.*, 1976, **102**, 731-746.
 83. L. J. Forney and T. C. Kwon, Efficient single-jet mixing in turbulent tube flow, *AIChE J.*, 1979, **25**, 623-630.

84. R. D. Reed and B. C. Narayan, Mixing fluids under turbulent-flow conditions, *Chem. Eng.*, 1979, **86**, 131-132.
85. T. Maruyama, S. Suzuki and T. Mizushima, Pipeline mixing between two fluid streams meeting at a T-junction, *Int. Chem. Eng.*, 1981, **21**, 205-212.
86. L. J. Forney and H. C. Lee, Optimum dimensions for pipeline mixing at a T-junction, *AIChE J.*, 1982, **28**, 980-987.
87. C. D. O'Leary and L. J. Forney, Optimization of in-line mixing at a 90.degree. tee, *Ind. Eng. Chem. Process Des. Dev.*, 1985, **24**, 332-338.
88. G. Tosun, A study of micromixing in tee mixers, *Ind. Eng. Chem. Res.*, 1987, **26**, 1184-1193.
89. C. Cozewith and M. Busko, Design correlations for mixing tees, *Ind. Eng. Chem. Res.*, 1989, **28**, 1521-1530.
90. Y. Wakashima, A. Suzuki, S.-i. Kawasaki, K. Matsui and Y. Hakuta, Development of a new swirling micro mixer for continuous hydrothermal synthesis of nano-size particles, *J. Chem. Eng. Jpn.*, 2007, **40**, 622-629.
91. T. Adschiri, Y. Hakuta, K. Sue and K. Arai, Hydrothermal synthesis of metal oxide nanoparticles at supercritical conditions, *J. Nanopart. Res.*, 2001, **3**, 227-235.
92. T. Adschiri, S. Takami, M. Umetsu, S. Ohara and T. Tsukada, Supercritical hydrothermal synthesis of nanoparticles, in *Characterization and Control of Interfaces for High Quality Advanced Materials*, eds. K. Ewsuk, K. Nogi, M. Reiterer, A. Tomsia, S. J. Glass, R. Waesche, K. Uematsu and M. Naito, 2005, vol. 146, pp. 3-10.
93. T. Adschiri, S. Takami, M. Umetsu and T. Tsukada, presented in part at the Sixth International Symposium on Supercritical Fluids, Versailles, France., April, 2003.
94. S.-I. Kawasaki, K. Sue, R. Ookawara, Y. Wakashima and A. Suzuki, Development of Novel Micro Swirl Mixer for Producing Fine Metal Oxide Nanoparticles by Continuous Supercritical Hydrothermal Method, *J. Oleo Sci.*, 2010, **59**, 557-562.
95. K. Mae, A. Suzuki, T. Maki, Y. Hakuta, H. Sato and K. Arai, A new micromixer with needle adjustment for instant mixing and heating under high pressure and high temperature, *J. Chem. Eng. Jpn.*, 2007, **40**, 1101-1107.
96. P. J. Blood, J. P. Denyer, B. J. Azzopardi, M. Poliakoff and E. Lester, A versatile flow visualisation technique for quantifying mixing in a binary system: application to continuous supercritical water hydrothermal synthesis (SWHS), *Chem. Eng. Sci.*, 2004, **59**, 2853-2861.
97. P. J. Blood, J. P. Denyer, E. Lester, M. Poliakoff, P. Hamley and D. Giddings, presented in part at the The Fourth Symposium on High Pressure Technology and Chemical Engineering, Venice, Italy, September, 2002.
98. J. P. Denyer, PhD thesis, University of Nottingham, 2003.
99. J. P. Denyer, E. Lester, P. A. Hamley, M. Poliakoff, D. Giddings, P. J. Blood and F. He, presented in part at the Eighth Meeting on Supercritical Fluids, Bordeaux, France, April, 2002.
100. E. Lester, P. J. Blood, J. P. Denyer, B. J. Azzopardi, J. Li and M. Poliakoff, Impact of reactor geometry on continuous hydrothermal synthesis mixing, *Mater. Res. Innovations*, 2010, **14**, 19-26.

101. E. Lester, P. J. Blood, J. P. Denyer, D. Giddings, B. Azzopardi and M. Poliakoff, Reaction engineering: The supercritical water hydrothermal synthesis of nano-particles, *J. Supercrit. Fluids*, 2006, **37**, 209-214.
102. E. H. Lester and 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., 7566436B2, 2009.
103. J. Li, PhD thesis, University of Nottingham, 2010.
104. E. Perez, M. L. Thomas, D. Housley, P. A. Hamley, J. Fraga-Dubreuil, J. Li, E. Lester and M. Poliakoff, Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 3: effects of geometry and mixing in laboratory scale continuous reactors, *RSC Adv.*, 2016, **6**, 11289-11294.
105. D. Housley, T. Huddle, E. Lester and M. Poliakoff, The use of dimensionless groups to analyse the mixing of streams with large density differences in sub- and supercritical water, *Chem. Eng. J.*, 2016, **287**, 350-358.
106. A. A. Peterson, J. W. Tester and F. Vogel, Water-in-water tracer studies of supercritical-water reversing jets using neutron radiography, *J. Supercrit. Fluids*, 2010, **54**, 250-257.
107. A. A. Peterson, P. Vontobel, F. Vogel and J. W. Tester, In situ visualization of the performance of a supercritical-water salt separator using neutron radiography, *J. Supercrit. Fluids*, 2008, **43**, 490-499.
108. A. A. Peterson, P. Vontobel, F. Vogel and J. W. Tester, Normal-phase dynamic imaging of supercritical-water salt precipitation using neutron radiography, *J. Supercrit. Fluids*, 2009, **49**, 71-78.
109. N. Takenaka, K. Sugimoto, S. Takami, K. Sugioka, T. Tsukada, T. Adschiri and Y. Saito, Application of Neutron Radiography to Flow Visualization in Supercritical Water, *Phys. Procedia*, 2013, **43**, 264-268.
110. J. Sierra-Pallares, D. L. Marchisio, E. Alonso, M. Teresa Parra-Santos, F. Castro and M. Jose Cocero, Quantification of mixing efficiency in turbulent supercritical water hydrothermal reactors, *Chem. Eng. Sci.*, 2011, **66**, 1576-1589.
111. C. J. Tighe, R. I. Guzar, C. Y. Ma, T. Mahmud, X. Z. Wang and J. A. Darr, Investigation of counter-current mixing in a continuous hydrothermal flow reactor, *J. Supercrit. Fluids*, 2012, **62**, 165-172.
112. K. G. Bemis, R. P. Vonherzen and M. J. Mottl, Geothermal heat-flux from hydrothermal plumes on the Juan-de-Fuca ridge, *J. Geophys. Res.: Solid Earth*, 1993, **98**, 6351 -6365.
113. J. B. Dunn and P. E. Savage, Economic and environmental assessment of high-temperature water as a medium for terephthalic acid synthesis, *Green Chem.*, 2003, **5**, 649-655.
114. N. Akiya and P. E. Savage, Hydrogen peroxide dissociation in supercritical water. 1 Reaction Equilibrium., *Abstr. Pap. Am. Chem. Soc.*, 1999, **217**, 692-693.
115. E. Croiset, S. F. Rice and R. G. Hanush, Hydrogen peroxide decomposition in supercritical water, *AIChE J.*, 1997, **43**, 2343-2352.
116. B. D. Phenix, J. L. DiNaro, J. W. Tester, J. B. Howard and K. A. Smith, The effects of mixing and oxidant choice on laboratory-scale measurements of supercritical water oxidation kinetics, *Ind. Eng. Chem. Res.*, 2002, **41**, 624-631.

117. Q. Jiang, H.-Y. Hu, C.-C. Guo, Q. Liu, J.-X. Song and Q.-H. Li, Aerobic liquid-phase oxidation of *p*-xylene over metalloporphyrins, *J. Porphyrins Phthalocyanines*, 2007, **11**, 524-530.
118. J. F. Connolly, Solubility of Hydrocarbons in Water Near the Critical Solution Temperatures, *J. Chem. Eng. Data*, 1966, **11**, 13-16.
119. K. G. Knauss and S. A. Copenhaver, The solubility of *p*-xylene in water as a function of temperature and pressure and calculated thermodynamic quantities, *Geochim. Cosmochim. Acta*, 1995, **59**, 2443-2448.
120. D.-S. Lee, E. F. Gloyna and L. Li, Efficiency of H₂O₂ and O₂ in supercritical water oxidation of 2,4-dichlorophenol and acetic acid, *J. Supercrit. Fluids*, 1990, **3**, 249-255.
121. G. I. Taylor, Dispersion of soluble matter in solvent flowing slowly through a tube, *Proc. Roy. Soc. A* 1953, **219**, 186-203.
122. G. I. Taylor, Conditions under which dispersion of a solute in a stream of solvent can be used to measure molecular diffusion, *Proc. Roy. Soc. A* 1954, **225**, 473-477.
123. G. I. Taylor, The dispersion of matter in turbulent flow through a pipe, *Proc. Roy. Soc. A*, 1954, **223**, 446-468.
124. O. Levenspiel, *Chemical Reaction Engineering*, John Wiley & Sons Inc., New York, 1999.
125. O. Levenspiel and K. B. Bischoff, Backmixing in the design of chemical reactors, *Ind. Eng. Chem.*, 1959, **51**, 1431 - 1434.
126. NIST - Physical properties of water, <http://webbook.nist.gov/chemistry>, (Accessed September, 2017).
127. P. Roffia, P. Calini, L. Motta and S. Tonti, By-product identification in the terephthalic acid production process and possible mechanisms of their formation, *Ind. Eng. Chem. Prod. Res. Dev.*, 1984, **23**, 629-634.

3 Equipment and Experimental

The first section of this Chapter details the basis of safety of the rigs. The next sections give a detailed specification of the rigs and the improvements that were made over the project. This however, excludes the reactor designs as these are covered in Chapter 2 (Section 2.3) and the evolution of reactor design is the subject of Chapter 7. The final section covers experimental formulations and operating procedures and the improvements that were made to these over the project.

3.1 The Basis of Safety of the Rigs

A summary of the requirements of the IP1 and K5 N/SCWO rigs' safety case is given in this section. This basis of safety was developed by others and was in place at the project start. It proved possible to undertake all the required work within this basis and therefore no modifications were made during the project. The precise process for determining a safety case depends on several factors and requires a careful safety systems review, specific to the rig under consideration.

The basis of safety for the IP1 and K5 N/SCW rigs is a combination of small inventory at temperature and pressure, and secondary containment within a steel and bullet resistant polycarbonate enclosure.

The maximum for the internal volume of the high-pressure regions of a rig was 100 cm³. The maximum tube size for process lines was ¼" O.D. Minimum tube wall thicknesses were in accordance with Table 3-1. The maximum unit operating pressure was 400 bar_g, although it may be necessary to reduce this if specific unit components (*e.g.* 25 mL/min Gilson pump heads) had lower pressure ratings. The design temperature of the units was 500 °C except the pre-heaters, which had a design temperature of 593 °C, and temperature trips were set below these values.

Table 3-1. The minimum wall thicknesses, that are allowed on IP1 and K5 N/SCW rigs, for various piping sizes at 400 bar_g.

Piping size O.D.	Minimum wall thickness
$\frac{1}{16}$ "	0.014"
$\frac{1}{8}$ "	0.028"
$\frac{1}{4}$ "	0.065"

The source of oxygen was H₂O₂ at a maximum concentration (in water) of 30 % w/w. This limited the average O₂:H₂O ratio and hence the concentration of oxygen that could occur under normal operating conditions.

Care in specifying the layout of the unit, together with regular inspections for corrosion reduced (but did not eliminate) the risk of a rupture and a loss of containment. Thus, secondary containment and extraction were an integral feature of the safety case.

3.2 Rig Design

The design of the IP1 and K5 rigs was similar to the UoN rigs 22 and 23 as described in Section 2.3.1 and Figure 2-1. Diagrams of the IP1 rig layout and instrumentation at the start of this project are given in Figure 3-2. The K5 rig had a similar configuration except for the use of a sand bath to heat the reactor. Both rigs were controlled by an OPTO 22, PC based system which was also used for data logging.

The author was not involved in the original design of the IP1 and K5 rigs. The components of the system and their experimental operation are described in the remaining sections of this chapter.

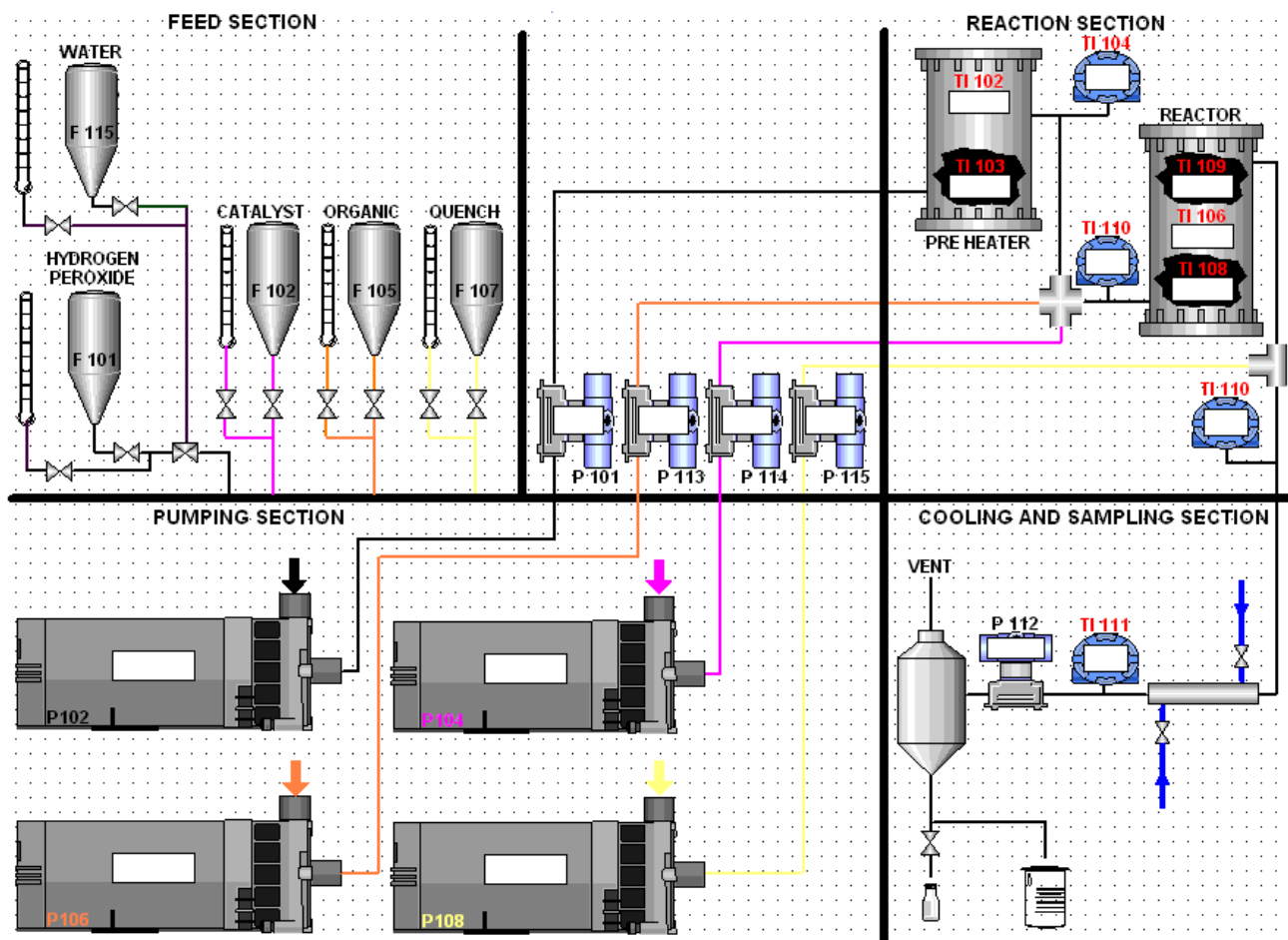


Figure 3-2 A schematic of the IP1 pX N/SCWO rig. The feed vessel section is shown top left and comprises 5 feed vessels each with a parallel burette that enables a feed rate measurement to be made. Later rigs added additional feed vessels. The water and hydrogen peroxide feed vessels fed to a common tee-piece and were alternative feeds for one pump; the choice of feed was controlled by valves. The feed section was low pressure and was not enclosed. The lines from the feed vessels passed to the pumping section which is shown bottom left; the detail of the lines is not shown though colour coded arrows show the line destinations. There were originally four HPLC pumps (as shown) but later rigs added additional pumps up to a total of nine. The delivery side of the pumps was high pressure and so this section was enclosed. The delivery lines passed through pressure transducers and then into the reaction section shown top right. The water and/or peroxide feed passed to a pre-heater and then to a mixer while the other feeds passed to the mixer. The mixer arrangements underwent considerable development during the project and are described in detail in Chapters 4 and 7; these descriptions should be consulted in preference to the layout shown in this figure. Likewise, the reactor arrangements underwent considerable development as detailed in Chapter 7. The discharge from the reactor passed to a quench addition point and then to the cooling and sampling section shown bottom right. In this section, the flow passed through a cooler, back-pressure regulator (BPR) and then to a gas liquid separator vessel and finally to a sampling point. Equipment downstream of the BPR was low-pressure and was not enclosed.

3.3 The Oxygen Feed System

The oxygen source on the rigs was hydrogen peroxide solution. Studies in the literature ¹⁻³ have shown that hydrogen peroxide can be decomposed to oxygen and water at elevated temperatures and this provided a convenient source of oxygen (in water) for these oxidations. The use of hydrogen peroxide solution as the source of oxygen was integral to the units' basis of safety as noted in Section 3.1.

3.3.1 Feed Vessels and Low Pressure Pipework

The hydrogen peroxide was obtained from Aldrich as a 30 % w/w solution that was stored in glass bottles in a fridge. Figure 3-2 shows that, on the IP1 rig, the peroxide feed pump was fed by two 2 litre vessels, one to contain distilled water and the other hydrogen peroxide solution. Each had a 100 mL burette arranged in parallel which enabled rate checks and calibrations using the rate of level fall in the burette. The water was used for start-up and for flushing operations while the peroxide solution was used during operation. The peroxide solution (as purchased) was diluted with distilled water as necessary and was charged to the glass feed vessel. These feed vessels and burettes can be seen in Figure 3-3.

During operation, it was found that the hydrogen peroxide was prone to decomposition while in the low-pressure section prior to reaching the pump head and pre-heater coils. This decomposition produced bubbles in the suction side of the system and caused problems such as:

- Gas locking of the HPLC pump.
- Incorrect dosing of oxygen.



Figure 3-3. Feed vessels for the IP1 rig. The peroxide and water feed vessels are the four towards the left, the quench feed vessel is central, the catalyst and water feed vessels are towards the right and the *pX* feed vessel is the small one at the right with a red top. Most of the feed vessels also have a parallel burette for feed rate measurement. The funnels and filter papers used to filter feed material are clearly visible. These were left in place during running to protect against the ingress of contamination while allowing material to be pumped without forming a vacuum in the vessel. Blue isolation valves are visible below the peroxide vessels and a network of plastic feed piping with white and blue fittings below these. The isolation valves below the catalyst, quench and *pX* vessels are metal and have green handles. There is a metallic drip tray below these on the top of the pump cabinet. The feed vessels are in a low-pressure area and are not enclosed. The edge of the (blue coloured) reactor cabinet is visible on the right. The large blue handle protruding through the wall of this cabinet is the control dial for a Pressure Tech back-pressure regulator. The metallic (quarter segment) segment of the drip tray below this handle covers the pipes that house the feed pipes from the pump cabinet (below) to the reactor cabinet. The cabinet to the left houses the degasser unit and a heater control box (which are visible) and additional HPLC pumps which are lower and out of shot. The hot plates on top of this cabinet and conical flask are components of a hot feed system which was intermittently used when feeding catalyst containing lower solubility components. Lagging and trace heating can be seen on sections of the feed lines from this system *e.g.* the top section wrapped in blue tape and lower sections wrapped in grey foam secured with silver coloured tape. The sections in between have hot water circulation over the feed pipes. The green cabling at the bottom are for thermocouples. Two electrical panels and the trunking of the cabinet extract can be seen at the top left and top right respectively.

The author developed and implemented several improvements to reduce these problems and these included:

- Eliminating all metal components upstream of the pumps. The original design used glass feed vessels and burettes and plastic feed tubing but these were connected by metal valves where peroxide decomposition to oxygen could be observed. The author had all the fittings replaced with plastic valves.
- Filtering all solutions when adding them to the feed vessels. The filter papers were left over the top of the feed vessels to allow air ingress (as the vessel level fell) but to prevent ingress of contamination.
- The plastic tubing seemed to accumulate adhered contamination over time that led to peroxide decomposition; the author therefore had the plastic tubing replaced every 4 to 6 months.
- The peroxide solution was kept in the fridge until immediately before its use to keep it cool for as long as possible.
- The analytical staff routinely use degassers to prevent gas locking of HPLC pumps during analysis and they suggested trying this on the rigs. Degasser units pass the liquid flow through a vacuum chamber lined with a PTFE membrane where entrained and dissolved gases pass through the membrane and are thus removed from the liquid stream. A degasser (model Jasco Degasys DG4413) was trialled to reduce gas bubbles in the peroxide stream prior to passing through the pump on the IP1 unit. This unit can be seen in the bottom left of Figure 3-3 though is obscured by the door frame in this picture. This was reasonably successful provided the degree of peroxide breakdown was not too great. A KNAUER AS328 degasser unit (capable of degassing up to 100 mL/min) was purchased for use on the K5 unit; the Jasco unit was also used to degas the three low peroxide feeds to the second, third and fourth oxygen stages.

The measures described in the first two bullet points can clearly be seen in Figure 3-3.

Flow rate checks were undertaken using timed level drop when feeding from the parallel burettes. Mass flow meters were not employed on peroxide lines because it was thought that their metal would provide surfaces where the peroxide could prematurely decompose.

The gassing problems tended to be worse in periods of hot summer weather. The author considered the use of jacketed feed vessels with circulation of cooling water (or even chilled water). However, this was not implemented because the other methods mentioned were successful at controlling the gassing problem.

As the project progressed, the author implemented oxygen staging and an additional peroxide feed was added to the IP1 rig to enable two peroxide feeds. An additional feed vessel (and associated burette) were therefore added, for a second peroxide solution. These can be seen in Figure 3-3.

The arrangement of vessels on the K5 rig was broadly similar. It originally had two 2 litre vessels for dilute peroxide and water. Later another feed vessel was added that contained more concentrated peroxide and this fed three additional oxygen stages. Later the vessel was modified for higher throughputs and the first peroxide vessel was replaced with a 5 litre vessel.

3.3.2 Pumps

The IP1 rig used Gilson HPLC pumps (Model 306 and 307) with 10 or 25 mL/min heads to feed the peroxide solution and water into the pre-heater. The pump cabinets and pumps for the IP1 rig can be seen in Figures 3-4.

The K5 rig used a Jasco HPLC pump (model PU-2086) with a 20 mL/min head as the peroxide pump. The pump and cabinet for this rig can be seen in Figure 2-7.

The pumps were banded and contained within a steel cabinet with windows of transparent polycarbonate sheeting. Both these features can clearly be seen in Figures 2-7 and 3-4. The cabinet was required by the safety case (as detailed in Section 3.1) which required shielding of high pressure sections of the rigs.



Figure 3-4. Feed pump cabinet on the IP1 rig containing the original four Gilson HPLC pumps. Additional pumps were added later in a second cabinet. Each pump has a stainless-steel drip tray bund. The discharge lines from the pumps pass to the reactor cabinet through the curved blue pipes that are visible top right.

As the project progressed, additional peroxide feed pumps were added to enable multiple oxygen feeds to the reactors. On tubular reactors, the later oxygen feeds used low flow rates of concentrated (30 % w/w) peroxide to minimise the additional dilution of the reaction medium. Thus, on the IP1 rig, the same model of pump was used but with 10 mL/min pump head for the second stage. The K5 rig was upgraded from one to two then to four peroxide feeds by adding further Jasco pumps of the same model.

Towards the end of the project the author investigated high throughput reactors with higher levels of turbulence and the K5 rig was upgraded for higher throughputs. Two Gilson 332 pumps with 50 mL/min heads were used for the first peroxide feed and the original Jasco pumps (but operated at higher flow rates) were used for the second to fourth peroxide feeds.

3.3.3 Pre-heaters

Pre-heaters were used on the water and hydrogen peroxide feed line to pre-heat the peroxide to a temperature at which it decomposed to oxygen and water. They were made by coiling metal tubing around cylindrical shaped brass blocks that had holes drilled out parallel to their axis into which electrical cartridge heaters were inserted. The design can be seen in Figures 2-6 and 3-5.

The first design used a 10 m length of $\frac{1}{16}$ " O.D. stainless steel tubing wrapped on a brass block. $\frac{1}{16}$ " O.D. tubing was chosen in order, to maximise heat transfer area and brass blocks were used because of the good heat transfer properties of that metal. Blocks were cylindrical, 75mm diameter and 140 mm long and contained two 15 mm diameter, drilled holes into which were inserted 1 kW electrical cartridge heaters. The pre-heater was mounted below the reactor to ensure a rising flow throughout the system, thereby reducing the risk of gas accumulation in the rig. Both the pre-heater and reactor were contained in metal housings into which lagging was inserted. The top and bottom of the brass block were insulated from the housing by disks of ceramic material. The use of $\frac{1}{16}$ " O.D. tube led to large pressure oscillations in the system. These oscillations tended to increase over time and could lead to a high-pressure trip and premature shutdown of the unit. The physics of this phenomenon were not well understood but the author believes that they could involve a complex, positive feedback between the peroxide decomposition rate and the effective heat transfer coefficient. The problem was solved by using $\frac{1}{8}$ " O.D. tubing. This could be 0.028" or 0.035" wall thickness though 0.035" was generally used due to its greater stock availability.



Figure 3-5. IP1 rig reactor cabinet. This photograph was taken when the reactor assembly was under construction; this enables more detail to be seen, as the final assembly was lagged and consequently detail was much less visible. The lower reactor chamber contained the pre-heater; the photograph to the right shows this with the housing open. The assembly comprised a brass block (the brass is just visible above the lower ceramic insulation disc) around which $\frac{1}{16}$ " (and later $\frac{1}{8}$ ") tubing was wrapped and was covered in metallic foil. The whole assembly was covered with lagging and a stainless-steel housing. The reactor was constructed in a similar fashion with $\frac{1}{8}$ " tubing and was located above the pre-heater. There were four pressure transducers to the right of the pre-heater, one on each of the feed lines from the pumps. The mixing cross assembly was just above the pre-heater. In this (early) deployment, the SCW/O₂ feed entered from below and the *p*X and catalyst entered from the side. There was a thermocouple assembly on the outlet (top of cross). The quench point and cooler assembly can be seen above the reactor. The extraction port is visible in the roof of the cabinet and a vent line can be seen discharging to this on the top left. The back-pressure regulator is just visible on the left.

The pre-heater was run with a maximum operating temperature of 495 °C and a trip temperature set at 550 °C. Temperatures were monitored with thermocouples embedded in the brass block and with an in-line thermocouple immediately downstream of the pre-heater block. The trip was set at this value because brass softens above this temperature and steel begins to weaken at higher temperatures.

The length of the pre-heaters was either 10 m of $\frac{1}{16}$ " O.D. tubing or 5.9 m of $\frac{1}{8}$ " O.D., 0.035" wall thickness tubing. Several heat transfer trials were run to ensure that the lengths of tubing employed provided adequate heating as monitored by

the thermocouple immediately downstream of the heater block. The conditions required for complete breakdown of the hydrogen peroxide are described in the literature.¹⁻³

No thermocouples were situated in the pre-heater coil on the block to avoid temperature losses and because the temperature profile was not critical at this point in the process. A thermocouple was placed on the outlet of the coil to ascertain the exit temperature that had been achieved. The in-line process temperatures obtained depended on the block temperatures (typically 495 °C) and on the process flow rates employed (12 - 24 mL/min at ambient) and were typically in the range 360 - 400 °C which was thought to be adequate to fully decompose the peroxide; the author more fully investigated this as described later in this section. The temperatures obtained exit the pre-heater were typically lower by ~20 – 40 °C when peroxide solution was pumped compared to water (containing no peroxide).

The distance between the pre-heater exit and the reactor was kept to a minimum to try to limit heat losses and all lines were heavily lagged for this reason. However, heat losses are inevitably high on such small-scale equipment because of its high surface area to volume ratio compared to plant scale. There were problems, on occasions, with attaining the required process temperatures in the downstream reactor and this aspect is discussed in the sections on reactor development in Chapter 7.

Lifetimes of pre-heater coils were quite variable. When Hastelloy C276 coils were used, they would often stress crack in < 20 hours of operation at temperature. The author attempted to solve this problem with the help of a consultant corrosion engineer. Attempts were made to stress relieve the coils by annealing the pre-heater assembly in an oven at 1120 °C. When doing this, it was necessary to use stainless steel blocks because brass would melt at this temperature and carbon steel would partially oxidise. However, annealing proved to be not very successful at prolonging the coil life. The author then tested stainless steel 316L as a coil material. It was found that coils of this material would often last for > 100 hours of operation; this is probably because stainless steel is more malleable than Hastelloy and so less likely to lock in stress during

the coiling operation. Stainless steel was thus adopted as the preferred pre-heater coil material. The author ensured that a replacement pre-heater block assembly was always available so that a rapid change over could be made upon coil failure.

As the project progressed multiple oxygen stages were implemented. Concentrated peroxide (30 % w/w) was used in the second and later oxygen stages to limit the amount of additional dilution of the reactor brew. Thus, the flow rates were relatively low at around 0.5 to 2 mL/min. Initially additional 5.9 m coils were used and these were wrapped on top of the main coil (that was in direct contact with the block). However, the author was concerned about the extent to which this design was compromising the exit temperatures obtained from both coils and this was shown to be the case in heat transfer trials. The author therefore tested designs where the pre-heater block was lengthened from 140 mm to 200 mm with longer cartridge heaters and the additional coils were wrapped on the extra block length available. These designs were again tested with heat transfer trials and it was found that because of the low flow rates, the additional coil(s) could be shortened to 3 m length (of 1/8" O.D. tubing) and still give adequate exit temperature.

The author was concerned about the extent of the peroxide decomposition in the pre-heaters and whether residual amounts of hydrogen peroxide were being slipped to the reactor and were effecting the chemistry. This was a concern also raised by Savage *et al.*⁴ The author therefore designed several studies to test this.

In the first study, 30 % peroxide was fed to the K5 pre-heater whose outlet was piped directly to the cooler and then to the BPR and sample point. Thus, the level of residual, undecomposed peroxide could be measured as a function of pre-heater temperature (400, 450, 490 °C) and peroxide solution flow rate (2 -20 mL/min). The process temperatures obtained were in the range 328 – 417 °C. Residual hydrogen peroxide concentrations were measured with peroxide assay sticks which were commercially available. In all the experiments undertaken, the residual peroxide concentration was measured as 1 – 2 ppm.

A further study investigated lower temperatures as shown in Figure 3-6.

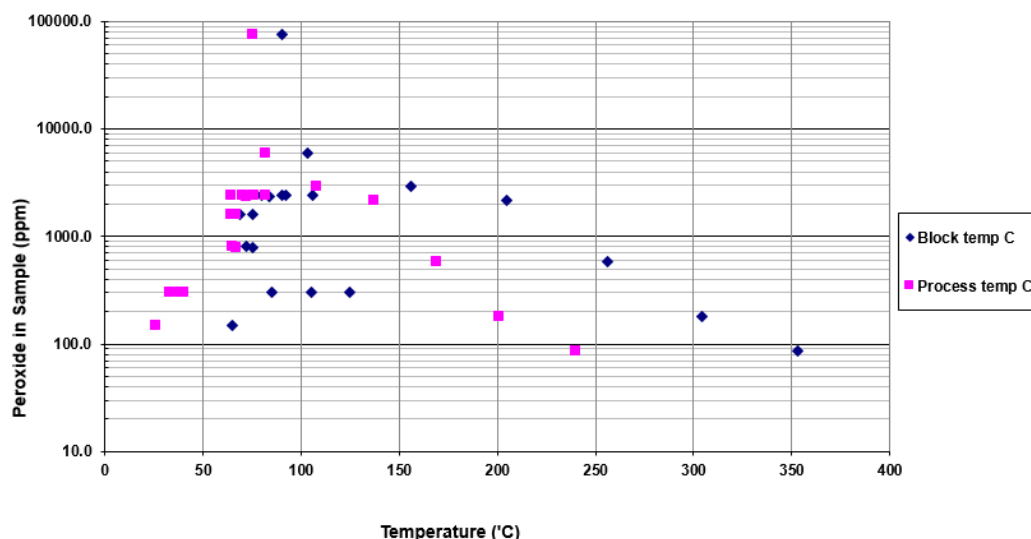


Figure 3-6. The decomposition of 30 % hydrogen peroxide solution in a pre-heater coil at variable temperature and a flow rate of ~2 mL/min. It showed that the decomposition is erratic at low temperatures and the residual concentration can vary by two orders of magnitude; this variability could be linked to residual contamination by metal oxide laydown within the cooling coil. At temperatures above ~150 °C, the degree of peroxide breakdown is well correlated with temperature.

The study showed that the peroxide decomposition was erratic at low temperatures and this was thought to be linked to residual contamination of metal oxides within the rig. However, the experiment demonstrated that it is likely that at least a few hundred ppm of undecomposed peroxide will persist at low temperatures.

In a final study, several *pX* SCWO runs were performed and the pre-heater temperature was varied between 50 °C and 495 °C. The reactor temperature was maintained at 380 °C and the *pX* SCWO reaction performance (particularly the total oxidation) was measured. This study was undertaken immediately after the installation of a new reactor which was washed with sulfamic acid and then water for several hours prior to the trial. This was to attempt to minimise any metal oxide contamination. It is thus highly likely that a substantial amount of undecomposed hydrogen peroxide was being fed to the reactor at the low pre-heater temperature conditions. The results are given in Section 6.4.8 and Figure 6-13 and showed that the reactor performance and the oxidation to carbon dioxide was invariant with the pre-heater temperature and the degree of hydrogen peroxide slippage into the reactor. Thus, it was concluded that the slippage of 1 -

2 ppm of hydrogen peroxide into the reactor under the normal operating conditions does not affect the results obtained. Though not demonstrated by these experiments, the author speculates that peroxide is rapidly and fully decomposed to oxygen in the presence of metal ions at NCW temperatures; this would explain why feeding substantial amounts of undecomposed peroxide into the reactor did not affect the *pX* N/SCWO chemistry.

3.4 The Catalyst Feed System

The catalysts used during the project were solutions of metal bromides. Additional additives were sometimes used.

3.4.1 Feed Vessels

The catalyst feed system on the IP1 rig was installed with a one litre catalyst feed vessel. Operation with a single vessel proved to be tedious because of the need for water flush and so a two-litre vessel for water was installed in parallel. The K5 rig was installed with two parallel feed vessels. These were originally of 1 and 2 litre size but this was changed to two 2 litre vessels during the K5 rig uprate.

The Mn based catalyst system is prone to precipitation of manganese oxides which are highly fouling. The author has published formulations that help stabilise the Mn based catalyst system;⁵ these predate this thesis and do not form part of the submission. However, the formulations were implemented on the IP1 unit as part of these studies. The most successful formulations added BA or TMA to the catalyst feed, however, these acids have limited water solubility at ambient conditions and a warm feed system was required to obtain useful compositions. The least soluble additive used was BA, the solubility of which in water is ~10000, 8000, 5000 ppm at 55, 50, 37 °C respectively. The hot feed system was implemented using a heated flask on a hot plate, with the feed tubing and pump head heated with circulating hot water. The original installation was prone to blockages when using 10000 ppm BA suggesting that the process temperature was falling below ~55 – 60 °C. The author therefore implemented a

series of improvements. The circulating water temperature was increased to 90 °C and the flow was made counter current (to the catalyst flow). The water bath that was used was that that was originally at 40 °C to warm the cooling water to the cooler to ~30 °C (warmed cooling water was necessary to prevent any unreacted *p*X from freezing in the cooler). Therefore, this system was redesigned so that a proportion of the cooling water by passed the bath (reset at 90 °C) so that the re-combined cooling stream remained at the original 30 °C temperature. The same bath was then used to feed the water jacketing on the catalyst feed lines. All the compression joints in the hot feed system pipework were electrically trace heated and all the pipework was lagged especially in the cabinet where the extraction airflow could significantly cool the pipework. The system can be seen in Figure 3-3. This system was discontinued after the successful implementation of cobalt and copper based catalysts which were much less fouling (than manganese based), and did not require the use of stabilising additives.

The catalyst brews were highly corrosive (as they contained bromides) and therefore the catalyst lines were flushed and filled with water when not in use.

3.4.2 Pumps

The IP1 rig used Gilson HPLC pumps (Model 306 and 307) with a 10 mL/min head to feed the catalyst solution into the reactor. These can be seen in Figure 3-4. The K5 rig used a Jasco model PU-2086 HPLC pump with a 20 mL/min head for the catalyst pumping duty. This can be seen in Figure 2-7.

The pumps were banded and contained within a steel and polycarbonate cabinet as required by the safety case, as detailed in Section 3.1. Both these features can be seen in Figures 2-7 and 3-4.

The author was concerned about the degree of catalyst hydrolysis that could occur in the catalyst feedlines, particularly after the insertion of the mixing assembly into the K5 sand bath. The mixer was moved into the heated zone to overcome the inability to get the mixer up to supercritical reaction temperatures as described

in Section 7.4. However, a consequence of this was that the catalyst solution was pre-heated by the hot sand before reaching the mixing point.

A typical catalyst solution comprising Co/Cu/Br was fed to the reactor at various flow rates and heated to subcritical (360 °C) or supercritical (380 °C) temperatures. The flow was then fed to the cooler and BPR and then sampled at the sampling point and analysed by XRF for the three catalyst components. The results are shown in Figure 3-7(a) to (c).

The results show high Co stability of 80 – 90 %, lower Cu stability of ~40 % and high bromide recoveries of ~90 % under normal reactor operating conditions.

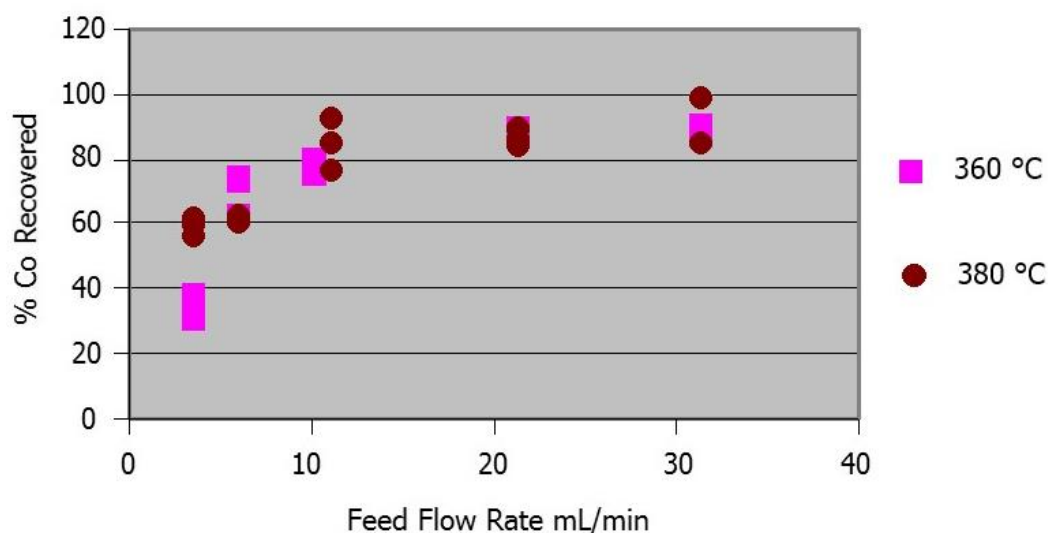


Figure 3-7(a). % Co recovered from Co/Cu/Br (Co:Cu):Br (0.85:0.15):2 by mole catalyst solution subjected to NCW and SCW conditions. The standard deviation (σ) of the recoveries (calculated as the square root of the weighted variances) is 3.8 %. Flow rates are ambient total reactor flows in mL/min; typical reactor feed flow is 24 mL/min.

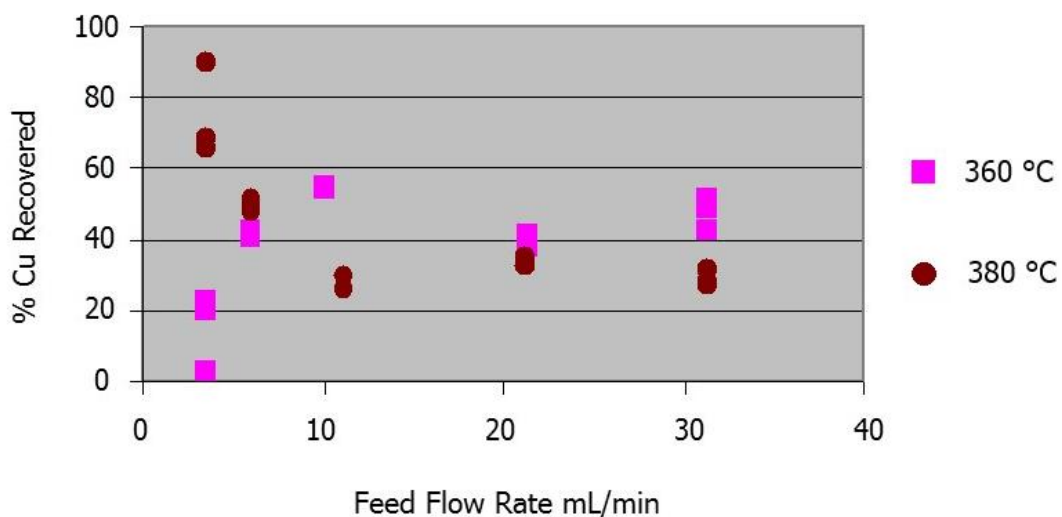


Figure 3-7(b). % Cu in fed catalyst recovered, standard deviation of recoveries measured $\sigma = 4.7\%$. See caption to Figure 3-7(a) for details.

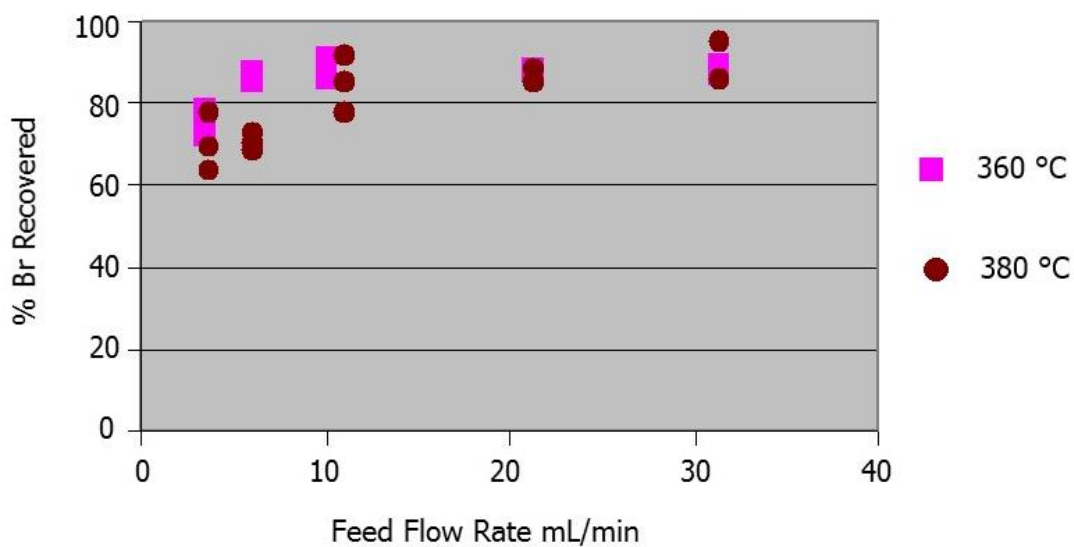


Figure 3-7(c). % Br in fed catalyst recovered, standard deviation of recoveries measured $\sigma = 3.2\%$. See caption to Figure 3-7(a) for details.

3.4.3 Mass Flow Meters

The original IP1 and K5 installations used timed level drop in parallel burettes to calibrate pump rates of catalyst solution.

Later in the project, thermal mass flow meters were installed on the catalyst lines of both the IP1 and K5 units. These were Bronkhorst L2-FGD-11-0 units that were ranged for 10 g/min and later (on the K5 uprate) for 16 g/min of catalyst solution.

3.5 The *p*-Xylene Feed System

3.5.1 Feed Vessels

pX was fed from a 0.5 litre and a 1 litre glass vessel on the IP1 and K5 rigs respectively. The vessels had parallel 10 mL burettes to enable timed flow rate checks to be made. 1/8" O.D. stainless steel pipework and fittings were used to connect the feed vessel to the pump.

pX was left in the system between runs as it is not corrosive and does not degrade in quality if left in contact with metal surfaces.

3.5.2 Pumps

The IP1 rig used Gilson HPLC pumps (Model 306 or 307) with 5 mL/min head for the *pX* pumping duty. The pump can be seen in Figure 3-4.

The K5 rig initially used a motorised, twin barrel syringe pump, manufactured by ISCO (model 260D). Twin syringes enable a switch to the second barrel while the first is reloading after discharge. This can be seen in Figure 2-7. This pump was later replaced by a double headed Jasco PU-2086 pump as described later in this section.

The pumps were banded and contained within a steel and polycarbonate cabinet. This was required by the safety case (as detailed in Section 3.1). Both these features can clearly be seen in Figures 3-4 and 2-7.

pX is prone to freezing at low ambient temperature and high pressure. Thus, the high-pressure feed line had to be heated to prevent freezing, particularly in winter. On the IP1 rig this was achieved with electrical trace heated and lagging. On the K5 rig, a Julabo F25-MC refrigerator/heater circulator fed Julabo Thermal H heat transfer fluid at ~50 °C to a jacketed section of the line. Heating (of this line) is not necessary when using *oX* which does not freeze under these conditions.

Unsurprisingly, the accurate pumping of *pX* proved to be critical to the achievement of a high carbon material balance on the units. It was believed that the syringe pump (which is driven by a stepper motor) would give a more continuous and more accurate feed profile than the reciprocating piston stroke of a HPLC pump and this was the reason that the ISCO pump was purchased. However, because of the persistent mass balancing problems on the K5 rig (described in Chapter 7), the author began to suspect that this might not be the case. Therefore, a study was undertaken of the relative performance of the two types of pump. *pX* was pumped (at the process flow rate of ~0.07 mL/min) through a thermal mass flow meter in series with a length of 1/16" O.D. piping that provided a substantial back pressure and the resulting flow rate was monitored over time. This revealed that the flow from a Jasco pump was pulsed as the piston reciprocated but that this pulse was steady and repeatable. In contrast, the flow from the ISCO pump was both variable and random in its variation. It was therefore decided to discontinue the use of ISCO pump.

3.5.3 Mass Flow Meters

As discussed in the previous section, the accurate pumping of *pX* was critical to obtaining good material balance. Measurement of pump rates by timed burette drop was tedious, especially when large numbers of samples were collected. Thermal mass flow meters are claimed to be accurate to within 1 % of their measurement range. Therefore, Bronkhorst L2-FGD-11-0 flow meters (for up to

5 g/min) were added on the *pX* feed line of both the IP1 and K5 rigs. These were positioned between the pump and the mixing point. However, this implementation was, in hindsight, flawed because 1 % of 5 g/min is 0.05 g/min $\sim$ 0.06 mL/min of *pX*. In many experiments, the *pX* flow rate was 0.07 mL/min so the errors were potentially large. Calibration checks against burette drop showed this to be the case. The Bronkhurst L1 instrument has a range of 0.5 g/min and this (or an equivalent) would be a better choice in any future studies. In later experiments, higher *pX* rates of $\sim$ 0.7 mL/min were employed for which the available instrument was better suited.

The K5 mass flow meter was damaged by back flow, particularly when using the ISCO pump which was prone to mis-sequencing. Therefore, two dissimilar non-return valves were installed downstream of the meter on both the IP1 and K5 rigs. This solved the problem and there were no further incidents of this type.

3.6 Reactors

The initial reactor designs employed on the IP1 and K5 rigs are described in Section 2.3.2. The evolution of reactor design is the subject of Chapter 7 which contains descriptions of the later designs.

3.7 Quench System

3.7.1 Feed Vessels

The quench fluids used in the experiment were dilute sodium hydroxide solution and water. Water was only suitable as a quench when using 0.5 % or lower *oX* feeds because of the higher solubility of *oPA* compared to *TA*.

IP1 rig used a 1 litre glass vessel and the K5 rig used a 5 litre glass vessel for quench solutions. Both rigs had parallel burettes for flow rate checking.

3.7.2 Pumps

IP1 rig used a Gilson HPLC pump (Model 306 or 307) with a 10 mL/min head and the K5 rig used a Jasco PU-2087 HPLC pump with a 50 mL/min head for the quench pumping duty.

3.7.3 Quench Point Design

The quenches used in this system were usually caustic solution and sometimes water. This served several purposes:

- Addition of caustic forms the sodium salt of the organic acids that had been formed. The sodium salts generally have much higher solubility than the corresponding organic acids and thus the quench prevents precipitation, fouling and blockages in the let down and product collection systems. This is not necessary when oxidising low levels (*i.e.* < 0.5 % w/w) of *o*X as the product, *o*PA, has sufficient water solubility at these concentrations.
- Partial cooling of the reactor liquor exiting the reactor. This can be achieved with either caustic or water quench.
- Addition of caustic to capture CO₂ as sodium carbonate. Organic acids have higher acid strength (lower pK_as) than carbonic acid. Thus, the organic acids are deprotonated before any carbonate is formed and it is thus necessary to add sufficient caustic to complete both, of these processes. If insufficient caustic is added, then some CO₂ loss (by degassing from the sample to atmosphere) occurs after discharge. When using water quench, CO is detected in the off gas but not when using caustic quench. It is probable that under hot, basic conditions the CO is captured, perhaps as sodium formate though this was not proven.

The range of sodium hydroxide strengths used was 0.5- 10 % w/w with the higher strengths being used when using higher *p*X concentrations.

On the IP1 rig, the quench was introduced in a 1/16" tee-piece just past the high point of the system. This was subsequently modified to a 1/8" tee-piece to avoid

blockage problems. On the K5 rig the quench was introduced downflow into a ¼" tee-piece but with no dip pipe. A lute arrangement was used to (try to) prevent back flow of caustic into the reactor. This was later modified to an up-flow addition point illustrated in Figure 7-5. The evolution of the quench point design is discussed further in Section 7.4

3.7.4 Cooler

The cooler was designed to cool the stream that has been quenched (and hence partially cooled) down to a temperature at which it could safely pass through the back-pressure regulator and be discharged at the sampling point. This discharge temperature was typically around 30-60 °C. At the caustic addition point, organic acids (such as benzoic acid, *p*-toluic acid, 4-CBA and TA) were captured in solution as their sodium salts. Catalyst metals were knocked out of solution as metal hydroxides. These metal hydroxides, though solid, are quite gelatinous and were easily conveyed without causing blockages.

On the IP1 and K5 rigs the construction of the cooler was with ⅛" O.D., 0.028" wall thickness tubing inside ⅜" O.D. tubing with materials being 316L stainless steel. It used counter current flow of the process fluids and cooling water. The cooler was 0.6 m long which was suitable for the process flows employed of 12-24 mL/min. All pipe work downstream of the cooler was ⅛" O.D., 0.035" wall thickness, 316L stainless steel.

A problem at start up (when incomplete reaction is occurring) or when using low conversion procedures was that *p*X would freeze in the cooler. This could block the cooler and cause a high-pressure trip on the unit. To overcome this problem, warmed cooling water (at ~30 - 40 °C) was deployed. Originally the water bath was set at ~40 °C but later it had to be raised to by ~90 °C to supply heating water for the hot catalyst feed system. The ~40 °C temperature for the cooler was maintained by diverting a proportion of the cooling water through a copper coil in the hot water bath and then recombining this flow with the main cooling water flow. A thermocouple was installed to monitor the cooling water temperature and a needle valve was used to control the proportion of cooling water diverted to the coil and hence to control the cooling water temperature.

Cooler blockages could also occur if insufficient caustic was used. This generally occurred if the caustic pump failed or an error was made in the start-up procedure, *e.g.* the quench pump was started late. Such failures would rapidly lead to blockage and a high-pressure trip.

When using water quench, it was necessary to pass TA slurry through the cooler and through the back-pressure regulator (BPR) and the valves of the sampling system. It was also necessary to remove the filters upstream of the BPR. The cooling water was isolated in this circumstance as cooling had been provided by a large water quench. It was possible to pump slurry in this way for short periods but the system would gradually block.

3.8 Pressure Let Down System

3.8.1 Back Pressure Regulators

Three types of back pressure regulators (BPR) were used on the IP1 and K5 rigs during the project, Tescom, Pressure Tech and Thar.

The successful deployment of BPRs for the pX N/SCWO duty was not easy to engineer. There were periods of good and poor performance and often the reasons for one or the other were not obvious. However, despite these difficulties, this section attempts to set out the key learning that was obtained.

It was necessary to have multiple BPRs to accommodate frequent change outs for maintenance. The first BPRs deployed were Tescom model 26-1762-22-043. These generally had to be serviced before every run. Their performance was eventually improved by using PEEK valve seats which could extend their service interval to about a week.

Subsequently Pressure Tech BP-LF690 BPRs were tested. These were initially disappointing but their performance was improved by using hardened stems with stainless steel seats. At their best, they could go approximately two weeks between services. Eventually the performance of the Pressure Techs began to decline. This was thought to be due to changes in the stem hardening process

used by the manufacturer. They became so unreliable that their use of was eventually discontinued.

The Thar (model BPR-A-200B-2) was designed to better handle solids and deployed an oscillating needle to try to keep the orifice hole clear. It proved difficult to configure and was not particularly reliable even with no TA solids present. Its use was therefore soon discontinued.

3.8.2 Filters

Two filters were deployed downstream of the cooler and prior to the back-pressure regulator (BPR). This was to protect the small orifice in the BPR from blockage by solids.

Different operating philosophies for filters were used on the UoN rig 22 and 23 and the IP1 and K5 rigs. On the UoN rigs, a large Highline filter was used with a fine 5 micron-mesh. This filter captured most of the precipitated catalyst solids. However, through the course of a run, the pressure drop over the filter increased and it was necessary to adjust the BPR to reduce its pressure drop to compensate. Eventually the whole of the pressure drop was being taken over the filter. The pressure in the unit then started to rise and it was necessary to shut the unit down. The IP1 and K5 rigs use two smaller filters, one coarse and one fine. The size of the meshes was varied and investigated but were generally 90 and 50 microns. These filters allowed some catalyst solids through and these solids could be seen in the samples collected and had to be filtered out (using filter paper) prior to analysis. However, the advantage of this procedure was that it allowed extended running without excessive pressure drop occurring over the filters.

3.9 Product Collection System

3.9.1 Gas Liquid Separator and Gas Analysis

Gas liquid separators (GLS) were deployed to separate gas from liquid prior to gas analysis and liquid sampling.

In the early experiments, the IP1 rig used a GLS. This was a metal Whitey cylinder with a lute for removing liquid and maintaining a constant liquid level. It was run at atmospheric pressure. This GLS had several problems:

- It was difficult to get material out of it and to adequately control level.
- It added residence time and a degree of back mixing to the system.
- It was prone to fouling with catalyst residues.

Due to these problems, the GLS had a by-pass installed for the collection of samples and a two-phase mixture was fed to the sampling point. Soon after this the GLS was completely removed from the system and a new technique was developed for obtaining gas samples.

In the new technique, a syringe (with its plunger fully pushed in) was attached to the sample point and a gas/liquid sample was collected by allowing the syringe plunger to be pushed out. This technique required large syringes (> 500 mL) and a good seal onto the sample point. The syringe material was plastic due to concerns about over pressurising and shattering glass, though this meant the quality of the plunger seal was poorer than would have been obtained with a ground glass seal. It was therefore necessary to analyse gas samples immediately after their collection. It was possible to estimate the relative volume of gas and liquid by observing the phases against the graduations on the syringe body. Gas tended to be mostly oxygen with small quantities of CO and CO₂ depending on the quench regime used. When caustic quench was used neither CO nor CO₂ were obtained (in significant quantity) and when using low exit oxygen (< ~115 % stoichiometric oxygen fed) very little if any gas could be obtained. Any gas samples obtained tended to be quite dirty (with liquid and catalyst residues contamination) and so an old Perkin Elmer GC was dedicated to this gas analysis

to avoid column damage on other, more modern GCs. It was not possible to measure organics (such as *p*X or toluene) in the gas phase due to the liquid contamination of the samples as the liquid phase also contained these components.

This syringe technique, though effective, proved not to be particularly important to the project because the majority of runs were quenched with caustic and thus the off gas did not contain CO and CO₂. Caustic captured CO₂ as sodium carbonate which could then be back titrated with HCl. It was thought that (at high temperatures, *i.e.* > ~300 °C) caustic may capture CO as sodium formate. Formate could not be determined by HCl titration and no method was developed to confirm formate or to estimate the levels obtained.

The K5 rig had a pressurised GLS; the pressure vessel can be seen in Figure 2-7. It comprised a narrow liquid containing section containing two level switches and a wide, gas disengagement section. The discharge from the BPR flowed into the vessel. Nitrogen was sparged through the liquid from the vessel base in order to strip dissolved gases out of the liquid. The nitrogen and gases from the rig were disengaged and flowed out from the top of the vessel, through a pressure control valve and into the Emerson Rosemount gas analysers. The liquid level oscillated between the two level control switches which opened and closed a liquid discharge valve to a liquid collection bucket. The pressure in the vessel of around 2 bar_g ensured a smooth and reliable discharge of liquid when the discharge valve was opened. This design of GLS worked well, the key feature being the over pressure to ensure smooth discharge. The GLS was primarily used for gas collection for analysis. It was possible to undertake ‘caustic drop’ experiments where the sodium hydroxide quench was progressively replaced with water quench and the CO₂ and CO progressively appeared in the analysed gas stream which also contained O₂. Under these conditions, the liquid discharge began to contain TA. By oscillating the ‘caustic drop’ up and down it proved possible to prevent the TA from building to levels where it clogged the discharge valves. Gas stripper trials were undertaken when known amounts of CO₂ calibration gas in nitrogen were fed to the GLS and the gas stripping efficiency was determined and found to be high. The ‘caustic drop’ measurements gave CO₂ levels that

agreed with the CO₂ determined by the HCl titration of carbonate method. This consistency increased the confidence in both methods.

3.9.2 Sample Points and Sampling

The GLS was not used for collecting liquid samples because of the issues around back mixing mentioned for the IP1 GLS.

On both IP1 and K5 rigs, the pipe work downstream of the cooler was 1/8" O.D. 0.028" wall thickness 316L stainless steel. The GLS discharge was from an open-ended pipe into a large plastic beaker. A sampling line was tee-ed off prior to the gas liquid separator vessel which comprised similar tubing with valves to control the direction of flow. The sampling discharge was into small glass vials which were sealed and appropriately labelled.

The residence time in the reactor was a function of reactor volume and operating conditions. A typically reactor volume was ~10 – 20 mL and its residence time fell in the range of 10 - 63 s when using NCW conditions. The volume of the hot pipe work from the reactor exit to the cooler was estimated at ~2 mL and the volume of the rig components from the cooler to the sampling point (excluding the GLS which was by passed) was ~24 mL. Thus, the residence time post the reactor was in the range of 60 – 120 s and the total residence time fell in the range of 70 – 183 s. A rule of thumb is that a back mixed system needs at least 5 residence times to ensure that the material within it has been substantially renewed. The laminar flow gives the unit some back mixed characteristic because of the tendency to axial dispersion along the pipe work in this flow regime. Thus, the sampling frequency needed to be at least every 15 minutes to ensure at least 5 residence times between samples and this was the frequency typically used. The sample sizes taken were typically ~20 mL though on occasions larger samples of ~50 - 100 mL were taken.

3.10 Experimental Procedures

Hazards caution: the experiments described in this report are potentially hazardous and should only be attempted after a rigorous hazard assessment

has been undertaken. The basis of safety is described in Section 3.1 of this thesis.

3.10.1 Pressure Testing

Post maintenance, the high-pressure sections of the unit were hydrostatically pressure tested at room temperature to normal operating pressure (~250 bar). Pressure was applied using a hydraulic hand pump. The BPR had to be isolated from the system prior to such a pressure test.

3.10.2 Formulations

The formulations in use at the commencement of the project are described in Section 2.4.1. The subsequent evolution of the chemistry and formulations is the subject of Chapter 6. The range of formulation parameters used in the project is detailed in this section.

All the chemicals were purchased from Sigma Aldrich and used without further purification.

Formulations typically comprised of the following streams:

- A stream of organic, typically *p*X or *o*X.
- A stream of catalyst solution, typically manganese bromide dissolved in water.
- A stream of oxidant comprising hydrogen peroxide solution in water. The peroxide is thermally decomposed prior to entering the reactor so that the actual oxidant used is oxygen.
- A quench stream, typically comprising of aqueous sodium hydroxide but sometimes of water.

The organic, catalyst and oxidant streams were fed to the mixer upstream of the reactor. The quench stream was added at the quench point after the reactor.

The total flow rates utilised were initially between 12 mL/min and 24 mL/min though later higher flows to 125 mL/min were used. Different flow rates allowed

varying residence times to be achieved for a given reactor volume and process condition (of temperature and pressure).

The flow rate of the organic was set to achieve between 0.5 % and 5.0 % by weight of organic in the reactor. This gave *pX* flows of between 0.061 and 1.28 mL/min.

The catalyst flow rates used varied between 4.0 mL/min and 9.7 mL/min. The concentrations of the manganese bromide solutions used were in the range of 0.0157 M to 0.0470 M. The most typical concentration was ~0.031M which corresponds to ~1700 ppm of Mn and ~5000 ppm of Br in the feed solution. These concentrations were diluted by a factor of ~3 in the mixer to thus give reactor concentrations of ~567 ppm of Mn and ~1667 ppm of Br. This level of catalyst (as defined by the bromide levels) is referred to as 100 % catalyst as this gives an easy, relative measure of different catalysts. Later formulations using other metals, particularly Co and Cu were adopted and these developments are described in Section 6.4.1 and in a paper by the author.⁶

The hydrogen peroxide stream used flow rates between 8.1 mL/min and 20 mL/min. The pre-heater construction is described in Section 3.3.3. It comprised 5.9 m of 1/8" O.D. tubing of wall thickness 0.035". This had a volume of 9.0 mL. The block temperature used was 495 °C and the exit process temperature achieved was 360 - 400 °C. This residence time in the pre-heater was difficult to estimate because of the wide range of temperature conditions that occur within it and because the density of supercritical water is strongly dependent on temperature under these conditions. However, a rough estimate indicated that was in the range of 20 - 40 s. Literature references indicate that these conditions were sufficient to ensure complete breakdown of the hydrogen peroxide to oxygen and water and thus to provide a homogeneous feed of oxygen and water to the mixing point of the reactor,¹⁻³ though this was tested as described in Section 3.3.3. The peroxide concentration used was varied to give an oxygen stoichiometry in the range of 30 – 200 % of that needed to fully oxidise the *oX* or *pX* to *oPA* or *TA* respectively.

The oxygen stoichiometry used fell into three categories:

- Sub stoichiometric runs that used between 30 % and 80 % of stoichiometric oxygen. These were used to study the pattern of production of early intermediates in the reaction.
- Stoichiometric runs that used between 115 % and 130 % of stoichiometric oxygen. It was necessary to have greater than 100 % of stoichiometric oxygen because the (unavoidable) side reactions that produce CO₂ and CO use a higher oxygen stoichiometry per mole of *p*X than the reaction to dicarboxy aromatic acid (the required stoichiometries are 3.0 and 10.5 moles of oxygen per mole of *p*X to produce the dicarboxy aromatic acid and CO₂ respectively).
- Excess oxygen runs that used > 130 % and up to 200 % of stoichiometric oxygen. These runs were used to study the effect of excess oxygen on the stability of the aromatics in the system (*i.e.* the reactants, intermediates and products).

Hydrogen peroxide was purchased as a 30 % w/w solution in water. It was diluted with water and was used at a strength that was between 1.28 % and 17.3 % w/w on the rig for the first oxygen feed. 30 % solution was used for additional oxygen feeds.

Quench solutions were either sodium hydroxide solutions of strength between 0.5 and 10 % w/w or water. The upper limit on caustic concentration (of 10 % w/w) was set for materials considerations as stainless steel alloys are prone to stress cracking in high pH, high temperature environments.⁷ Water was only suitable for 0.5 % *o*X procedures because *o*-phthalic acid has moderate solubility in water (the solubility of *o*PA is ~0.6 % w/w or 6000 ppm at 20 °C; the comparable solubility of TA is ~10 ppm). Sodium hydroxide is necessary to dissolve the organic acids produced (and prevent their precipitation in and blockage of the cooler). Sufficient sodium hydroxide can also (optionally) be added to convert any carbon dioxide produced to sodium carbonate. (Note that the relevant pK_as are TA 3.51, 4.82, H₂CO₃ 6.35, HCO₃⁻ 10.33, H₂O 15.74 so caustic will preferentially take protons from the organic acids over the carbonic acid). The advantage of converting the carbon dioxide to carbonate is that it prevents it from gassing off at the sampling point and enables the carbonate to be subsequently

back titrated with HCl to quantify the CO₂. The required rate of quench sodium hydroxide addition was set to provide a 10 % excess over that needed to dissolve the acids and trap the estimated amount of carbon dioxide. The CO₂ production rate (for this calculation) was set at that resulting from ~5 % and ~12 % total oxidation of *o*X and *p*X respectively. The flow rate (of caustic solution) used was between 4.2 and 25 mL/min.

3.10.3 Start-Up Procedure

The first procedure for bringing the various streams on was:

- Feed water through the pre-heater to produce HTW and bring the unit up to temperature.
- Switch the feed to the pre-heater to a water/peroxide mix and thus produce a water/oxygen stream.
- Turn on the organic feed. The line was kept full of organic between runs so the organics entered the mixing point immediately.
- Wait 20 seconds then switch on the catalyst feed. The catalyst line contains water at start up and so there is ~90 second delay before catalyst enters the mixing point.
- Switch on the quench feed.

The problem with this procedure was that organic contacted oxygen in the absence of catalyst for a period, until the catalyst feed broke through at the mixing point. Under these conditions, organic oxidises unselectively, which can cause a considerable exotherm (a temperature rise of up to 80 °C) especially when using higher organic concentrations.

When considering other possible start up procedures, those that contact catalyst solution and oxygen in the absence of organic should be avoided as this would cause excessive formation of metal oxides that would likely foul the mixer. Other possible start-up procedures considered were:

1. Keep the same procedure but bring the organic on at a low feed rate then increase the organic feed rate once catalyst break through has occurred.
2. Feed water heated to HTW, bring on organic, bring on catalyst (initially pumps water), bring on quench, switch to water/peroxide feed
3. Feed water heated to HTW, switch to water/peroxide feed, bring on catalyst (initially pumps water), immediately bring on quench, immediately bring on organic

Option 1 contacts catalyst and oxygen with a shortage of organic and will likely lead to excessive fouling. Option 2 is probably better but catalyst solution can hydrolyse in hot water and foul. In option 3, the lag in the time to catalyst breakthrough ensures that the organic reaches the mixing point before the catalyst and so avoids the problem of excessive catalyst hydrolysis and fouling. Also, the tendency to exotherm is reduced by the extra water flow through the catalyst line compared to the original start up procedure. This start up procedure was trialled, found to be effective and adopted.

The situation is subtly different during a restart, *i.e.* the situation where the rig has been started up, has tripped out and is then restarted. During a trip, the peroxide feed is switched to water feed. However, the catalyst line remains full of catalyst solution. Thus, during a subsequent restart, there is not the delay on catalyst entering the mixing point. Thus, it was important that the catalyst feed pump and the *pX* feed pump were started simultaneously in this circumstance to prevent catalyst contacting oxygen in the absence of organic which would lead to excessive fouling of the mixer from catalyst precipitation.

3.10.4 Shutdown Procedure

At shutdown, the *pX* flow was stopped and the catalyst feed and water/peroxide feed were switched to water flushes. These were continued for up to 2 hours in order to cool the rig. It was found that the *pX* line could be left full between runs. It was important that the catalyst line was water flushed as leaving it charged with

catalyst solution was found to cause excessive corrosion in that line. It was thought that much of this corrosion occurs during the start-up procedure when this line becomes warm from thermal conduction from the reactor. After cooling the reactor was cleaned by pumping a cleaning solution through it. The cleaning procedure adopted was as follows:

- Pump water through the peroxide feed and catalyst feed lines until the reactor was cooled to 60 °C. This could take up to 2 hours. The heaters were set to 60 °C to maintain this temperature for the remainder of the wash cycle.
- Pump 5 % caustic through the peroxide feed line for 15 minutes. This was to remove any TA and other organic acid residues.
- Pump water through the line for 5 minutes to remove caustic.
- Pump 10 % aqueous sulfamic acid through the line at 10 mL/min, for 30 minutes. This removes manganese oxide deposits. The discharged cleaning fluid was collected as 4 samples, one every 15 minutes and these were analysed by XRF to determine the levels of Mn and metals from corrosion such as Fe, Cr, Ni. The first sample tended to be brown and the subsequent samples became progressively lighter in colour. XRF was used for metals analysis of the sulfamic acid washes. The samples showed a drop across the 4 samples typically from 20 ppm to < 10 ppm for Cr and Fe and from 100 ppm to < 10 ppm for Ni - it is presumed that corrosion causes these metals to leach out of the reactor walls but they are only flushed out when dissolved in the sulfamic acid. There were typically constant levels of Co at 10 ppm and Br at 2 ppm across the 4 samples. Mn levels typically dropped from ~1000 ppm to 100 ppm.
- The heaters were switched off and the unit was flushed with water until the reactor temperature fell to 40 °C. The pump was then switched off. This procedure ensured that the peroxide and catalyst feed lines and the reactor were full of water during unit shutdown.

3.10.5 Analytical Procedures

The analytical techniques and instrumentation that were used for the analysis of the products from the N/SCWO of xylenes are given in Table 3-8.

The details of the industrial partner's analytical methods are proprietary and not available for publication. However, the methods used by the UoN are similar and are detailed in their reports that are referenced in Section 2.2.3 of this thesis.

Table 3-8. The analytical techniques and instruments used for the analysis of given components. The 'minor components' are those described in Section 1.3.3.

Technique	Instruments	Components
HPLC	Agilent 1050 & 1100 series	<i>p</i> -Tol, 4-CBA, TA, BA, <i>o</i> PA, <i>i</i> PA, minor components
GC	Agilent 6890 FID	<i>p</i> X, <i>p</i> -tolualdehyde, benzene, toluene, benzaldehyde, benzyl alcohol, 4-methyl benzyl alcohol/bromide/acetate
IR/paramagnetic	Fisher Rosemount NGA 2000. FID & MLT analysers	CO ₂ , CO, O ₂
Titration	Metrohm auto titrator	Br ⁻ , CO ₃ ²⁻
XRF	Spectro X Lab 2000	Metals (<i>e.g.</i> Co, Mn, Cu, Fe <i>etc.</i>)

3.10.6 Data Reporting Conventions and Error Assessment

The author has adopted the convention of presenting all yield data of product components on the basis, of the molar percentage of the fed xylene converted to that component. Thus:

$$Y_X = \frac{100 M_X w_{pX}}{M_{pX} w_X}$$

where Y_X is the % mass yield of component X, M_X is the mass of component X obtained over a given time-period, w_X is the molecular mass of component X and M_{pX} is the mass of *p*X fed to the unit over that time-period.

This convention has been used throughout this thesis. Where referenced data, that is reported in different ways, has been quoted, the author has converted that data to this basis.

Experimental errors were assessed using several methods, as detailed in the following paragraphs.

For some experimental techniques, calibration and capability studies were undertaken. Examples include the degree of peroxide breakdown, detailed in Sections 3.3.3, and the degree of catalyst hydrolysis, detailed in Section 3.4.2. Estimates of standard deviations for those studies are given.

In some cases, multiple measurement techniques were applied, where this was possible. An example was the measurement of flow rates by timed burette level drops and by thermal mass flow meters on *pX* and catalyst feed lines, as detailed in Sections 3.4 and 3.5; errors are discussed in these sections. A further example was the use of carbonate titration (described in Section 2.5.1) and the ‘caustic drop’ technique with IR gas analysers (described in Section 3.9.1) for the measurement of CO₂ production rates.

The *pX* N/SCWO chemistry experiments made extensive use of repeat measurements. This was at several levels *e.g.*

- In each experiment, 5-6 samples were typically collected over a 2 hour period.
- Experiments were periodically repeated, especially ‘standard’ experiments.
- Experimental studies were often repeated when a new (and improved) reactor became available. This was particularly the case with the introduction of the welded tubular reactor described in Section 7.4 which was superior to the previous reactors employed.

The chemistry studies described in Sections 5.8.2 to 5.8.4 and Figures 5-10 to 5-12 were performed in the best reactors deployed during this project *i.e.* the welded TBR and the STR as described in Sections 7.4 and 5.6.3 respectively. The standard deviations in these experiments were assessed by the methods

described above and are given in the captions of Figures 5-10 and 5-11. The same TBR was used for the *p*X concentration experiments in Section 6.3 and the errors will be similar. The other studies described in Chapter 6 used earlier reactor designs that were less capable. Figure 7-9 shows the evolution of TBR errors over the course of the project; this figure shows that the standard deviations of results from these earlier reactors (*i.e.* experiments performed around year 0.75 to 1.5) were about twice those achieved with the welded TBR (at low throughputs).

3.11 References

1. N. Akiya and P. E. Savage, Hydrogen peroxide dissociation in supercritical water. 1 Reaction Equilibrium., *Abstr. Pap. Am. Chem. Soc.*, 1999, **217**, 692-693.
2. E. Croiset, S. F. Rice and R. G. Hanush, Hydrogen peroxide decomposition in supercritical water, *AIChE J.*, 1997, **43**, 2343-2352.
3. B. D. Phenix, J. L. DiNaro, J. W. Tester, J. B. Howard and K. A. Smith, The effects of mixing and oxidant choice on laboratory-scale measurements of supercritical water oxidation kinetics, *Ind. Eng. Chem. Res.*, 2002, **41**, 624-631.
4. P. E. Savage, J. B. Dunn and J. L. Yu, Recent advances in catalytic oxidation in supercritical water, *Combust. Sci. Technol.*, 2006, **178**, 443-465.
5. J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, E. Perez, I. Pearson, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Prevention of Manganese Precipitation during the Continuous Selective Partial Oxidation of Methyl Aromatics with Molecular Oxygen in Supercritical Water, *Adv. Synth. Catal.*, 2009, **351**, 1866-1876.
6. E. Perez, J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, M. L. Thomas, C. Yan, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 2. The discovery of better catalysts, *Green Chem.*, 2011, **13**, 2397-2407.
7. G. J. Theus, Caustic Stress-Corrosion Cracking of Inconel-600, Incoloy-800, and Type-304 Stainless-Steel, *Nucl. Technol.*, 1976, **28**, 388-397.

4. Mixer Design and Development

4.1 Overview

This chapter describes the work that has been undertaken to optimise the mixing of the three inlet streams of water/oxygen, catalyst solution and *pX* in a *pX* N/SCWO reactor.

It first considers the effect of poor mixing of these streams. It references the mixing literature that was reviewed in Chapter 2 Section 2.2.4. The work undertaken to improve and optimise the mixing is summarised; a fuller account has been published in two papers ^{1,2} which are reproduced in Appendix 1.

The author developed the data analysis presented in this chapter. The Light Absorption Imaging technique was developed and the experimental work was undertaken by Ed Lester's group in the Department of Chemical Engineering at the University of Nottingham.

4.2 The Effects of Poor Mixing

It was noted in Chapter 1 that *pX* N/SCWO is thought to proceed by a similar mechanism to that in the acetic acid process, involving free radical chain oxidation with peroxide and bromine radicals as the propagating species. This is evidenced by:

- The necessity for bromide in the catalyst system to obtain high yields of TA.
- A similar pattern of intermediates and by-products in the two processes.

This section gives some thoughts on the effect of poor mixing on the course of the reactions in such a system.

Most of the N/SCWO reactor configurations in this thesis have three inlet pipes, feeding the liquid *pX*, the gaseous oxygen (mixed with some of the water), and the dissolved catalyst in further water. Ideally, prior to the initiation of the

reaction, these three streams would completely mix to a homogeneous composition. However, the streams are treated in different ways before entering the mixing region:

- The *pX* stream is of low volumetric flow compared to the other two. *pX* is prone to freezing when at low ambient temperatures and particularly when pressurised. This is particularly problematic during winter months. *pX* feed lines are therefore best trace heated and the *pX* is thus pumped and fed to the mixing zone at slightly above ambient temperature (around 30 – 40 °C). There is little advantage in further preheating the *pX* because its flow rate is too low for it to carry significant sensible heat to the mixing zone.
- The catalyst stream is of intermediate volumetric flow typically representing 15 – 35 % of the total flow. The catalysts comprise transition metal salts and the metal cations are Lewis acids which are prone to hydrolysis and precipitation (of metal oxides and hydroxides) in water. This process is accelerated in hot water and, for this reason, it is preferable to feed the aqueous catalyst at ambient temperature and to mix it rapidly with the hotter streams at the mixing point.
- The oxygen feed is generated by decomposing a stream of hydrogen peroxide solution at high temperatures to generate water and oxygen.³⁻⁵ This is the largest volume stream and it must be heated to supercritical temperatures above 400 °C so that it carries sufficient enthalpy to enable the final mixed stream to reach the target temperature.

Thus, two streams enter the mixing zone at low temperatures and thus have densities around 850 - 1050 kgm⁻³. The third stream enters as supercritical water and thus has a density of around 100 - 200 kgm⁻³. Densities are estimated from those of pure water using the NIST databank.¹⁰

The efficient mixing of streams with large density differences is potentially problematic because buoyancy can cause stream stratification. From the acetic acid process, we know that poor mixing can significantly affect the product yields and selectivity of the reaction. Thus, it is to be expected that in a N/SCW system,

subtle changes in the reactor geometry and the feed pipe orientation will have a significant effect on the outcome. Some reasons for this are now considered.

If the reaction is initiated before the feed streams are completely mixed, there will be a variation of the concentration of the pX , oxygen and the catalyst in the reactor. The undesirable reactions that can occur in each of these regimes are considered.

The desired reaction is that the organic free radicals, denoted as $R^\bullet$, react with the oxygen. This is a very rapid, spontaneous, spin-allowed reaction:



This ultimately leads to the desired intermediates and carboxylic acid product as is illustrated in Figure 1-6.

4.2.1 Low Oxygen Concentration Regions

If there is poor mixing, there will be regions in the reactor with unusually low oxygen concentrations and the frequency of the dimerisation of the organic free radicals will increase:



Or the free radical will react with another hydrocarbon:



Reactions (4-2) and (4-3) are detrimental in two ways:

- In free radical chain reactions, the overall rate of reaction is dependent upon the steady-state concentration of chain carrier radicals. Reactions (4-2) and (4-3) decrease the steady-state concentration of these radicals hence the rate of reaction.
- Reactions (4-2) and (4-3) and the subsequent oxidation of the products give undesirable, highly coloured by-products, as described in section 1.3.3, which must be separated from the TA before it is used in polyester manufacture.

4.2.2 High *p*-Xylene Concentration Regions

Improper mixing will lead to regions in the reactor with higher *p*X concentration than average in which the rate of (the undesirable) reactions (4-2) and (4-3) will be enhanced.

4.2.3 Low Catalyst Concentration Regions

Improper mixing can lead to regions in the reactor with lower catalyst concentrations than average. It is well-established in these systems that the catalyst concentration affects both the rate of reaction and its selectivity. This can be understood by reference to Figure 1-7. As the catalyst concentration increases, the terephthalic acid yield increases and by-products such as CO₂, CO and rate-inhibiting phenols decrease. The catalyst reduces the number of (less selective, uncatalysed) free-radical pathways (reaction (1)) to the products and reduces the steady-state concentration of the highly unselective hydroxyl radicals by promoting the highly selective metal-catalyzed pathways (reaction (2)). Thus, low catalyst regions will have lower selectivity to the desired products.

4.3 Literature

The literature in this area is reviewed in Chapter 2, Section 2.2.4 and in the author's published paper.¹

4.4 Mixer Characterisation

The performance of mixers were characterised by Light Absorption Imaging (LAI) methods developed by Lester *et al.*^{7, 8} in which fluids of differing densities were contacted in mixers made from acrylic blocks and the observed mixing behaviour was captured on video. The experimental work in the paper¹ was commissioned by the author and undertaken by Post-Doctoral students in Lester's group at the UoN. The analysis presented was developed by the author and is summarised here.

The aims of the study were:

- to assess the mixing that occurred in a tee-piece under varying flow conditions and to compare this to the performance in the buoyancy mixers developed by Lester *et al.*^{8, 9} for the mixing of streams with appreciable density differences for the production of nano-particles in SCW.
- To develop a model framework to allow the results to be extrapolated to:
 - the mixer geometries and conditions in use on the laboratory scale experimental rigs
 - plant scale mixers and conditions.

These behaviours were captured by LAI and were mapped onto a matrix plot of Reynolds Numbers for the two mixer inlet streams, as shown in Figure 4-1.

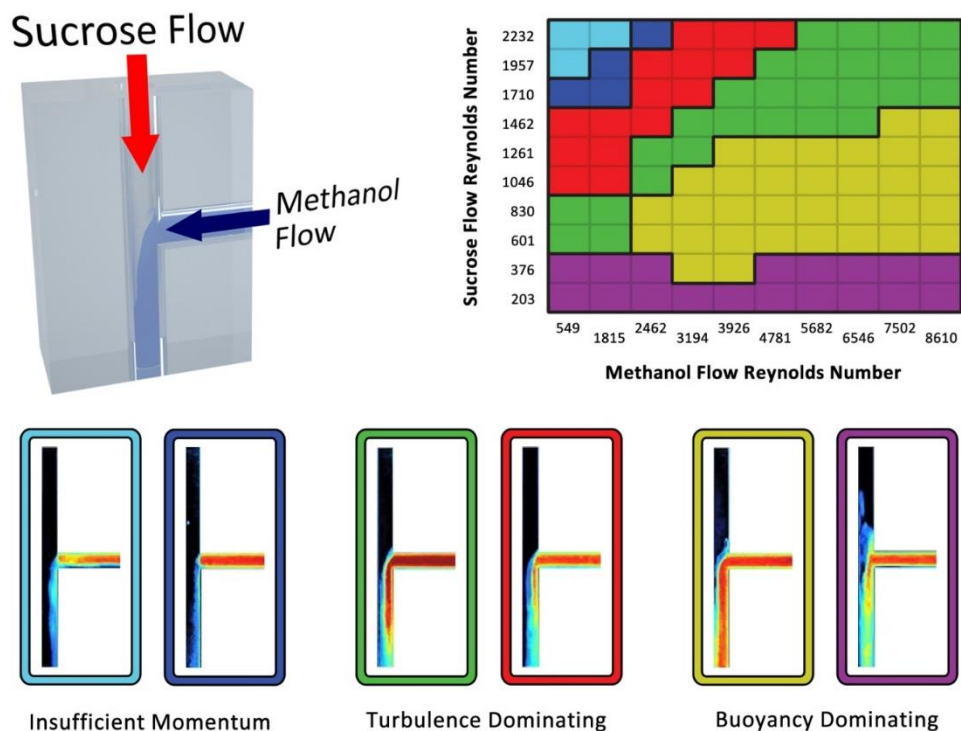


Figure 4-1. The mixing performance of a tee-piece mixer fed with a low-density methanol stream with a higher density sucrose solution stream at varying flow rates. The mixing performance is mapped onto a Reynolds matrix and is illustrated by LAI images; these can be linked by the colour coding. Regions dominated by turbulence, buoyancy and relative momentum are apparent.

The concept of mapping performance onto a Reynolds matrix was developed by Lester's team; the author can see some merit in this approach but it also raises some issues. The advantage is that it enables a wide range of fluid properties,

pipe sizes and fluid flow rates to be captured on a consistent and comparable basis. However, it raises the question of how fundamental this approach is and whether matrices constructed from data obtained at differing scales and with different fluids would be consistent. Vogel *et al.*¹⁰⁻¹² and Adschiri *et al.*¹³ have applied neutron radiography to directly image NCW and SCW mixing. Adschiri's study provides images on such mixing in a tee-piece which are reproduced in Figure 4-2.

Copyrighted material removed.

Figure 4-2. Neutron radiography images of the mixing of NCW (from side arm) with down flowing SCW. NCW has greater attenuation and shows up darker than SCW on the images. 'NCW inlet mixing' (where SCW pushes into the NCW inlet) occurs at all NCW flow rates but reduces with increasing flow. Some 'SCW inlet mixing' appears at the highest NCW flow rate. Source Adschiri *et al.*¹³

The flow regimes for this mixer configuration, mapped onto a Reynolds matrix as measured by Lester are shown in Figure 4-3.

Analysis of Adschiri's data shows that the SCW has a $Re \sim 880$ and the NCW a Re of $\sim 150, 380, 760, 1520$ with increasing NCW flow rate. Thus, Adschiri's transition from 'NCW inlet mixing' to 'SCW inlet mixing' occurs at the same Reynolds number as Lester's transition from 'sucrose inlet mixing' to 'methanol inlet mixing'. While this doesn't rigorously validate the assumption noted above, it provides some assurance that the extrapolation of Lester's Reynolds matrix to other fluids and scales has some merit.

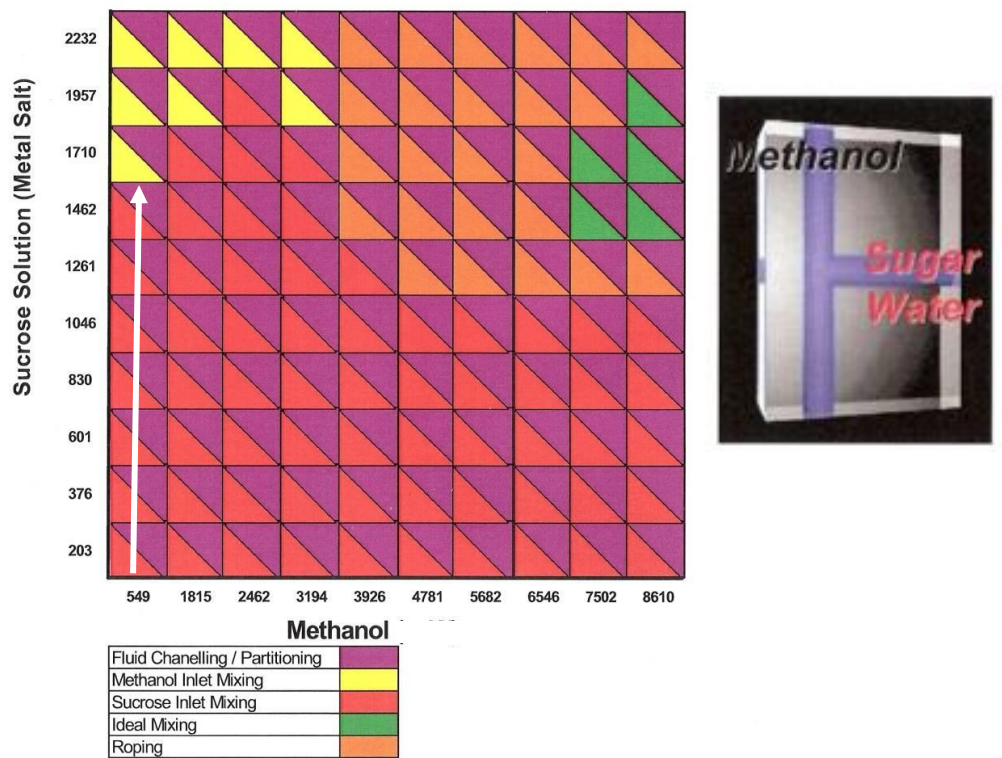


Figure 4-3. The flow regimes for a tee-piece mixer of the illustrated orientation mapped onto a Reynolds matrix. Inlet mixing was defined in the caption to Figure 4-2. Roping is where two streams wrap around each other (like strands of rope) but fail to fully mix. The white arrow shows the range of conditions covered in Adschiri's data.

The review of the literature highlighted how the various metrics that had been used to characterise the performance of a tee-piece mixer could be grouped into those describing turbulence, buoyancy and relative stream momentum. Therefore, the dimensionless groups of Reynolds number, Richardson number and momentum ratio were selected as promising groups with which to characterise the system and these numbers were calculated for each flow condition and mapped onto the same Reynolds matrix (as used in Figure 4-1) as shown in Figure 4-4.

It was then possible to compare the experimental Reynolds matrix in Figure 4-1 with the dimensionless groups Reynolds matrices in Figure 4-4 and determine the physics dominating the mixer performance for the various flow regimes observed.

The various mixer geometries that were investigated by these techniques are illustrated in Figure 4-5.

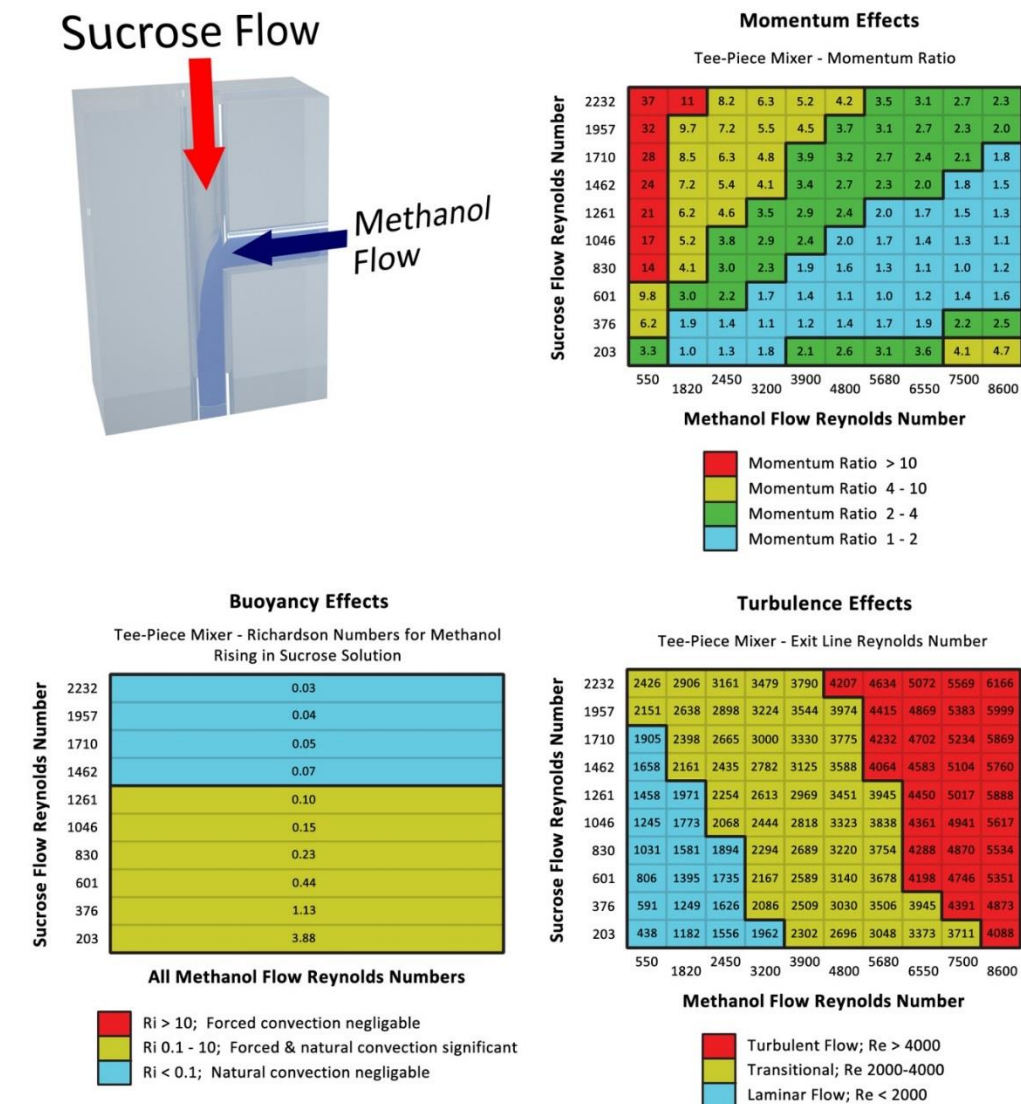


Figure 4-4. Dimensionless groups mapped onto the Reynolds matrix for a tee-piece mixer. Note that momentum effects cut across the matrix from bottom left to top right, buoyancy effects horizontally and turbulence effects from bottom right to top left.

The determination of their Reynolds matrices (of flow regimes), as measured by LAI, were undertaken by Lester. The best tee-piece mixer for this mixing duty was found to be the one third from left, top row as characterised in Figures 4-1 and 4-4. The Lester buoyancy mixer, top left, was also effective and is further analysed in Figures 4-6 and 4-7.

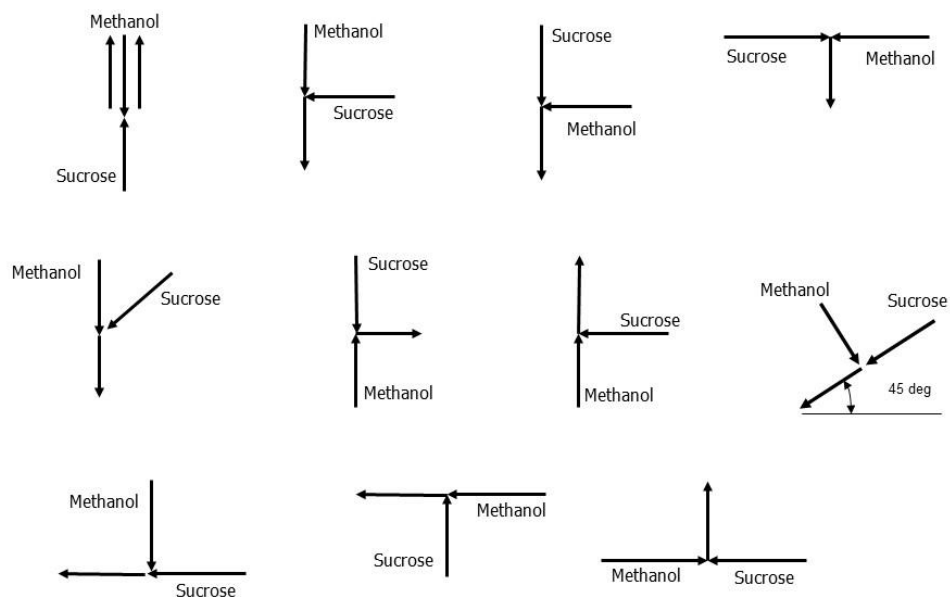


Figure 4-5. The mixer designs that were characterised by LAI of mixers made from acrylic blocks.

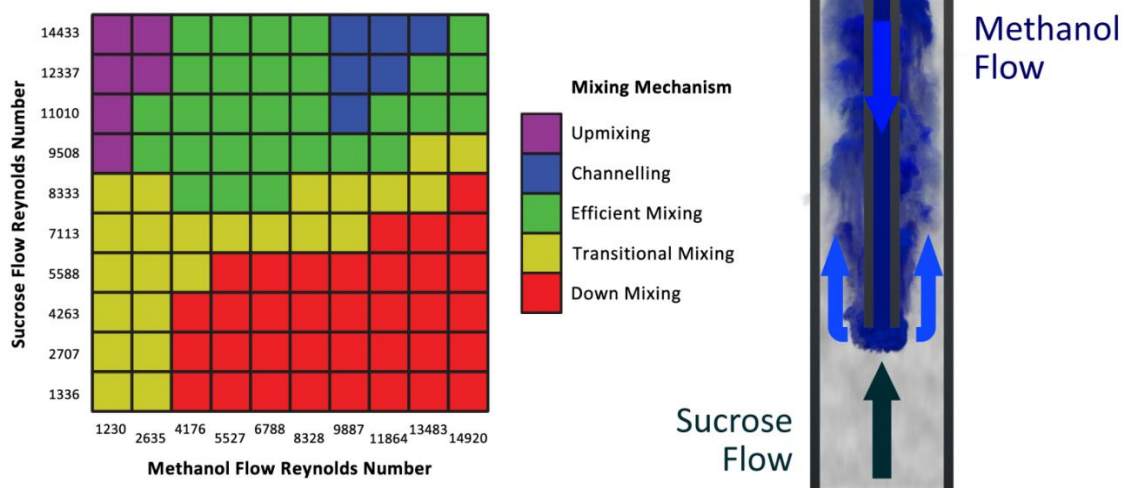


Figure 4-6. The Reynolds matrix plot of the buoyancy mixer geometry shown in the schematic as determined by Lester *et al.*¹

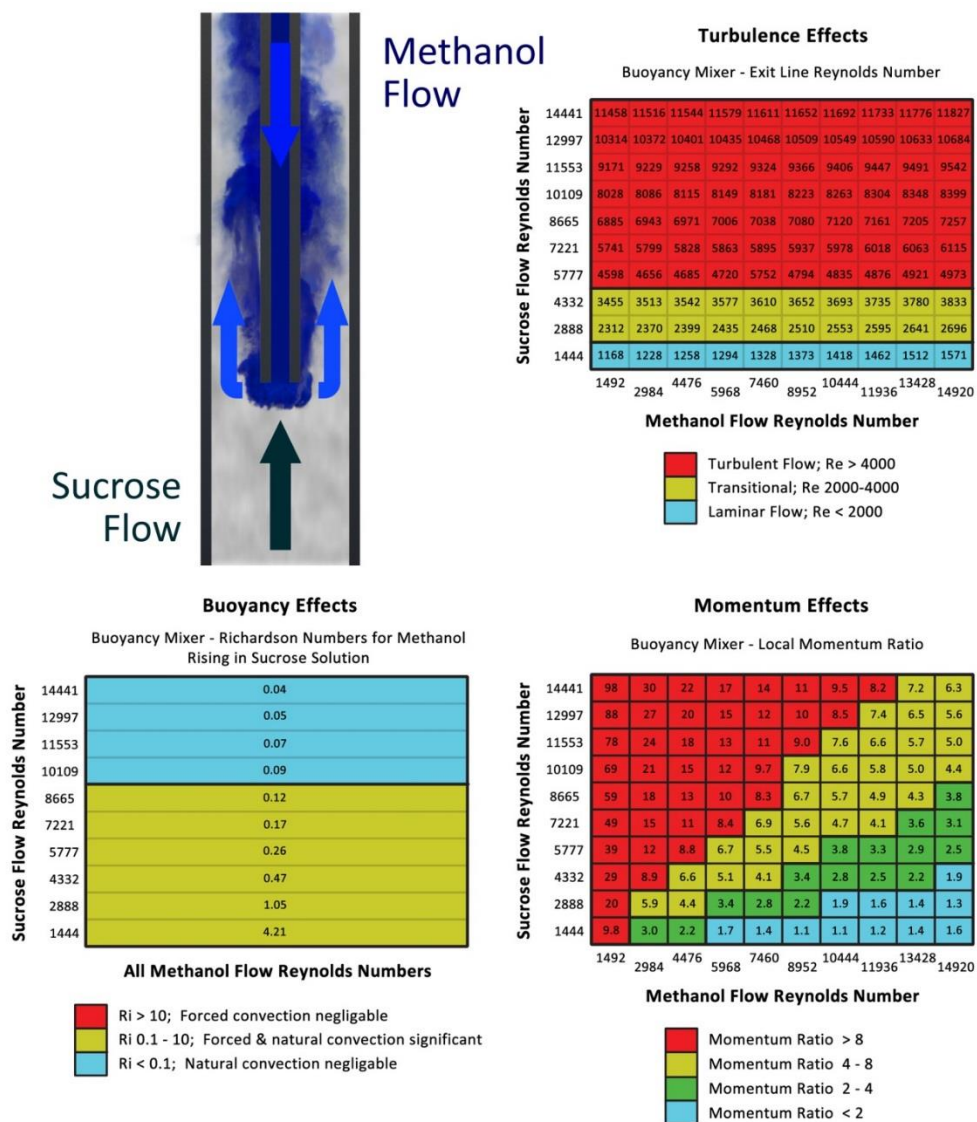


Figure 4-7. Dimensionless groups mapped onto Reynolds matrices for the buoyancy mixer geometry shown in the schematic.

In Figure 4-6 the colour contours generally cut from bottom left to top right, suggesting that the performance of the buoyancy mixer is dominated by momentum effects. “Up-mixing” is the (transient) forcing of methanol back up its feed pipe by the sucrose. Cross referencing Figure 4-6 with Figure 4-7 suggests that this phenomenon can occur with a methanol/sucrose solution local momentum ratio of ~ 30 . Down mixing is the (transient) forcing of sucrose down its feed pipe by the methanol. This occurs with a methanol/sucrose solution momentum ratio below ~ 5 .

Efficient mixing occurs in the region where the flow is turbulent and momentum ratios are not too great. The onset of transitional mixing coincides with natural convection (*i.e.* buoyancy) becoming significant as indicated by the Richardson number.

Channelling is the separation of the sucrose solution and methanol components in the outer annulus. It occurs in the region where buoyancy effects are unimportant and the sucrose solution flow is high relative to the methanol flow.

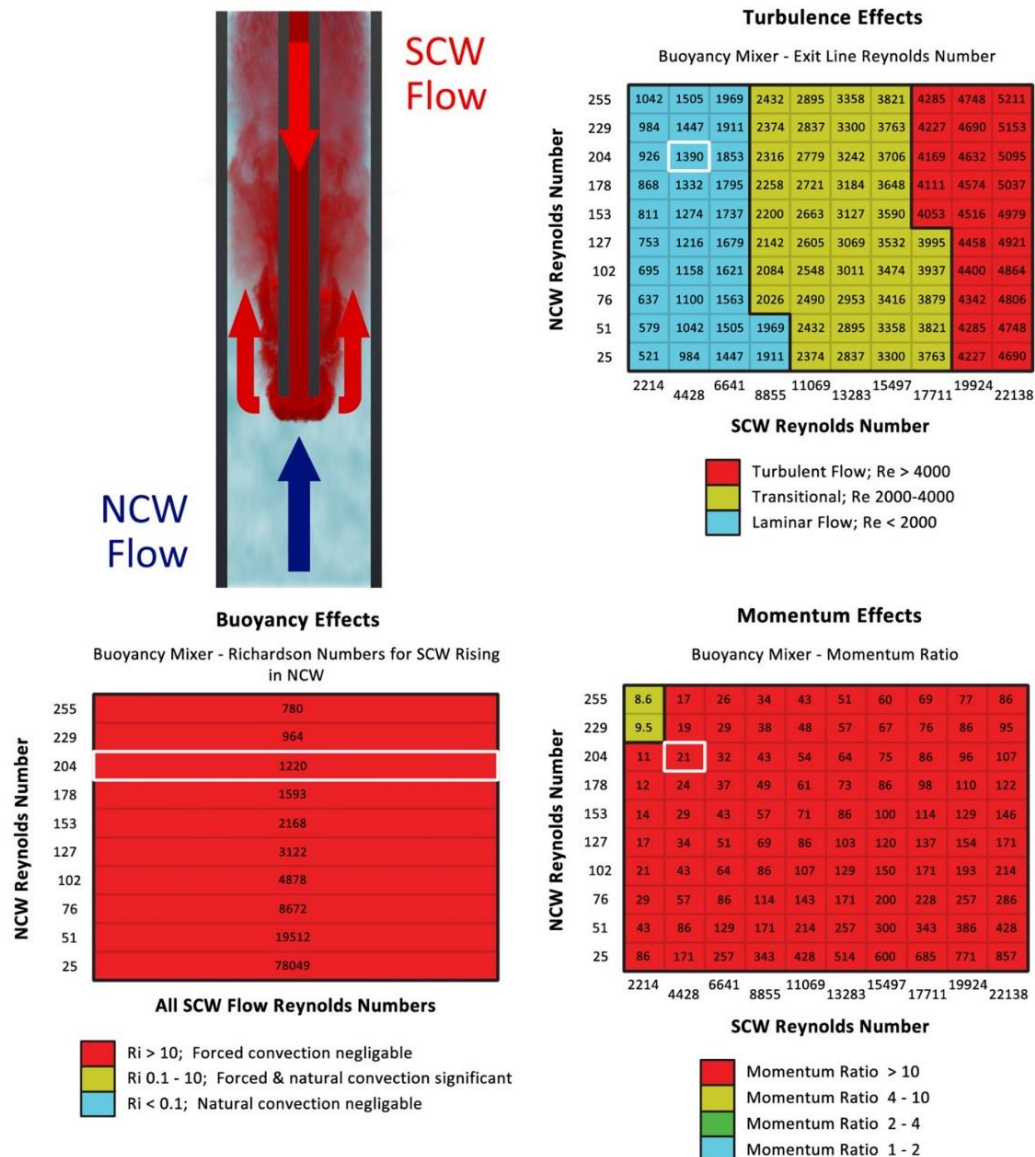


Figure 4-8. Dimensionless groups mapped onto Reynolds matrices for the laboratory buoyancy reactor illustrated in the schematic at typical N/SCW conditions, for differing inlet stream Reynolds numbers. The normal operating condition is framed in white.

Figure 4-8 shows the dimensional analysis for an actual laboratory scale, supercritical fluid buoyancy reactor. This reactor has inner and outer tube internal diameters of 1.40 mm and 4.57 mm respectively and a normal operating throughput of 0.72 kg/hr.

To interpret Figure 4-8 by referring to the preceding figures, one must assume (as noted earlier) that Reynolds matrices are independent of the scale of the measurement and nature of the fluids; the analysis of Adschiri's neutron imaging data of NCW/SCW mixing, in Figure 4-2, provided some reassurance on this.

With this assumption, the analysis shows that in this reactor, the annular flow is laminar with a Reynolds number of ~ 1400 . The momentum ratio of the supercritical water (SCW) stream is approximately 21 which is high enough to enable down mixing. The Richardson number is approximately 1200 meaning that the flow is being dominated by the buoyancy of the SCW in the cooler fluid as it enters the annular gap. Thus, the buoyancy helps to generate mixing in this region and it can be seen why the downwards injection of SCW into NCW is beneficial in this application.

4.5 Mixer Scale Up

The dimensionless analysis approach can be used to assess the likely mixing effects that would occur on scale up of the buoyancy reactor.

Throughput rates from a laboratory scale of 0.72 kg/hr (12 mL/min) to a large continuous petrochemical process scale of 360 te/hr were considered. At larger scale, fluid velocities can be higher because wall effects such as pressure drop become less important and two sets of cases were considered as summarised in Figure 4-9.

The mixer dimensions were increased by a factor of the throughput raised to the power of ~ 0.41 and ~ 0.30 for the higher diameter, lower velocity and lower diameter, higher velocity cases respectively. The significance of these scale up factors can be seen by considering the dimensionless hydrodynamic factors obtained for the cases, shown in Figure 4-10.

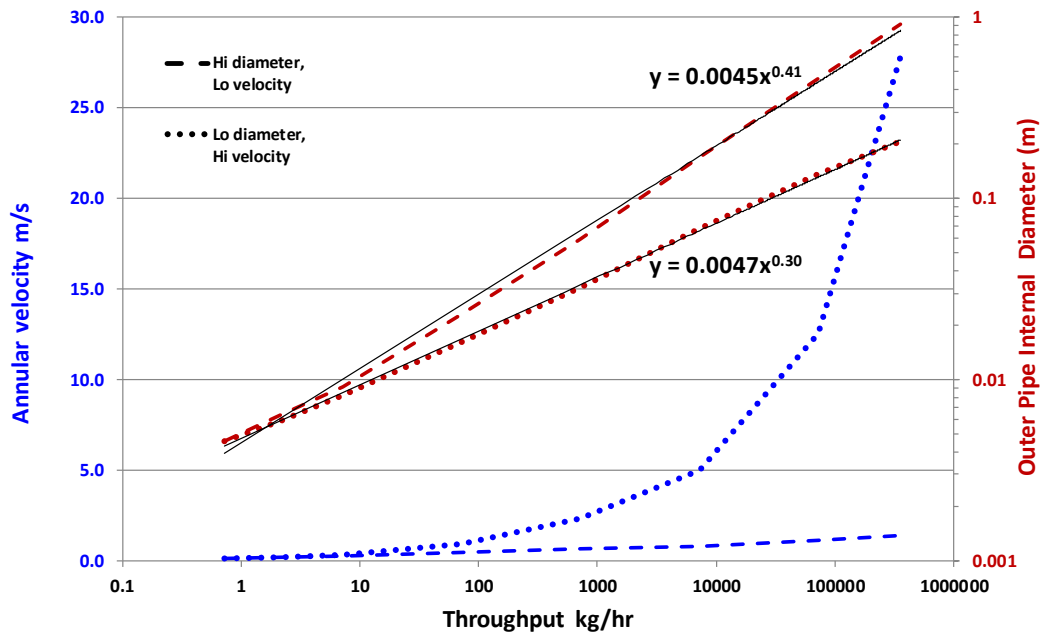


Figure 4-9. The cases assessed for buoyancy mixer scale up. Lower diameter, higher velocity (dots) and higher diameter, lower velocity (dashes) cases were assessed. The inner to outer pipe diameter was kept constant.

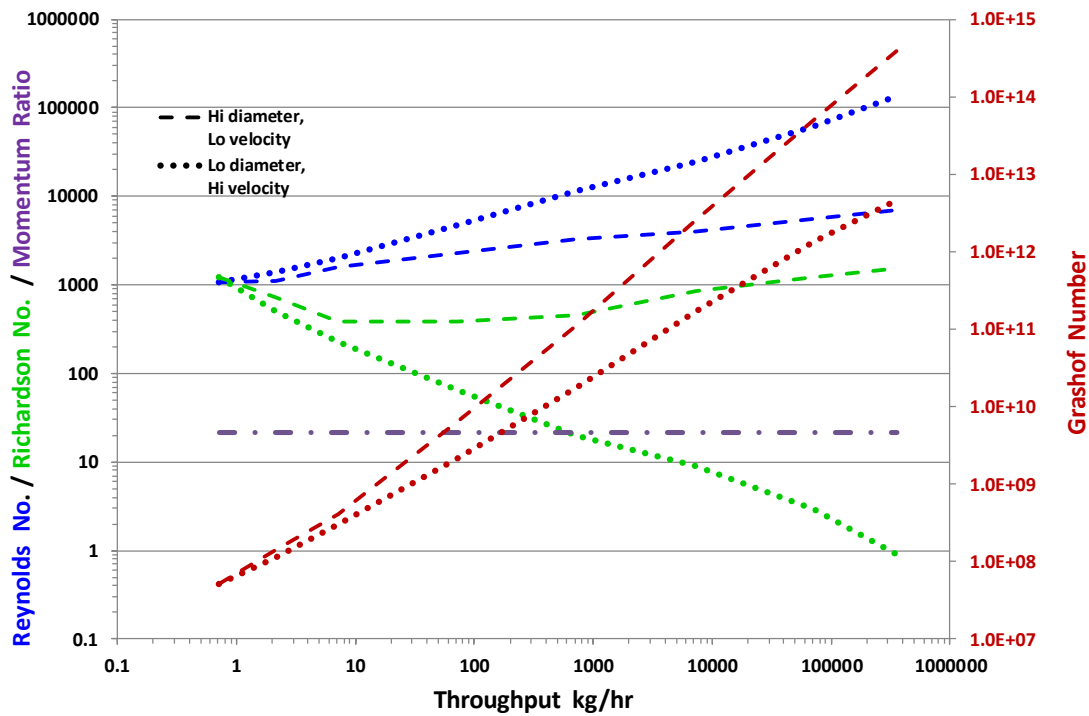


Figure 4-10. The dimensionless hydrodynamic factors obtained for the scale up cases. Lower diameter, higher velocity (dots) and higher diameter, lower velocity (dashes) cases are assessed.

For both scale up approaches, the momentum ratio is invariant with scale and is about 20 with the SCW having the larger momentum; this is the down mixing regime. Buoyancy and convection can generate turbulence at Grashof numbers of $\sim 10^8 - 10^9$ and Reynolds numbers of $\sim 2000 - 4000$ respectively; these transitions occur at throughputs of ~ 3 kg/hr and ~ 30 -100 kg/hr respectively. Thus, at small, laboratory scale, we have laminar flow with down mixing and this gives rise to transitional mixing. Turbulence becomes progressively more important at larger scales. However, the relative importance of buoyancy and convection induced turbulence varies with geometry. Buoyancy becomes unimportant (relative to convection) at a Richardson number of < 1 . Thus, buoyancy remains significant in higher diameter, lower velocity mixers where the Richardson number shows a minimum of ~ 300 . However, with low diameters and high velocities, buoyancy becomes progressively less important at larger scale and becomes unimportant at very large scale.

4.6 References

1. D. Housley, T. Huddle, E. Lester and M. Poliakoff, The use of dimensionless groups to analyse the mixing of streams with large density differences in sub- and supercritical water, *Chem. Eng. J.*, 2016, **287**, 350-358.
2. E. Perez, M. L. Thomas, D. Housley, P. A. Hamley, J. Fraga-Dubreuil, J. Li, E. Lester and M. Poliakoff, Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 3: effects of geometry and mixing in laboratory scale continuous reactors, *RSC Adv.*, 2016, **6**, 11289-11294.
3. N. Akiya and P. E. Savage, Hydrogen peroxide dissociation in supercritical water. 1 Reaction Equilibrium., *Abstr. Pap. Am. Chem. Soc.*, 1999, **217**, 692-693.
4. E. Croiset, S. F. Rice and R. G. Hanush, Hydrogen peroxide decomposition in supercritical water, *AIChE J.*, 1997, **43**, 2343-2352.
5. B. D. Phenix, J. L. DiNaro, J. W. Tester, J. B. Howard and K. A. Smith, The effects of mixing and oxidant choice on laboratory-scale measurements of supercritical water oxidation kinetics, *Ind. Eng. Chem. Res.*, 2002, **41**, 624-631.
6. NIST - Physical properties of water, <http://webbook.nist.gov/chemistry>, (Accessed September, 2017).
7. P. J. Blood, J. P. Denyer, B. J. Azzopardi, M. Poliakoff and E. Lester, A versatile flow visualisation technique for quantifying mixing in a binary system: application to continuous supercritical water hydrothermal synthesis (SWHS), *Chem. Eng. Sci.*, 2004, **59**, 2853-2861.

8. E. Lester, P. J. Blood, J. P. Denyer, D. Giddings, B. Azzopardi and M. Poliakoff, Reaction engineering: The supercritical water hydrothermal synthesis of nano-particles, *J. Supercrit. Fluids*, 2006, **37**, 209-214.
9. E. Lester, P. J. Blood, J. P. Denyer, B. J. Azzopardi, J. Li and M. Poliakoff, Impact of reactor geometry on continuous hydrothermal synthesis mixing, *Mater. Res. Innovations*, 2010, **14**, 19-26.
10. A. A. Peterson, J. W. Tester and F. Vogel, Water-in-water tracer studies of supercritical-water reversing jets using neutron radiography, *J. Supercrit. Fluids*, 2010, **54**, 250-257.
11. A. A. Peterson, P. Vontobel, F. Vogel and J. W. Tester, In situ visualization of the performance of a supercritical-water salt separator using neutron radiography, *J. Supercrit. Fluids*, 2008, **43**, 490-499.
12. A. A. Peterson, P. Vontobel, F. Vogel and J. W. Tester, Normal-phase dynamic imaging of supercritical-water salt precipitation using neutron radiography, *J. Supercrit. Fluids*, 2009, **49**, 71-78.
13. N. Takenaka, K. Sugimoto, S. Takami, K. Sugioka, T. Tsukada, T. Adschiri and Y. Saito, Application of Neutron Radiography to Flow Visualization in Supercritical Water, *Phys. Procedia*, 2013, **43**, 264-268.

5 The Optimisation of Residence Time Distribution

The importance of the reaction flow regime and of residence time distribution (RTD) was introduced in Section 2.5.3. This discussed how any RTD can be represented as combinations of the idealised RTDs of plug flow and fully back mixed arranged in series and/or parallel. Back mixing is often engineered using a continuous stirred tank reactor (CSTR) though other approaches to back mixing are possible and are discussed later in this chapter. The term CSTR is often used to describe the theoretical, idealised concept of a fully back mixed reactor in which mixing is instantaneous. In practice, a continuous stirred tank reactor has a finite mixing time though a reasonable approximation to the theoretical condition occurs provided the vessel's average residence is much greater than its mixing time. This thesis will henceforth use the term CSTR to describe the idealised concept (or a close approximation to it) and the term stirred tank reactor (STR) to describe the experimental set up which may or may not approximate to the idealised concept under a given condition. This section considers how the reactions in *pX* NCWO are affected by the RTD and considers what would be the optimal RTD to deploy and how this might be engineered.

5.1 Reaction Concentration Profiles

The main reaction pathway in *pX* oxidation has sequential reactions as discussed in Section 1.2 and illustrated in Figure 1-2.

The distribution of reactants, intermediates and products was measured for *pX* oxidation (in acetic acid solvent) in a batch reactor by Aleksandrov.¹ This work used a batch reactor which approximates to plug flow as all material is subjected to the same residence time.

The effect of RTD on reactant, intermediate and product distributions for sequential reactions has been analysed in reaction engineering texts^{2, 3} and is briefly summarised here.

Consider a system in which A reacts with O₂ to form B and B reacts with O₂ to form a final product C, where both reactions have first order kinetics. O₂ is supplied at a rate sufficient for its concentration to remain constant at its solubility (*i.e.* there is no mass transfer limitation). Thus, the reaction equation is:



And kinetic equations are:

$$-\frac{dA}{dt} = k_A[A] \quad (5-2)$$

$$\frac{dB}{dt} = k_A[A] - k_B[B] \quad (5-3)$$

$$\frac{dC}{dt} = k_B[B] \quad (5-4)$$

The component concentration equations for a fully back mixed reactor (*e.g.* a CSTR) can be summarized as:

$$C_A = C_{Ao}/(1 + k_B\tau) \quad (5-5)$$

$$C_B = (C_{Bo} + k_B\tau (C_{Ao}/(1 + k_B\tau))) \quad (5-6)$$

Where C_X is the concentration of X, C_{Xo} is the initial concentration of X, k_X is the rate constant for the consumption of X and τ is the residence time.

The component concentration equations for a plug flow reactor (PFR) can be summarized as:

$$C_A = C_{Ao} \exp(-k_B\tau) \quad (5-7)$$

$$C_B = k_B C_{Ao} / (k_C - k_B) \{ \exp(-k_B\tau) - \exp(-k_C\tau) \} + C_{Bo} \exp(-k_C\tau) \quad (5-8)$$

Conversion can be defined as:

$$\text{conversion} = \{2C_{Ao} - (2C_A - C_B)\} / (2C_{Ao}) \quad (5-9)$$

Figure 5-1 plots the concentration profiles as determined by these equations as a function of conversion for a CSTR and PFR.

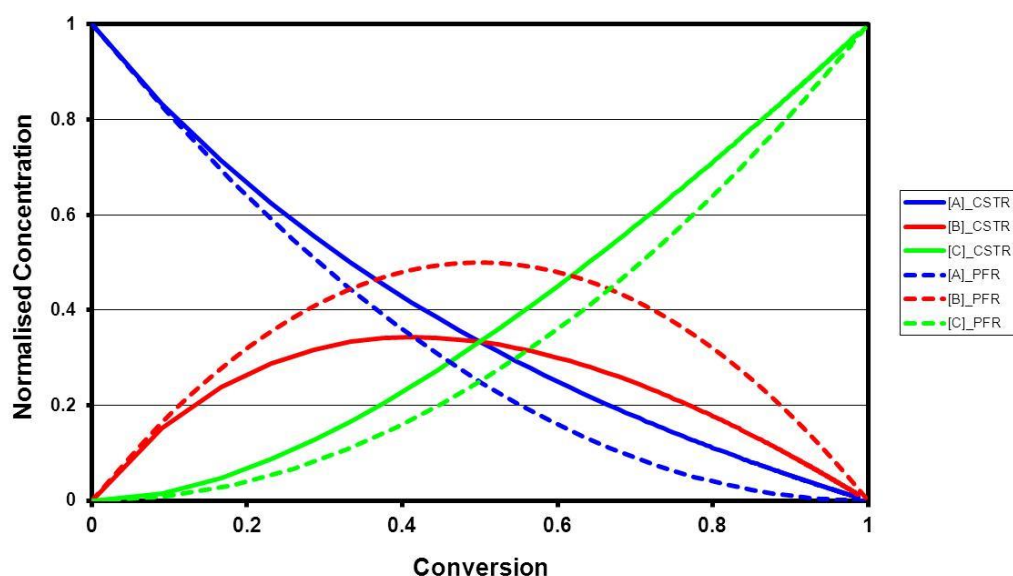


Figure 5-1. Concentration profiles in idealised reactors. Concentration profiles as a function of conversion for sequential reactions in a continuous stirred tank reactor (CSTR) and plug flow reactor (PFR). The profiles were generated with the equations given in the text using kinetic parameters: $k_B = 0.2$, $k_C = 0.1$, $C_{A0} = 1.0$, $C_{B0} = 0$.

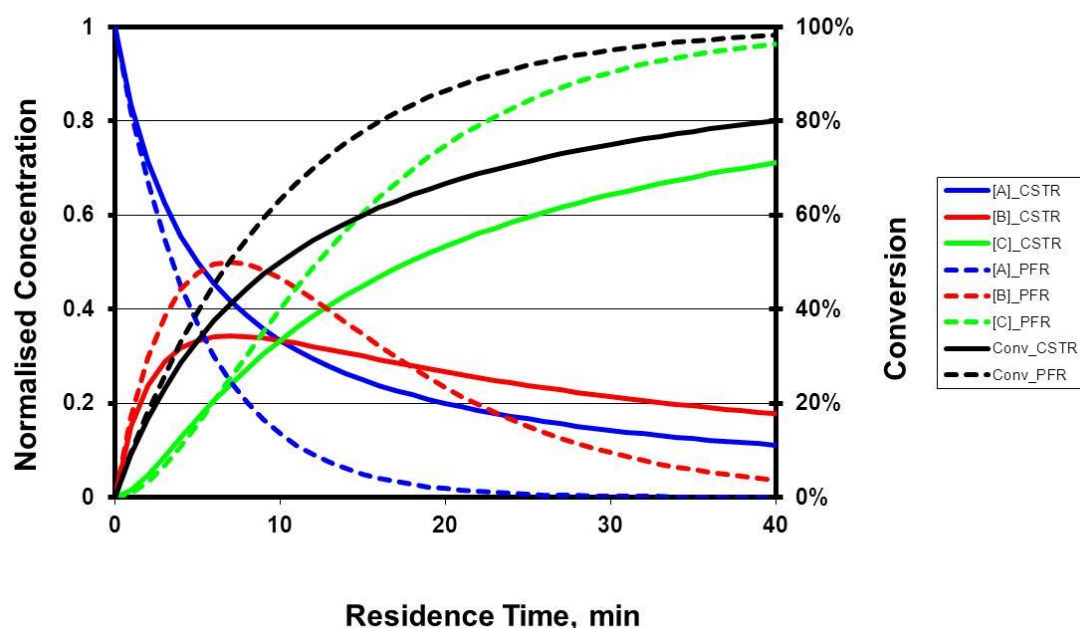


Figure 5-2. Concentration profiles as a function of residence time for sequential reactions in a continuous stirred tank reactor (CSTR) and plug flow reactor (PFR). The kinetic parameters used to generate this plot are the same as those given in Figure 5-1 and these give a reaction time typical of that used for *p*X oxidation in a CSTR in acetic acid solvent. Reaction times in NCWO are an order of magnitude lower.

This figure demonstrates that, in a PFR relative to a CSTR at a given conversion, the concentration of intermediate B is higher while the concentration of product C is lower.

Figure 5-2 shows the profiles and conversion as a function of residence time.

This figure illustrates that a PFR has higher (space time) productivity than a CSTR by a factor of ~ 2.7 (times for 80 % conversion are ~ 15 minutes and ~ 40 minutes respectively) and is better suited to drive the reaction to completion. However, there are several other considerations for the selection of the preferred reactor type. These include the removal of heat from the reactor, the co-crystallisation of TA with the reaction intermediates to produce CTA and the production rate of by products such as CO_2 , CO and the minor aromatic species, many of which are coloured and which discolour the TA. These aspects were introduced in Sections 1.3.2 through 1.3.6 of this thesis and are considered again here with regards to the RTD aspect.

The concentration profile of oxygen differs between plug flow and back mixed reactors as illustrated by profiles in Figure 5-3. In a PFR (with 1 stage of oxygen addition) all the oxygen is added at the start and is consumed along the reactor causing the concentration to fall to its exit value. An excess of oxygen is generally required, partly because in a real system oxygen is also consumed by side reactions, but also to enable the reaction to proceed to completion. The high oxygen concentration can encourage side reactions and this can create a 'vicious circle' where more oxygen is needed and this encourages further side reactions. The high oxygen concentrations in a PFR can be, at least partly, overcome by staging the oxygen, the effect of which is illustrated. In a CSTR, oxygen is added continuously and can never be fully consumed. Thus, there is an excess which can be controlled and is seen (and can be measured) as the outlet concentration. The average concentration is always lower than for a PFR for the same outlet oxygen excess.

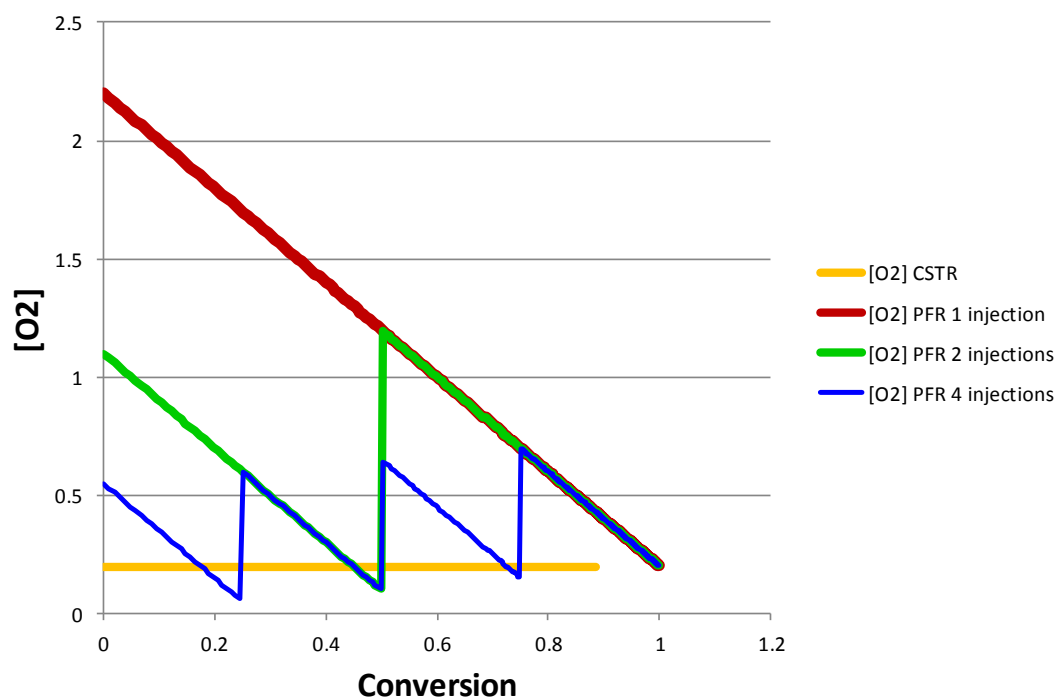


Figure 5-3. Oxygen concentration profiles for a CSTR and a PFR with 1, 2 or 4 stages of oxygen addition for the sequential reactions $A + O_2 \rightarrow B$ then $B + O_2 \rightarrow C$ where 2 moles of O_2 are required for complete conversion of A to C. For all profiles, a 10 % excess of oxygen is added. For 2 PFR O_2 stages, the additions are made at 0 and 50 % conversion and for 4 stages at 0, 25, 50 and 75 % conversion. For CSTR, oxygen is added continuously with a 10 % O_2 excess such that the exit O_2 concentration is 0.2

5.2 Heat Removal Considerations

The oxidation of pX is highly exothermic and requires heat removal for isothermal operation. In the industrial, acetic acid, STR based process heat is removed by the boiling of the acetic acid/water solvent. Heat removal cannot be by heat transfer surfaces (*e.g.* cooled walls, cooling coils *etc.*) because TA precipitates on and fouls such surfaces. Tubular PFRs are not suited for boiling and thus heat removal is problematic for such reactors. This restriction cannot be overcome by adiabatic operation (*i.e.* having no cooling and allowing the reaction temperature to rise) because the heat rise would be excessive for this system at the high pX concentrations required for commercial operation. However, the restriction could be overcome by the use of multiple CSTRs in series which would approximate to PFR operation.²

5.3 Conversion and Recycle

In the industrial TA process, the reaction is performed at very high conversion (> 99 %) because the reaction is highly selective to TA even under these forcing conditions. Not all industrial oxidations are like this *e.g.* the oxidation of ethylene to ethylene oxide ⁴ is undertaken at low conversion because of poor selectivity at higher conversions. Unconverted ethylene is recycled and this requires a large recycle stream. This illustrates a dominating factor for industrial commodity chemicals reactors, that in general the need for high selectivity trumps all the other aspects of design. In other words, large and expensive plant is usually economic provided it delivers a (relatively) high overall selectivity to the desired product compared to other (probably capitally cheaper) designs giving lower selectivity.

A CSTR operates at a single condition throughout the reactor. Figure 5-1 illustrates that at high conversion (to the final product C), the concentration of the final reaction intermediate (B) has been driven to a low level and in the acetic based, industrial process this is an important advantage because the incorporation of 4-CBA into CTA by co-crystallisation is minimised. In contrast, a PFR operates under the full range of conversions along its length and TA can therefore precipitate in regions containing high 4-CBA thus producing highly impure CTA that cannot subsequently be economically purified. A PFR is therefore unsuitable for this duty. However, in a solution based process such as *pX* N/SCWO, the TA does not precipitate and therefore this constraint does not apply.

5.4 Effect on By-Products

We now need to consider the effect of RTD on the production rate of by-products such as CO₂, CO and minor aromatic products. Such products can represent significant yield losses and create highly problematic product quality issues. Often yield loss can represent a significant process variable cost and determine the industrial viability of the process. For this reason, these by-product formation rates are given detailed consideration in this section while the variable cost, process economics and viability will be considered in Chapter 8.

The minor products formed in *pX* N/SCWO are discussed in Sections 1.3.2 to 1.3.4 of this thesis. The effect of RTD on by-product formation was studied by measuring the formation rate of these species for plug flow and back mixed reactor configurations.

5.5 The Engineering of a Plug Flow Reactor

The designs of reactor used historically to develop *pX* N/SCWO were tubular reactors as discussed in Section 2.3.1. Section 2.5.3 considered the reactor Reynolds number that could be achieved with these designs and demonstrated that the flows being achieved were laminar in nature. It showed that axial dispersion occurs in laminar flow as illustrated in Figure 2-9 and that the UoN reactors are therefore not plug flow under these conditions. To achieve plug flow in tubular reactors, it is necessary to work at higher (non-laminar) Reynolds numbers. Table 2-3 demonstrates that higher Reynolds numbers can be achieved by using lower diameter tubing, however in the *pX* N/SCWO system such small bores are likely to block as discussed in Section 2.5.3. However, plug flow can be achieved by using higher flow rates (and hence higher Reynolds) with ¼" O.D. reactor tubing. It was determined that larger HPLC pumps were available from Gilson (as discussed in Section 3.3.2) with flow rates of 50 mL/min and the hydrodynamic conditions that could be achieved with these pumps are detailed in Figure 2-10 and Figure 5-4. This illustrates that using two 50 mL/min and one 25 mL/min pump, it was possible to achieve a Reynolds number of $\sim 10^4$ under sub critical conditions. In pipe flow, the transition to turbulent flow starts at Reynolds numbers of ~ 2000 . Figure 2-9 quantifies the degree of axial dispersion achieved as a function of Reynolds number and shows that at Re of 10^4 , $\sim 90\%$ of full turbulence has been achieved. It was decided that this was the best that could be practically be engineered at reasonable cost with the resources available.

Reactor volume ml	6.4	6.4	6.4	6.4	6.4	6.4	17.1	17.1
Ambient flow rate mls/min	24	24	24	24	12	24	57	124
Temperature C	300	330	360	380	330	330	330	330
Pressure bar	230	230	230	230	230	230	230	230
Phase	liquid	liquid	liquid	supercritical	liquid	liquid	liquid	liquid
Density kg/m ³	740	675	576	209	675	675	675	675
Viscosity cP	0.091	0.080	0.066	0.031	0.080	0.080	0.080	0.080
Flow rate at T&P mls/min	32.4	35.5	41.7	115.0	17.8	35.5	84.4	183.6
Residence time s	11.8	10.8	9.2	3.3	21.6	10.8	12.2	5.6
Reynolds Number	1836	2092	2519	5443	1046	2092	4968	10808

Figure 5-4. This illustrates the Reynolds numbers that can be achieved with near critical and supercritical conditions and with higher flow rate subcritical conditions. It illustrates that under near critical conditions, turbulent flow could not be achieved with the 25 mL/min pumps. Larger pumps enable $Re \sim 10^4$. The residence time of the reactor was reduced because the original ~ 21.6 s had been shown to be excessive and because of space restrictions in the sand bath.

Thus, with the use of these larger HPLC pumps it was possible to study the transition from laminar to turbulent flow in a tubular reactor.

5.6 The Engineering of a Back Mixed Reactor

Various approaches to back mixing for a reactor suitable for pX N/SCWO were considered. These were:

- Jet mixed venturi loop reactor
- Jet mixed reactor
- Thermosiphon reactor
- Stirred tank reactor (STR)

All these concepts were considered and (to varying extents) prototyped as is described in the following sections.

5.6.1 Jet Mixed Reactors

A jet mixed venturi loop reactor comprises a reactor loop containing a jetted venturi injection point, which drives the loop circulation, and an outlet line. Material is introduced to the reactor through the jet and this entrains material in the loop and imparts momentum to it thus driving the loop circulation giving rise to reactor back mixing. A prototype reactor was built using $\frac{1}{4}$ " O.D. tubing and some water trials were undertaken using ink (whose concentration could be

measured by absorption) to determine the degree of back mixing that was being obtained. The trial showed that little circulation could be achieved in the loop at this scale and that most of the material was passing from the injection jet to the outlet pipe without undergoing circulation. It is probable that the high surface area to volume ratio at such small scale causes excess pressure drop (through friction of the fluid with the walls) and makes it difficult to achieve the necessary pressure profile to drive a circulation. This approach to obtaining back mixing was therefore abandoned.

A jet mixed reactor uses the energy and momentum of the injected material to mix a reaction chamber. A reactor was built using this concept is illustrated in the drawings and photographs of Figures 5-5 and 5-6.

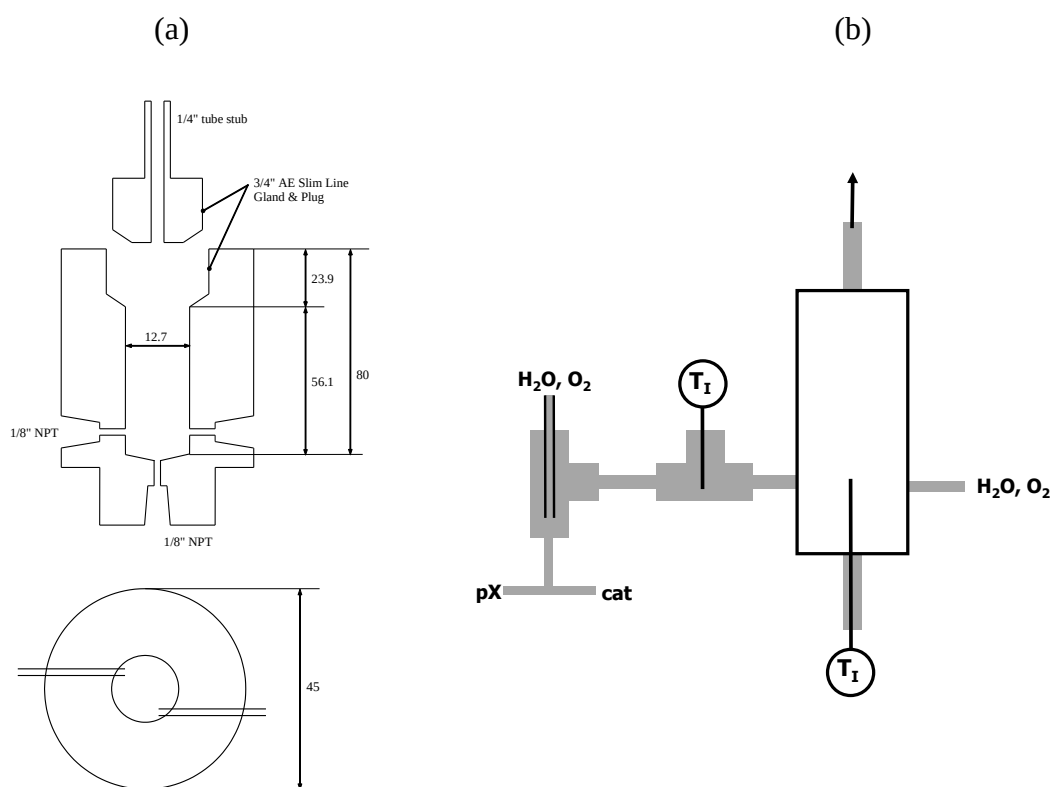


Figure 5-5. The jet mixed reactor. (a) shows the construction and sizing and (b) shows the layout of the feeds. This scheme used staged oxygen injection with the first oxygen slug injected into a buoyancy mixer and a second slug into the jet mixed reactor.

Two problems were encountered with this reactor design. First a flow simulation, commissioned by the author, using the technique of computational fluid dynamics (CFD) demonstrated that the flow being obtained was plug flow in nature as

illustrated in Figure 5-6(b). The technique of CFD and its application to flows in N/SCW systems is described in the literature.^{5, 6} Secondly, Section 3.4.2 describes how the metal bromide catalysts in this system are prone to hydrolysis and precipitation as metal oxides, especially when using manganese based catalyst. The outlet of this reactor proved to be ineffective at removing the precipitated catalyst material causing the reactor chamber to gradually fill up with precipitated metal oxide and this design was thus highly prone to blockage. For these reasons, the jet mixed reactor approach to achieving back mixing was discontinued.

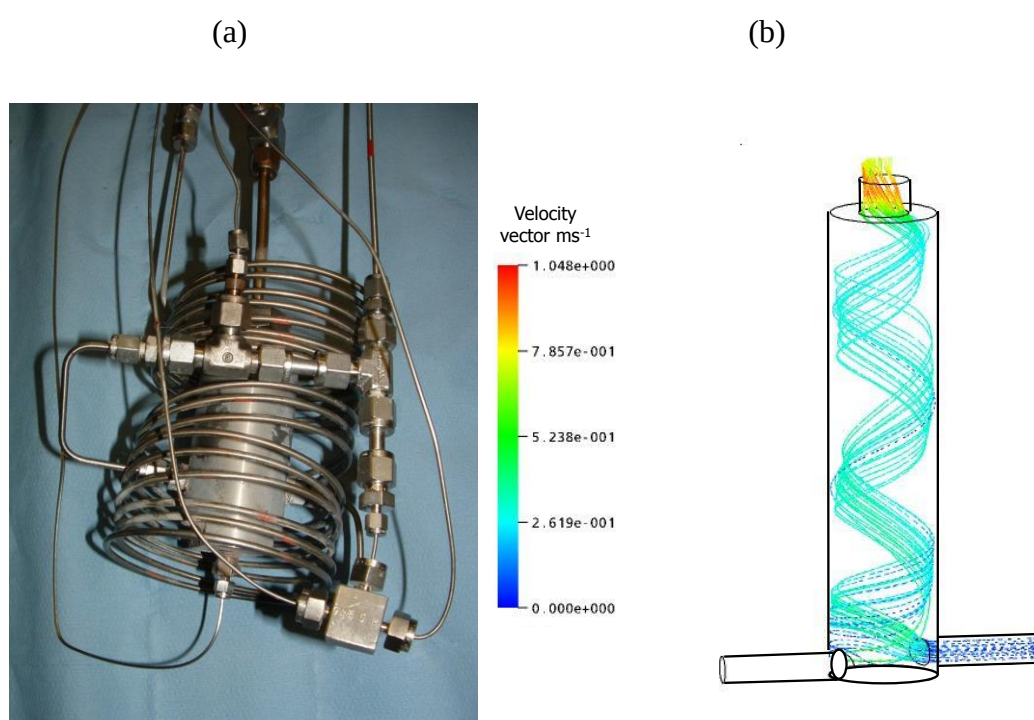


Figure 5-6. (a) shows a photograph of the jet mixed reactor as constructed. This arrangement was suitable for insertion into the sand bath. The layout of the feeds can be discerned referencing Figure 5-5. The coil around the reactor forms a pre-heater for the second O_2 /water injection. (b) is output from a CFD simulation of the jet mixed reactor. It shows velocity vectors and stream lines for the flow. It shows an upward swirling flow from feed points to the reactor exit with minimal recirculation of the flow. Thus, the flow is largely plug flow in character.

5.6.2 Thermosiphon Reactor

A thermosiphon reactor uses density differences to drive a fluid circulation in a vertically orientated, donut shaped loop. For pX N/SCWO, the concept could be implemented as follows. pX and oxygen would be injected into NCW at the low

point of the reactor loop. The *pX* oxidation would generate heat causing the reactor liquor to become supercritical and its density to fall. The buoyancy of this low-density material would drive the circulation in the up-flow section of the loop. As the flow reaches the high point of the reactor, it would enter a cooling section where colder water is injected, the liquor would cool to sub critical, its density would increase and its negative buoyancy would drive circulation in the down flow section of the loop. A paper study of this thermosiphon concept for *pX* N/SCWO was commissioned by the author. This study concluded that this concept could likely be made to work at large scale but was unlikely to be successful at small scale because of the high heat losses associated with small scale equipment. It would also be difficult to determine the degree of circulation occurring in the loop and hence the degree of back mixing being achieved. For these reasons, the author decided not to prototype this reactor concept.

5.6.3 Stirred Tank Reactor

A stirred tank reactor (STR) comprises a reaction space that is agitated by a rotating impeller. For a flowing system, reactants continuously flow in and products, reaction intermediates and unreacted reactants continuously flow out. Such a reaction system, suitable for the high pressure and temperature conditions of *pX* N/SCWO, was identified and procured. The manufacturer was Inox Design Limited and the supplier was Labtex Limited. Photographs of the unit's components parts are given in Figure 5-7.

The unit comprised a reaction chamber of diameter 32 mm. A plug could be inserted into the chamber on which were welded four baffles. Two plug sizes were available which enabled the reactor volume to be either 50 mL or 20 mL. The reactor exit was at the base of the vessel and a hole was drilled through the baffle mounting plug to allow vessel contents to flow to this outlet. The contents were stirred with an impeller comprising one or two flat blades turbines of diameter 16 mm suitable for agitating the 20 mL and 50 mL reaction volumes respectively. The impeller was driven by an air driven motor with a magnetic coupling between the external and internal stirrer shafts. The hydrodynamic conditions that could be achieved with this reactor are shown in Figure 5-8.

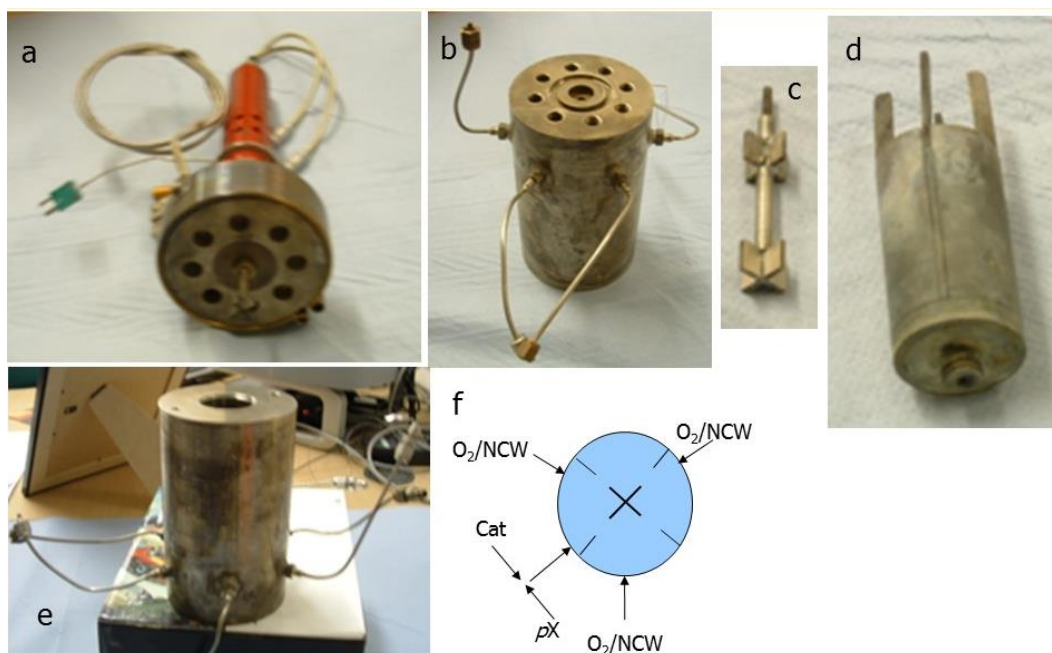


Figure 5-7. Photographs of the constituent parts of the stirred tank reactor deployed for *pX* N/SCWO. (e) shows the main body of the reactor (upside down) with the reaction chamber visible. (d) shows the threaded titanium plug with baffles that is inserted into the chamber and secured by screwing it into position – the plug shown is sized to give a 20 mL reaction volume; a smaller plug was also available which gave a 50 mL reaction volume. The plug has a hole drilled down its middle which terminates in a fitting which is clearly visible and this provides the outlet channel to the base of the reactor. (c) shows the impeller shaft (with two sets of flat impeller blades) suitable for use with the 50 mL reactor volume; a shorter impeller with one set of blades, suitable for the 20 mL reaction volume, was also available. This shaft and impeller assembly was made from titanium. (a) shows the head assembly with the shaft motor. The coupling between the motor and the impeller shaft was by magneto drive (*i.e.* a magnetic coupling). This assembly slotted onto the main body, shown in its upright position in (b), and was secured in place with 8 bolts whose bolt holes are clearly visible. The impeller shaft could then be inserted into the main chamber and screwed to the shaft and the base plug (with baffles) inserted and screwed into place. In (b), (four of) the six feed points and feed lines into the reactor are clearly visible and these feed into the top part of the reaction chamber. (f) shows how the feeds were orientated with three oxygen/NCW feeds and one catalyst/*pX* feed; only four of the six available feed points were used. The exact positioning of the feed points relative to the baffles was not recorded.

There were six feed points to the vessel through feed lines that fed into the top of the reaction space though only four were used as illustrated in Figure 5-7(f). The vessel shell material was Hastelloy C276. The internals (plug, baffles and impellers) were constructed from titanium. The vessel pressure rating was 400 bar and its temperature rating was 500 °C.

Agitator speed rpm	41	200	400	600	800	1000	1200	1400	1400	1400
Temperature C	300	300	300	300	300	300	300	300	330	360
Pressure bar	200	200	200	200	200	200	200	200	200	200
Density kg/m3	735	735	735	735	735	735	735	735	667	548
Viscosity (cP)	9.0E-02	9.0E-02	9.0E-02	9.0E-02	9.0E-02	9.0E-02	9.0E-02	9.0E-02	7.8E-02	6.3E-02
Reynolds number	1427	6962	13924	20887	27849	34811	41773	48735	50737	52122
Mixing Time, T90 (s)	251	11.2	2.92	1.32	0.75	0.49	0.34	0.25	0.25	0.25

Reactor Volume ml	20	20	20	20
Ambient flow rate ml/min	11	22	33	44
Temperature C	300	300	300	300
Pressure bar	200	200	200	200
Density kg/m3	735	735	735	735
Viscosity (cP)	9.0E-02	9.0E-02	9.0E-02	9.0E-02
Flow rate at T&P ml/min	15.0	29.9	44.9	59.9
Residence time s	80.2	40.1	26.7	20.0

Figure 5-8. The hydrodynamic conditions that could be achieved with the STR design as installed. The upper table shows the Reynolds numbers and mixing times obtained with different impeller speeds. 41 rpm was the lowest possible impeller speed and gives laminar conditions (*i.e.* $Re < 2000$). Operation with a stationary shaft was not considered wise because of the risk of shaft seizure. All the other operating conditions gave turbulent conditions (*i.e.* $Re > 2000$). T&P is temperature & pressure. The highest Reynolds number that could be achieved was ~50000 and this was ~5 times higher than that possible on the tubular reactors employed as can be seen by comparison to the tubular reactor hydrodynamic conditions given in Figures 2-10 and 2-11. The lower table shows the residence times that could be achieved with differing flow rates. At higher agitation speeds the vessel mixing times are much shorter than the residence time and so the reactor approximates to a CSTR. However, at lower agitator speeds ($< \sim 200$ rpm), mixing times are similar to the residence times so the reactor will have some plug flow characteristic and the CSTR approximation is not valid. CSTR mixing times were estimated from the correlation $T_m = 3.9(P/V)^{-0.333}/N$ where T_m is mixing time (s), (P/V) is power/unit volume (kW/m^3) and N is impeller speed (s^{-1}).

This CSTR approach to engineering a back mixed reactor was successful and the reactor was used in the studies described in the following sections.

5.7 Summary of Hydrodynamic Regimes Achieved

The preceding sections have discussed the extent to which the tubular and stirred vessel reactors achieved the idealised flow regimes of plug flow reactor (PFR) and continuous stirred tank reactor (CSTR). The hydrodynamic regimes that could be achieved with each reactor type are summarised in Figure 5-9.

	Tubular	Stirred vessel
Laminar	Axial dispersion but short diffusion path lengths. Plug flow(ish)	Residence time < mixing time. Long diffusion path lengths. Plug flow(ish) & poor O₂/<i>pX</i> mixing
Turbulent	Plug flow	Back mixed CSTR

Figure 5-9. Summary of the hydrodynamic regimes that were achieved for *pX* NCWO using tubular and stirrer tank reactors. Under turbulent flow conditions, both reactor types closely approximated the desired, idealised flow regimes. Under laminar flow conditions, both reactor types deviated significantly from the idealised flow regimes.

5.8 Experimental Studies

5.8.1 Introduction

In the preceding sections, we have discussed how plug flow and back mixed reactors were engineered for the *pX* N/SCWO system using a TBR and STR respectively.

In the next sections, we look at experiments which were undertaken to address these important mixing questions with regards this system:

- What is the effect of the transition from laminar flow to turbulent flow on reaction outcomes?

- How does the use of a tubular and STR affect the reaction outcome?
- What could be the optimum reactor configuration for this reaction?

These questions are considered with regards to the key industrial metrics for *pX* oxidation, *i.e.* the total oxidation to CO₂ and CO and the formation of minor colour components.

5.8.2 The Transition from Laminar to Turbulent Flow in a Stirred Tank Reactor

The hydrodynamic conditions that could be achieved in the *pX* N/SCWO STR are given in Figure 5-8 and summarised in Figure 5-9. The STR could operate well into the turbulent regime at higher stirrer speeds. At low impeller speeds (below ~50 rpm) laminar flow occurred and the vessel was poorly mixed and no longer approximated to an idealised CSTR.

A series of *pX* NCWOs were run over this range of hydrodynamic conditions. Figure 5-10 gives the process conditions used and the reactor outputs that were obtained as a function of Reynolds number. In the laminar to turbulent transition (*i.e.* over the Reynolds number range 0 to 10000) the *p*-toluic acid concentration fell indicating an increase in reaction conversion. In the turbulent regime (*i.e.* at Reynolds numbers above 10000) the conversion was reasonably constant. Oxidation to produce CO₂ showed a similar pattern, dropping in the laminar to turbulent transition and being constant in the turbulent regime. The total oxidation to CO₂ was approximately double under the laminar condition and this is probably caused by the poor mixing and the vessel no longer being an idealised CSTR.

The figure also shows the dependence of by-product formation on the Reynolds number. The aryl radical derived and benzyl radical derived minor species show differing patterns of dependence on Reynolds number.

The mechanisms for the formation of cross linked aromatic by-products were discussed in Section 1.3.3 of this thesis. Some species (*e.g.* DCF, BPTC and diphenic acid) are formed by the reaction of aryl radicals with aromatic

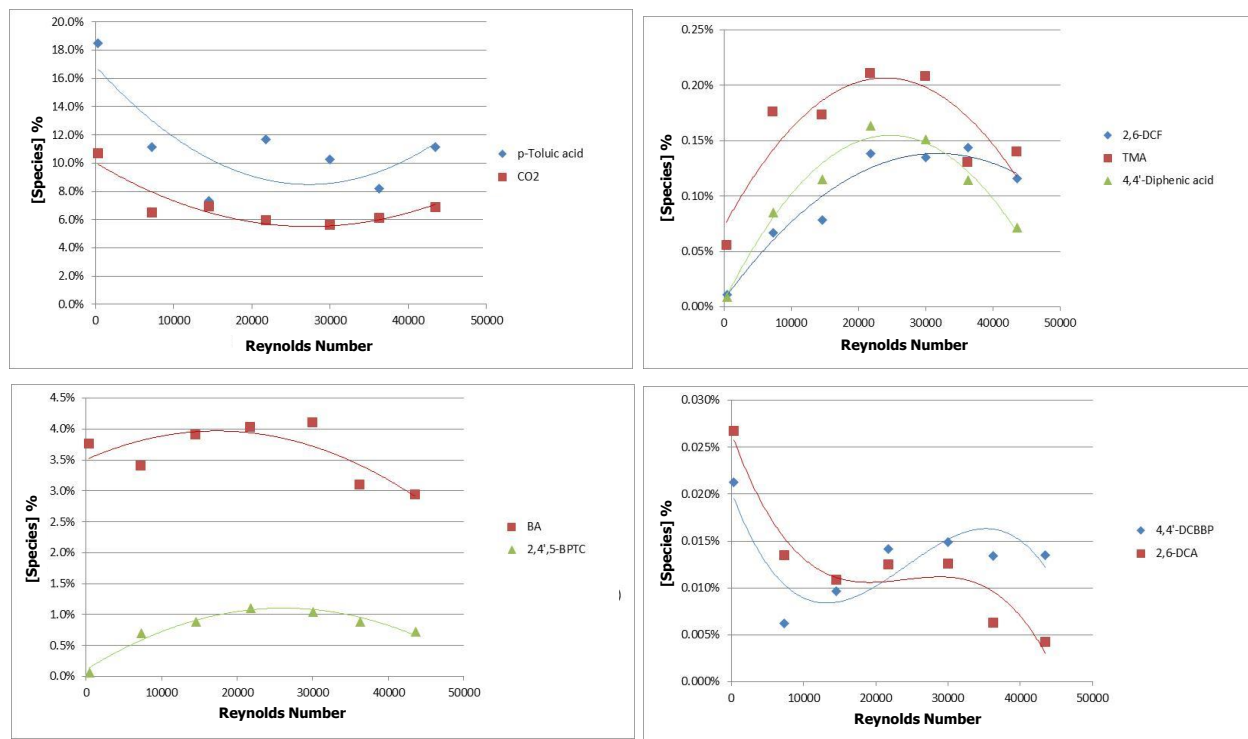


Figure 5-10. The formation of the intermediate *p*-toluic acid, of the oxidation product CO₂ and of minor by-products as a function of Reynolds number for *p*X NCWO in a stirred tank reactor. [Species] is species concentration expressed as % of *p*X fed converted to that species. Aryl radical derived species are 2,6-dicarboxyfluorenone (DCF), 2,4',5-biphenyltricarboxylic acid (BPTC), 4,4'-diphenic acid and benzoic acid (BA). Benzyl radical derived species are 2,6-dicarboxyanthraquinone (DCA) and 4,4'-dicarboxybenzophenone (DCBBP). The system contains no acetic acid and so trimellitic acid (TMA) is likely to be derived by intermolecular transfer of labile methyl groups. Lines are Excel fits (2nd or 3rd order polynomials) and are for guidance of the eye. Conditions were 20 mL reactor volume, 18 s residence time, 330 °C, CoBr₂/CuBr₂/HBr catalyst, 130 % stoichiometric oxygen (for full conversion of *p*X to TA) except for the lowest Reynolds number (41 rpm) case where conditions were 27 s, 300 °C, 115 % O₂. Each data point is the average of ~6 separate measurements with standard deviations (σ) as follows $\sigma(p\text{-toluic})$ 1.61 %, $\sigma(\text{CO}_2)$ 0.43 %, $\sigma(\text{DCF})$ 0.024 %, $\sigma(\text{TMA})$ 0.022 %, $\sigma(\text{diphenic})$ 0.024 %, $\sigma(\text{BA})$ 0.245 %, $\sigma(\text{BPTC})$ 0.125 %, $\sigma(\text{DCBBP})$ 0.0033 %, $\sigma(\text{DCA})$ 0.0033 %.

intermediates species in solution. These species show a peak in formation rate at a Reynolds number of $\sim 20000 - 30000$. The lower formation rate at higher Reynolds numbers probably reflects better mixing and the contacting of aryl radicals with oxygen which encourages oxidation of the radicals and suppresses by-product formation. At lower Reynolds numbers, mixing becomes progressively worse and the aryl radicals have less opportunity to contact oxygen. The formation of the (fully oxidised) by-products proceeds through precursors in which the methyl groups are un-oxidised or only partially oxidised *e.g.* 2,6-dimethyl fluorenone would be a precursor to 2,6-dicarboxy fluorenone. The reduced levels of (the fully oxidised) by-products seen is thus likely attributable to reduced oxidation of these precursors species. Unfortunately, HPLC methods to measure these partially oxidised precursors were not available and these compounds are not available to purchase. Thus, it was not possible to develop suitable HPLC methods within the scope of this PhD project.

The pattern of formation of benzoic acid differs from the other aryl derived by-products in that its formation rate does not fall away as strongly at low Reynolds numbers. This probably reflects the difference in the mechanism of formation of this species; the aryl radical does not need to cross link with another aromatic but merely needs to abstract a hydrogen and to oxidise. The aryl precursor is mono methyl substituted and thus more easily oxidised than the di and tri substituted precursors of the other aryl radical derived by-products. It is thus more easily formed in the oxygen lean conditions that occur at low Reynolds numbers with poor mixing.

Other types of by-products (*e.g.* DCBBP, DCA) are formed by the reaction of benzyl radicals with aromatic intermediates species in solution. Figure 5-10 shows that these species show a different pattern of dependence on Reynolds number to the aryl radical derived species. They show a high formation rate at low Reynolds number and a flatter response at increasing turbulence. This could suggest that these side reactions favour the more highly oxidised (*i.e.* carboxy substituted) benzyl radicals over the less highly oxidised (*i.e.* methyl substituted) benzyl radicals.

The pattern of TMA formation is similar to that of the aryl radical derived minor species. TMA is thought to occur by the coupling of methyl radicals onto the ring of disubstituted intermediates. In the acetic acid system, the major source of methyl radicals is acetic acid. In N/SCWO, methyl radicals cannot arise from this source and the presence of TMA (as a product) suggests that the methyl groups are (to some extent) labile. The drop in the TMA levels at low and high Reynolds numbers is probably due to similar mechanisms to the drop in the aryl derived species such as DCF.

From these discussions, it can be seen that the dependence of the formation rate of the cross-linked by-products on Reynolds number varies somewhat and that these variations can be attributed to a complex interaction between their mechanisms of formation and the mixing that is occurring.

It is clear, that in a stirred tank reactor, high Reynolds number and its associated good mixing is the preferred hydrodynamic regime for *pX* NCWO.

5.8.3 The Transition from Laminar to Turbulent Flow in a Tubular Reactor

The hydrodynamic conditions that could be achieved in a tubular reactor were summarised in Figure 5-4. A series of *pX* NCWOs were run over this range of hydrodynamic conditions. The formation rates of intermediates and by-products obtained under these conditions are given in Figure 5-11.

In a tubular reactor, the easiest method of varying Reynolds number is by changing flow rate but this also changes the residence time. To keep residence time constant, it would be necessary to build multiple reactors of differing volumes and this is expensive and time consuming. As a compromise, these experiments were conducted in two reactors of volumes 17.1 and 6.4 mL. The conditions that were achieved were residence times of ~24, 12, 13 and 6 seconds at Reynolds numbers of 920, 1840, 4360 and 9480 respectively. This variation (in residence time) is not ideal and this needs to be born in mind when interpreting the results. The transition to turbulence begins at a Reynolds number of 2000; Figure 2-9 shows that at a Reynolds number of 10^4 , a flow is about 90 % turbulent as measured by the reduction in the degree of axial dispersion.

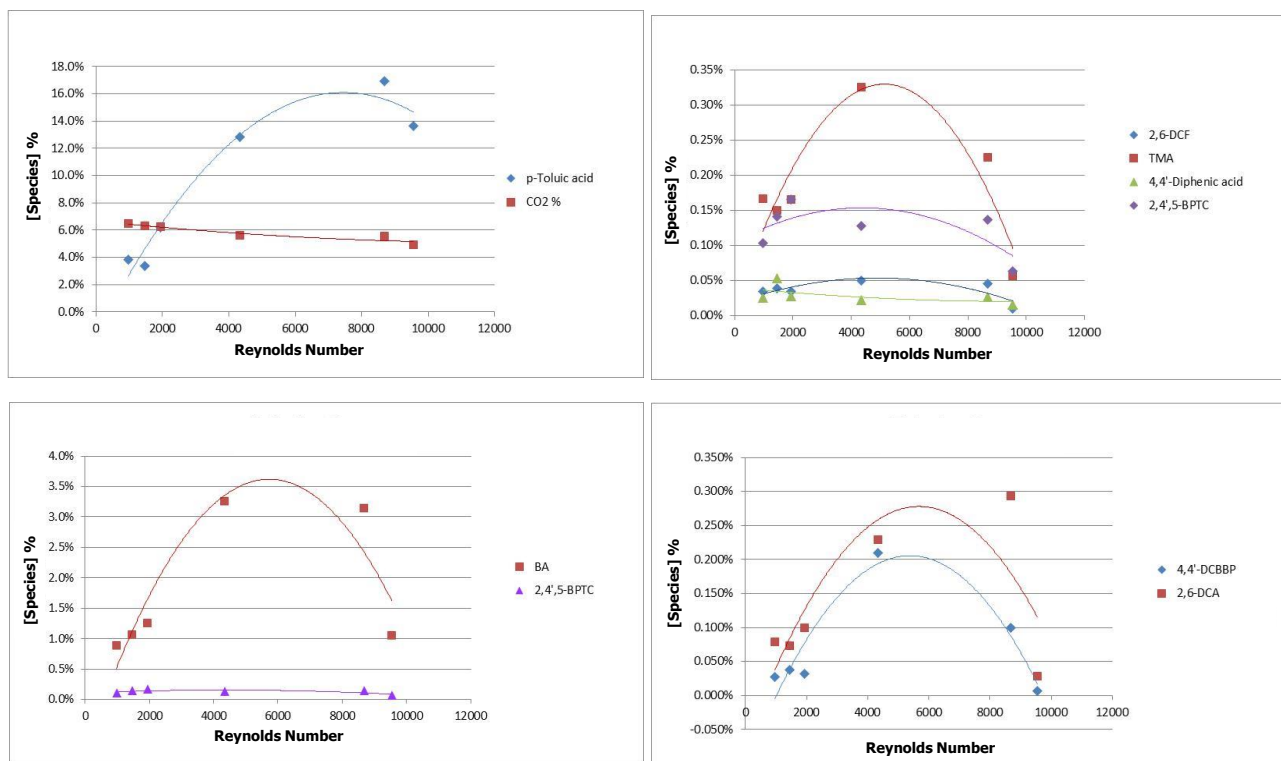


Figure 5-11. The formation of the intermediate *p*-toluic acid, of the oxidation product CO₂ and of minor by-products as a function of Reynolds number for *p*X NCWO in a tubular reactor. [Species] is species concentration expressed as % of *p*X fed converted to that species. Lines are Excel fits (2nd order polynomials) and are for guidance of the eye. Conditions were kinetics rig, welded reactor, 6.4mL and 17.1 mL reactor volumes, 12.7-125 mL/min ambient flow rates, 1.82 % *p*X in feed, 4 stage O₂ addition through tee-pieces, CoBr₂/CuBr₂/HBr catalyst, 300 °C, 230 bar, 115 % stoichiometric oxygen (for full conversion of *p*X to TA). Each data point is the average of between 7 - 29 separate data points with standard deviations (σ) as follows σ (*p*-toluic) 7.03 %, σ (CO₂) 1.01 %, σ (DCF) 0.016 %, σ (TMA) 0.087 %, σ (diphenic) 0.019 %, σ (BA) 0.538 %, σ (BPTC) 0.064 %, σ (DCBBP) 0.046 %, σ (DCA) 0.108 %.

Figure 5-11 shows that at low Reynolds numbers (1000 – 4000), as turbulence is increased, the *p*-toluic acid is also increasing. The dependence of an intermediate (such as *p*-toluic acid) on conversion and residence time is illustrated in Figures 5-1 and 5-2 respectively; the data is probably climbing the left side of this intermediate curve, *i.e.* conversion is increasing with turbulence. In the Re range 4000-10000 the *p*-toluic acid response is much flatter suggesting that we have reached the peak region of the intermediate curve. The formation of by-products, in these experiments, shows two patterns of response. CO₂ and 4,4'-diphenic acid decrease as Reynolds number increases while all the other by-products increase, peak and then decline. The interpretation of these observations needs to consider both the variation of conversion (*i.e.* the variation of *p*-toluic acid) and the variation in mixing (*i.e.* Reynolds number).

Section 1.3.2 discusses the aromatic total oxidation mechanisms, Section 6.4.2 illustrates that oxidation to CO₂ increases as conversion is increased and Section 4.2 discusses the mechanisms by which poor mixing increases total oxidation. The response of the CO₂ in these experiments (*i.e.* a decrease with increasing conversion and increasing turbulence) suggests that the improved mixing is dominating.

Section 1.3.3 discusses the mechanism of formation of the aromatic by-products, Section 6.4.2 illustrates that aromatic by-products increase as conversion is increased while the mixing discussion in the preceding CSTR section considered the way in which the formation of (undetected) precursors to by-products can mask by-product formation. Section 4.2 discusses the mechanism by which poor mixing increases by-products. The response of the aromatic by-products in these experiments (*i.e.* an increase, peak then decrease with increasing conversion and increasing turbulence) suggests that at low Reynolds numbers and conversions the mixing effect and conversion effects are combining while at higher Reynolds numbers and conversions the mixing effect is dominating. The exception is the 4,4'-diphenic response and this perhaps reflects the difference in formation

mechanism of this species (arising from the coupling of an aryl radical and a mono-substituted aromatic) as discussed in Section 1.3.3.

5.8.4 The Comparison of Tubular and Stirred Tank Reactors

In the preceding sections, we have considered the response of reaction by-products to the degree of mixing in a stirred vessel and a tubular reactor. We can use this data to undertake a comparison of these reactor types. There was some variation in the experimental conditions used in these experiments as summarised in Table 5-1.

Table 5-1. Comparison of experimental conditions for *p*X NCWO STR and TBR comparison.

	Stirred Tank Reactor	Stirred tank Reactor	Tubular Reactor
Temperature °C	330	300	300
Pressure bar	200	200	230
[<i>p</i> X] %	2	2	2.0
Catalyst	(Co:Cu):Br (0.85:0.16):3.23 by mass added as CoBr ₂ /CuBr ₂ /HBr		
[Br] M	0.024	0.024	0.049
Oxygen stoichiometry %	130	115	115
Oxygen profile	1 feed to mixer, 2 feeds to STR	1 feed to mixer, 2 feeds to STR	4 stages
Reactor volume mL	20	20	6.4 & 17.1
Residence time s	18	27	24, 12, 13, 6
Reynolds numbers	~7000-43000	1427	920, 1840, 4360, 9480

Figure 5-12 directly compares the levels of intermediates and by-products obtained in these two reactor types.

Figure 5-2 shows the theoretical response of intermediates (such as *p*-toluic acid) to CSTR and PFR residence time distributions as a function of average residence time. The response is flatter for a CSTR than for a PFR and this pattern can be seen in the experimental results in Figure 5-12. Section 6.4.2 shows that the level of oxidation to CO₂ increases with conversion. Thus, in the TBR, the level of oxidation to CO₂ is clearly being more impacted by the degree of mixing than by the conversion. Also, the oxidation to CO₂ is significantly lower in the TBR than

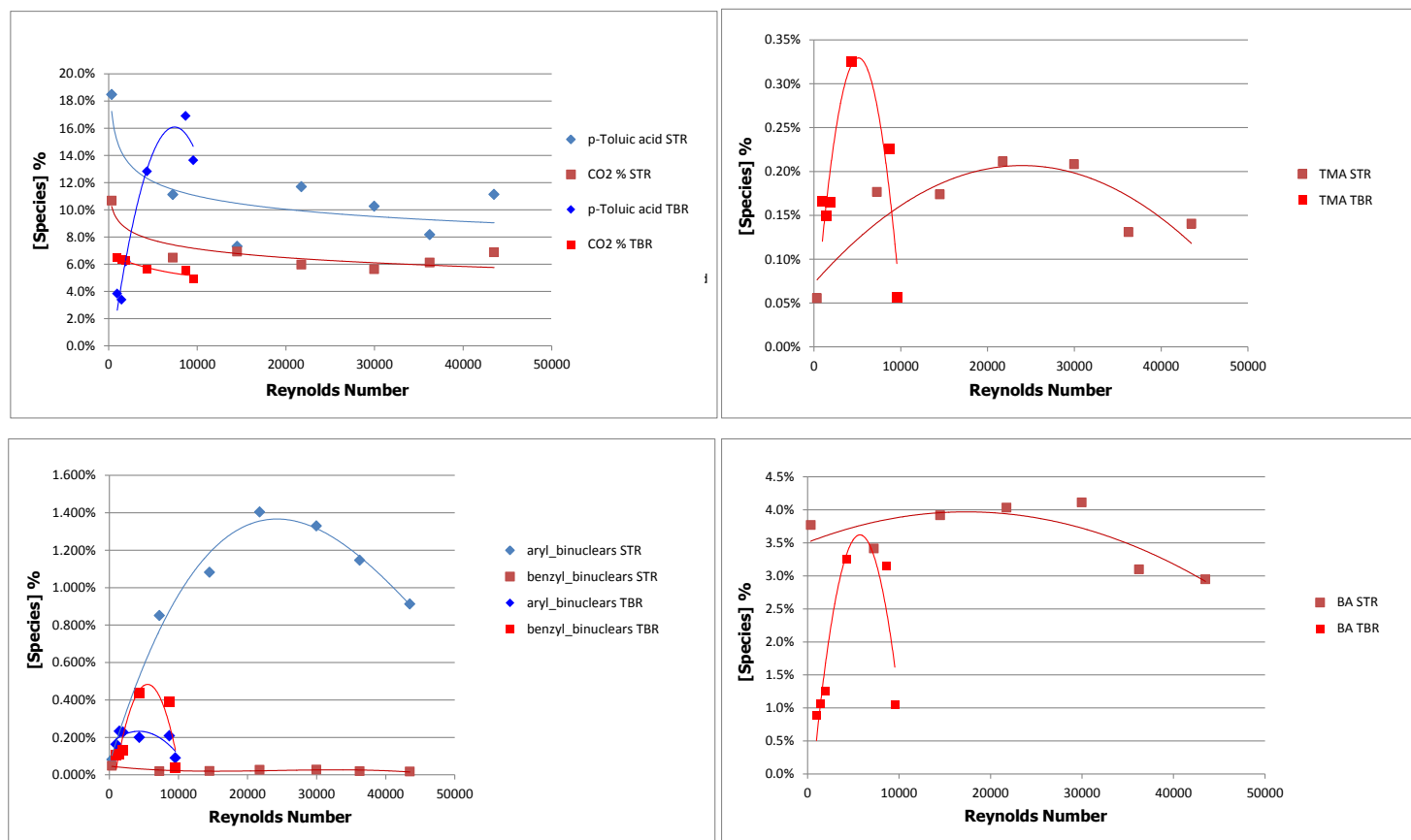


Figure 5-12. The comparison of intermediate and by-product formation as a function of mixing in stirred tank and tubular reactors. This comparison uses the same data as was presented in Figures 5-10 and 5-11 and the experimental conditions are as given in Table 5-1. Note that the STR achieved much higher Reynolds numbers. The individual binuclear species have been combined into aryl radical derived and benzyl radical derived, see captions of the previous figures for details and estimates of errors.

in the STR by around 30-40 % for a given degree of turbulence. The TBR is likely the more effective mixing device (at least in these experiments) because of its low length scale and short diffusion paths.

The pattern of binuclear by-products is:

- Aryl derived species in STR > in TBR
- Benzyl derived species in TBR > in STR
- For STR, aryl derived species >> benzyl derived species
- For TBR, aryl derived species ~ benzyl derived species

Section 1.3.3 discusses the mechanisms of formation of the binuclear by-products. These involve the reaction of either aryl or benzylic radicals with aromatic species such as *pX*, intermediates or TA. The radical species can be either methyl substituted or carboxy substituted. Carbonyl substituted radicals are also possible though these are probably less likely because of the higher reactivity of the carbonyl group to further oxidation. The likely dominant interactions of the various radicals and aromatics for differing residence time distributions are summarised in Figure 5-13.

The high aryl radical derived by-products in a STR compared to a TBR suggest that the dominant formation is from the reactions of:

- Methyl aryl radicals with late intermediates/TA and/or
- Carboxy aryl radicals with *pX*/early intermediates

The former is more likely because:

- Methyl substituted radicals are more reactive than carboxy substituted radicals.
- Aryl radical formation is likely front end loaded in the reactions as evidenced by the high formation rate of toluene, as described in Section 6.4.2.
- Late intermediates and TA are more persistent in the system than early intermediates which are more easily oxidised away.

	<i>pX</i> Early intermediates	Late intermediates TA
Me aryl• Me benzylic•	CSTR PFR	CSTR
Carboxy aryl• Carboxy benzylic•	CSTR	CSTR PFR

Figure 5-13. The likely dominant interactions between aryl and benzylic radicals and aromatics for idealised residence time distributions in *pX* NCWO. Radicals are characterised as methyl substituted or carboxy substituted while aromatics are characterised as *pX* and early intermediates (*e.g.* *p*-tolualdehyde) or as late intermediates (*e.g.* *p*-toluic acid, 4-CBA) and TA. A CSTR is fully back mixed and so interactions occur between both radical and both intermediate classes. A PFR tends to contact *pX* and early intermediates with methyl substituted radicals and late intermediates and TA with carboxy substituted radicals.

These experiments were performed under NCWO conditions. It is probable that under SCWO conditions that the reaction of carboxy aryl radicals with TA becomes important due to higher decarboxylation rates, as described in Section 6.2.

The opposite pattern is seen for benzyl radical derived by-products, *i.e.* they are higher in a TBR than in a STR. This suggests that the primary interaction is methyl derived benzyl radicals with *pX* and early intermediates which are at higher concentrations in a PFR.

Benzyl radicals are on the main reaction pathway while aryl radicals are formed in undesirable side reactions. Both preferentially react with oxygen (rather than aromatics), benzyl radicals to form desirable products, aryl radicals to ultimately

form CO₂ and CO with only small amounts forming binuclear by-products. Figure 5-3 illustrates the higher oxygen levels in a PFR compared to a STR. Thus, the results suggest that oxygen is relatively more reactive with aryl radicals than benzyl radicals and can thus better suppress aryl derived by-products in a TBR.

In conclusion, these have proved to be very nice experiments with highly satisfying results which have been able to demonstrate the interaction between chemical mechanisms and mixing effects. The next section considers the implications of this for reactor scale up and for process design.

5.8.5 The Comparison of Minor Components in NCWO and the Acetic Acid Based Process

The minor components produced in the acetic acid based *pX* oxidation process are described by Roffia *et al.*⁷ and are reviewed in Section 1.3. Roffia provides data from which the formation rate of BA and TMA can be estimated. In addition Eastman Chemical Company has published a number of patents^{8, 9} which give data from which the formation rate of 2,6-DCF and 4,4'-diphenic acid (in the acetic acid process) can be estimated. Comparing these estimates to the formation rates of these components estimated for *pX* N/SCWO (given in Figures 5-10 and 5-11) shows that the formation rates are higher in the N/SCWO process by a factor of ~5, 15, 50, 3 for BA, DCF, diphenic acid and TMA respectively.

These figures suggest that both aryl and methyl radical concentrations are high in the N/SCWO process compared to the acetic acid based process. It seems likely that the formation rates of the other minor components (for which this comparison hasn't been made) will also be high. These high formation rates are probably caused by keeping intermediates and TA product in solution at high temperatures for too long. This demonstrates a weakness of this process as the BA represents a significant TA yield loss while the more minor components are contaminants that must be removed in the purification plant.

5.9 Scale Up Considerations

The range of concentration of *pX* used in the experiments in this PhD were in the range 0.5 – 5.0 % w/w. The effect of *pX* concentrations on the reaction chemistry is considered in Section 6.3. The concentration is a considerable economic driver because it impacts the reactor size and the sizing of the product separation and solvent recycle equipment. It is believed that for an economic industrial process, operation at a concentration of 10 – 20 % w/w would be necessary; the economics are considered in Chapter 8.

Oxygen concentration is higher in a PFR than a CSTR as illustrated in Figure 5-3. In a CSTR, the lower concentrations of reactants, particularly *pX* and oxygen, make it more suitable than a PFR for higher concentration operation. A PFR is more problematic because the injections of the reactants lead to high local concentrations and the possibility that, under NCW conditions, the oxygen solubility can be exceeded. This is a dangerous situation because the contacting of *pX* and oxygen without water diluent can give explosive decomposition as shown in Figure 2-4.

Information on the solubility of oxygen and *pX* in NCW is available^{10, 11} and using this data, the following solubility expressions were fitted:

$$S_{pX} = 0.00141T^2 - 0.6324T + 71.317 \quad (5-10)$$

$$S_{O_2} = P(0.0167T - 3.26)/250 \quad (5-11)$$

Where S_x is the solubility of x in % w/w, P is pressure in bara and T is temperature in °C. These expressions are only applicable in NCW as oxygen and *pX* are fully miscible with SCW.

These expressions can be used to assess the number of oxygen and *pX* stages that are required in a plug flow reactor to prevent phase separation at the injection point. The result of this analysis is shown in Table 5-2.

It can be seen, that up to 3 stages of *pX* and 9 stages of oxygen are required to avoid feed point phase separation at the higher feed concentration operation required for commercial operation.

Table 5-2. The number of stages of *pX* and oxygen addition required to ensure that the solubility limits of these components are not exceeded at the injection points in a PFR. Calculations performed using solubility equations 5-10 and 5-11 at 350 bara and the temperatures shown. The use of hydrogen peroxide as an oxygen source is largely impracticable at higher *pX* feed concentrations because it has insufficient oxygen content and so O_{2(g)} is used.

Temp C	<i>pX</i> solubility %	O ₂ solubility %	Feed [<i>pX</i>] %	O ₂ Source	Required <i>pX</i> stages	Required O ₂ stages
360	26.4	3.85	10	50% H ₂ O ₂	1	5
			10	O ₂	1	3
			15	O ₂	1	5
			20	O ₂	1	6
330	16.2	3.15	10	O ₂	1	4
			15	O ₂	1	5
			20	O ₂	2	7
300	8.5	2.45	10	O ₂	2	5
			15	O ₂	2	7
			20	O ₂	3	9

5.10 Implications for Process Design

This final section considers the optimum reactor configuration and residence time distribution for the *pX* N/SCWO process.

We have seen that a CSTR has the advantage that it back mixes the reactants, *pX* and oxygen to low concentrations and so is suited to the addition of these components at higher, commercial concentrations. However, a CSTR suffers from high formation rates of undesirable by-products and struggles to drive the reaction to high conversion. A PFR has higher concentration of reactants and needs multiple staged additions to keep these concentrations down. It reduces the contact of early intermediates with the TA product and this reduces the formation of undesired by-products. It allows a long ‘tail-out’ to drive down intermediates to low concentrations and produce high overall conversion but it is important to avoid excessive residence time in the presence of oxygen that can lead to additional oxidation to CO₂ and CO.

Overall a PFR with multiple *pX* and oxygen stages is better suited to this reaction, producing fewer by-products and allowing the reaction to be driven to

high conversion. Another possible reactor configuration could be to have a low conversion CSTR followed by PFR. This gives the advantages of a CSTR for feed mixing but allows ‘tail-out’ to high conversion in the PFR. However, it is difficult to predict the level of by-product formation that such an arrangement would give. Unfortunately, time constraints did not allow for the engineering and experimental testing of this reactor arrangement and so this remains a recommendation for possible future work in this area.

5.11 References

1. V. N. Aleksandrov, Mechanism of *p*-xylene oxidation in acetic-acid solution with cobalt-manganese-bromide catalyst, *Zh. Org. Khim.*, 1978, **14**, 1517-1522.
2. O. Levenspiel, *Chemical Reaction Engineering*, John Wiley & Sons Inc., New York, 1999.
3. O. Levenspiel and K. B. Bischoff, Backmixing in the design of chemical reactors, *Ind. Eng. Chem.*, 1959, **51**, 1431 - 1434.
4. *Ethylene Oxide.*, IHS Chemical Consulting, London, 2016.
5. E. Lester, P. J. Blood, J. P. Denyer, D. Giddings, B. Azzopardi and M. Poliakoff, Reaction engineering: The supercritical water hydrothermal synthesis of nano-particles, *J. Supercrit. Fluids*, 2006, **37**, 209-214.
6. J. Sierra-Pallares, D. L. Marchisio, E. Alonso, M. Teresa Parra-Santos, F. Castro and M. Jose Cocero, Quantification of mixing efficiency in turbulent supercritical water hydrothermal reactors, *Chem. Eng. Sci.*, 2011, **66**, 1576-1589.
7. P. Roffia, P. Calini, L. Motta and S. Tonti, By-product identification in the terephthalic acid production process and possible mechanisms of their formation, *Ind. Eng. Chem. Prod. Res. Dev.*, 1984, **23**, 629-634.
8. A. G. Wonders, G. G. Lavoie and C. E. J. Sumner, Optimised liquid-phase oxidation, US Pat., 7 361 784, 2008.
9. A. G. Wonders, R. B. Sheppard and M. De Boer, Polycarboxylic acid production system employing hot liquor removal downstream of oxidative digestion, US Pat., 7 420 082, 2008.
10. H. Weingartner and E. U. Franck, Supercritical water as a solvent, *Angew. Chem., Int. Ed.*, 2005, **44**, 2672-2692.
11. K. G. Knauss and S. A. Copenhaver, The solubility of *p*-xylene in water as a function of temperature and pressure and calculated thermodynamic quantities, *Geochim. Cosmochim. Acta*, 1995, **59**, 2443-2448.

6 Chemistry Studies

6.1 Introduction

There were many *pX* N/SCWO chemistry studies undertaken during this PhD study, the main ones being:

- The stability of TA in NCW/SCW/O₂ environments.
- The effect of *pX* concentration.
- The nature of catalyst and the effect of catalyst concentration.
- The effect of oxygen concentration and the effect of oxygen addition strategies.
- The effect of residence time.
- The effect of temperature.
- The effect of phase.
- The effect of quench on the chemistry.
- The effect of residual undissociated hydrogen peroxide on the chemistry.

The first two studies are described in detail in Sections 6.2 to 6.3. Catalyst studies were published ¹ by the author and co-workers and a copy of the paper is available in Appendix 1. The remaining studies are summarised more briefly and cross references are provided to other parts of the thesis (*e.g.* the experimental section) where they provide more detail. The impact of these studies on the mass balance and process selectivity is covered in Chapter 7.

The chemistry also interacts with the reactor designs, so for example the efficiency of mixing affects the amount of the chemistry that occurs with stoichiometries away from the mean while the residence time distribution can affect the profiles of *pX* and oxygen concentrations within the reactors. The evolution of mixing, RTD and reactor designs is extensively discussed in Chapters 4, 5 and 7 respectively. Cross references are provided where these chapters give relevant information on chemistry aspects.

Some of the studies were performed several times, being repeated as more capable reactors became available; the results from the most capable reactor used are reported. The reactors used and the associated experimental error is detailed in Section 3.10.6.

6.2 Stability of TA in NCW/SCW/O₂ Environments

Conditions in SCWO are harsh and this environment is used for the degradation and disposal of organic chemical waste. TA is prone to degradation through decarboxylation, both thermal and catalysed. The process suffers from the propensity of the intermediate 4-CBA to co-crystallise with TA during work up and thus the process requires harsh conditions to attain high conversion and drive 4-CBA to low levels. Intermediates and TA tend to degrade in the harsh conditions and this damages the process selectivity and yield.

This topic is reviewed by Savage *et al.*² They studied the hydrothermal stability of six aromatic carboxylic acids, including TA, in water in the temperature range 250 – 410 °C using a batch reactor heated in a sand bath. They found TA was stable at 300 °C for 1 hour but formed 10 – 15 % BA after 1 hour at 350 °C. Trimellitic anhydride was found to decompose to TA and *i*PA after 30 minutes at 350 °C. BA was stable at 350 °C for 1 hour. The standard deviations and material balance in their work was relatively poor. The author thinks that this is likely due to their use of a sand bath as our experience is that non-welded joints are prone to leakage under these conditions as described in Section 7.4.

Savage's study has limited applicability for flow conditions with short residence time and in addition he did not cover supercritical conditions. The author therefore decided to study TA stability under these conditions.

Two possible techniques for assessing TA stability in a flow reactor are:

- Provide the reactor with additional residence time beyond that necessary for full conversion.
- Feed TA product to the reactor with no *p*X SCWO occurring.

*p*X and intermediates are degraded, to an extent, during SCWO to the same by-products as occur from TA degradation *e.g.* CO₂, CO and benzoic acid. Thus, the first approach requires the deconvolution of by-products formed during conversion from those formed after conversion is complete. Such an experiment would require a wide variation of reactor residence time – techniques to vary this and their relative merits are discussed in Section 2.5.4. Varying residence time

would ideally be done at constant flow rate but this is awkward because it requires multiple reactor rebuilds. The alternative, of constant reactor volume and varying flow rate, leads to unwelcome variations in the hydrodynamic flow regime.

The second approach requires that TA is fed as an aqueous solution. TA has very low solubility in water at room temperature but the solubility rises appreciably above about 250 °C. Its sodium salt also has appreciable solubility. Thus, it would be possible to dissolve TA in a high temperature dissolver and feed the exit solution to the reactor. Alternatively, a solution of the sodium salt could be fed and TA regenerated in the reactor by an injection of an acid such as hydrochloric acid. This would however give a mixed solution of TA and sodium chloride.

Another possible technique is to decarboxylate trimellitic acid (TMA). TMA is benzene-1,2,4-tricarboxylic acid and has an appreciable solubility in water of ~2 % at 20 °C and ~1 % at 15 °C. Savage's study showed that the ortho carboxylic acid groups decarboxylate more easily to give an (approximately) equimolar mixture of TA and *i*PA in solution. The author considered that this technique could be applied on the IP1 and/or K5 rigs by using the pre-heater to affect the TMA decomposition.

The author favoured methods that could be applied on the existing rigs without the need for a reactor rebuild, *i.e.* the sodium terephthalate method and the TMA decomposition method. The former has the disadvantage that the TA is generated in the presence of an equi-molar amount of a sodium salt (such as sodium chloride) and it is well known that inorganic salts are prone to precipitation and fouling in SCW reactors. In addition, it was possible that the presence of the salt and any excess acid could modify the stability of the TA and compromise the experiment. The disadvantage of TMA decomposition method is that it would produce a mix of TA and *i*PA. However, the author thought it unlikely that these would significantly interact and affect their decomposition behaviour.

An initial experiment was performed to determine whether the decomposition could produce the required result and to determine the optimum conditions. The work was undertaken in the K5 reactor with its 5.9 m long, 1/8" O.D. pre-heater. In this experiment, the pre-heater was hot and the reactor was unheated. A 0.86

% aqueous solution of TMA was fed to the pre-heater at a range of flow rates of 6-12 mL/min and heated to temperature in the range of 455-495 °C. The mixture was quenched with an aqueous sodium hydroxide of strength 3.5 % fed through the first oxygen inlet at the start of the unheated reactor. The liquor was passed through the reactor and cooler to the gas/liquid separator and samples were collected from the sampling system. These were analysed for the carboxylic acids TMA, TA, *i*PA, *o*PA, BA by HPLC and for carbonate (from CO₂) by titration with HCl.

The results from this experiment are given in Figure 6-1 and 6-2. TMA decomposed to an (approximately) equi-molar solution of TA and *i*PA. A small amount of BA was also produced. The level of CO₂ measured corresponded to the amount expected if the measured TA, *i*PA and BA were formed from decarboxylation of TMA. The overall mass balance achieved was high being mostly ~100 % though at times between ~85 – 110 %. There was a trade-off between the amount of residual TMA and over decarboxylation to BA though the latter is preferable since BA is more thermally stable than TMA and will thus be less disruptive to subsequent studies on TA/*i*PA stability. The optimum decomposition conditions were therefore determined as an ambient pump flow rate of 9 mL/min and pre-heater temperature of 475 °C which produced a total decomposition of the TMA without excessive over decarboxylation to BA.

In a second stage of the experiment, the effect of oxygen and of metal bromide catalyst on the stability of the *i*PA/TA mix was investigated. The optimised decomposition conditions were used to produce a TA/*i*PA solution exit the pre-heater that was then fed forward to the reactor. Oxygen (produced from the decomposition of hydrogen peroxide) or metal bromide catalyst solution was added through the injection point at the start of the reactor. The oxygen levels used were 100 – 600 % of that that would be necessary to affect an oxidation of *p*X to TA at an equivalent feed concentration; the starting TMA concentration

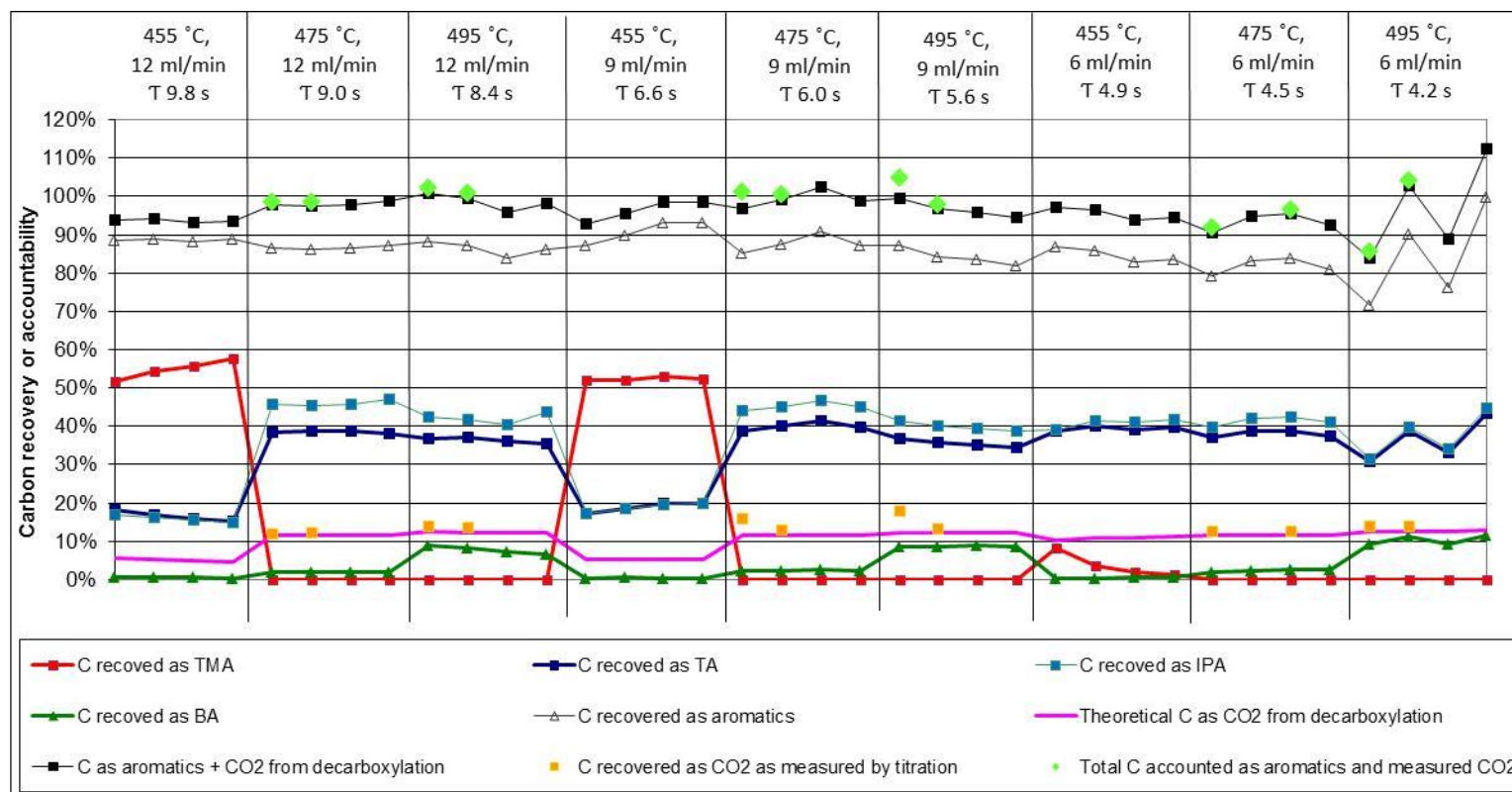


Figure 6-1. The thermal decomposition products of TMA. Each experimental period is delimited by the vertical lines and the conditions of temperature, ambient pump rate and estimated pre-heater residence time (τ) are given. Carbon recoveries and material balances are plotted based on the amount of TMA being fed. Residual TMA is shown in red. The major products *i*PA and TA are shown in light and dark blue respectively. The minor product BA is shown in dark green. The theoretical amount of CO₂ from decarboxylation of TMA to *i*PA/TA and of *i*PA/TA to BA is shown in magenta. CO₂, as measured by titration, is shown in yellow, but was only measured for only a selection of points. Aromatic recovery is plotted in black (with open symbols) and aromatic recovery plus theoretical CO₂ is plotted in black with closed symbols. The total carbon material balance as aromatic recovery plus measured CO₂ are shown as green points – these points are only available where CO₂ was measured. More detail on the minor components can be seen in Figure 6-2.

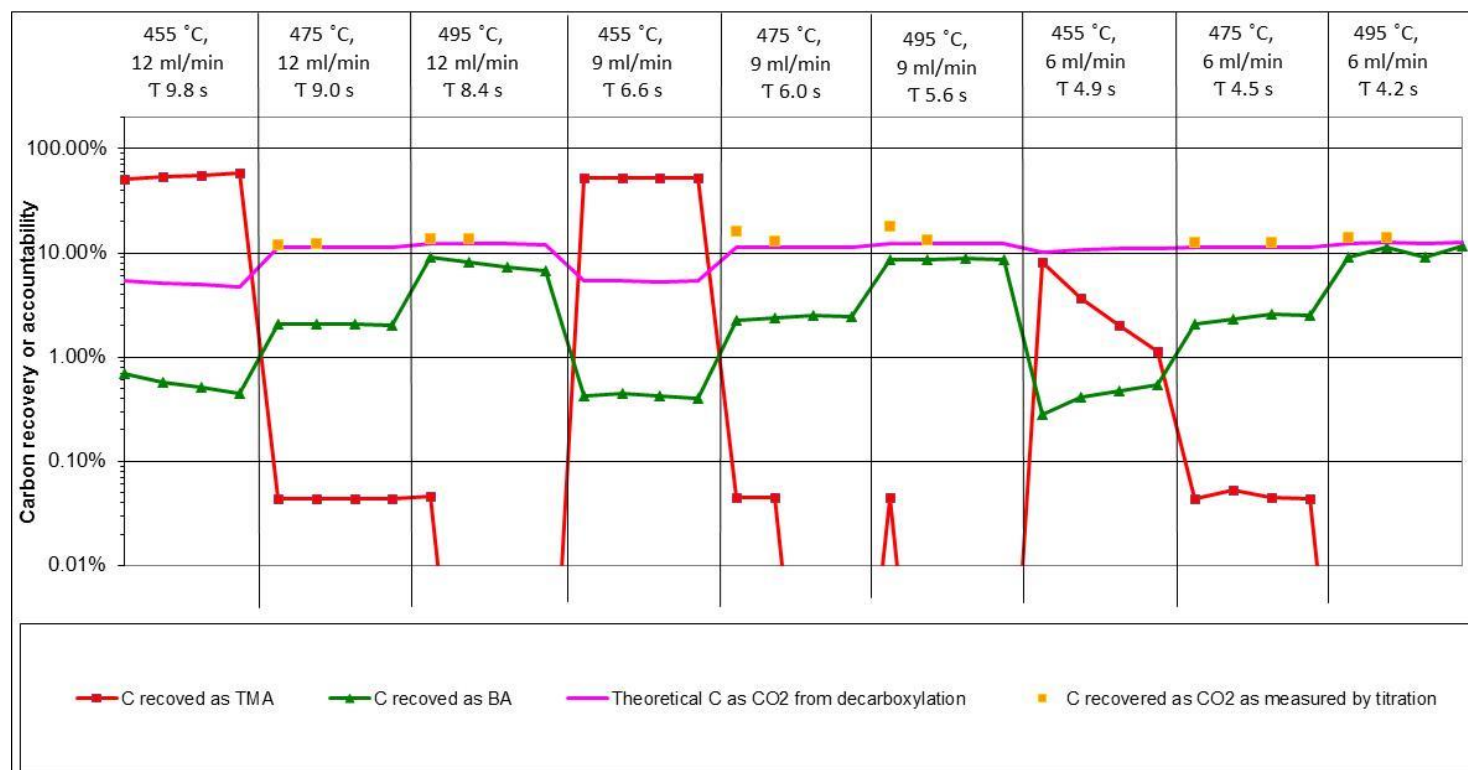


Figure 6-2. Detail on the minor products from the thermal decomposition of TMA. The same information as in Figure 6-1 is plotted with the same colour scheme but using a logarithmic scale. Each experimental period is delimited by the vertical lines and the conditions of temperature, ambient pump rate and estimated pre-heater residence time (τ) are given. Carbon recoveries and material balances are plotted based on the amount of TMA being fed. Residual TMA is shown in red; points off the bottom of the graph were measured as zero and these cannot be captured on a log scale though have been plotted as 10^{-7} %. Note that there was sometimes a lag in response after a change in flow rate. The minor product BA is shown in dark green. The theoretical amount of CO₂ from decarboxylation of TMA to *i*PA/TA and of *i*PA/TA to BA is shown in magenta. CO₂, as measured by titration, is shown in yellow, but was only measured for only a selection of points.

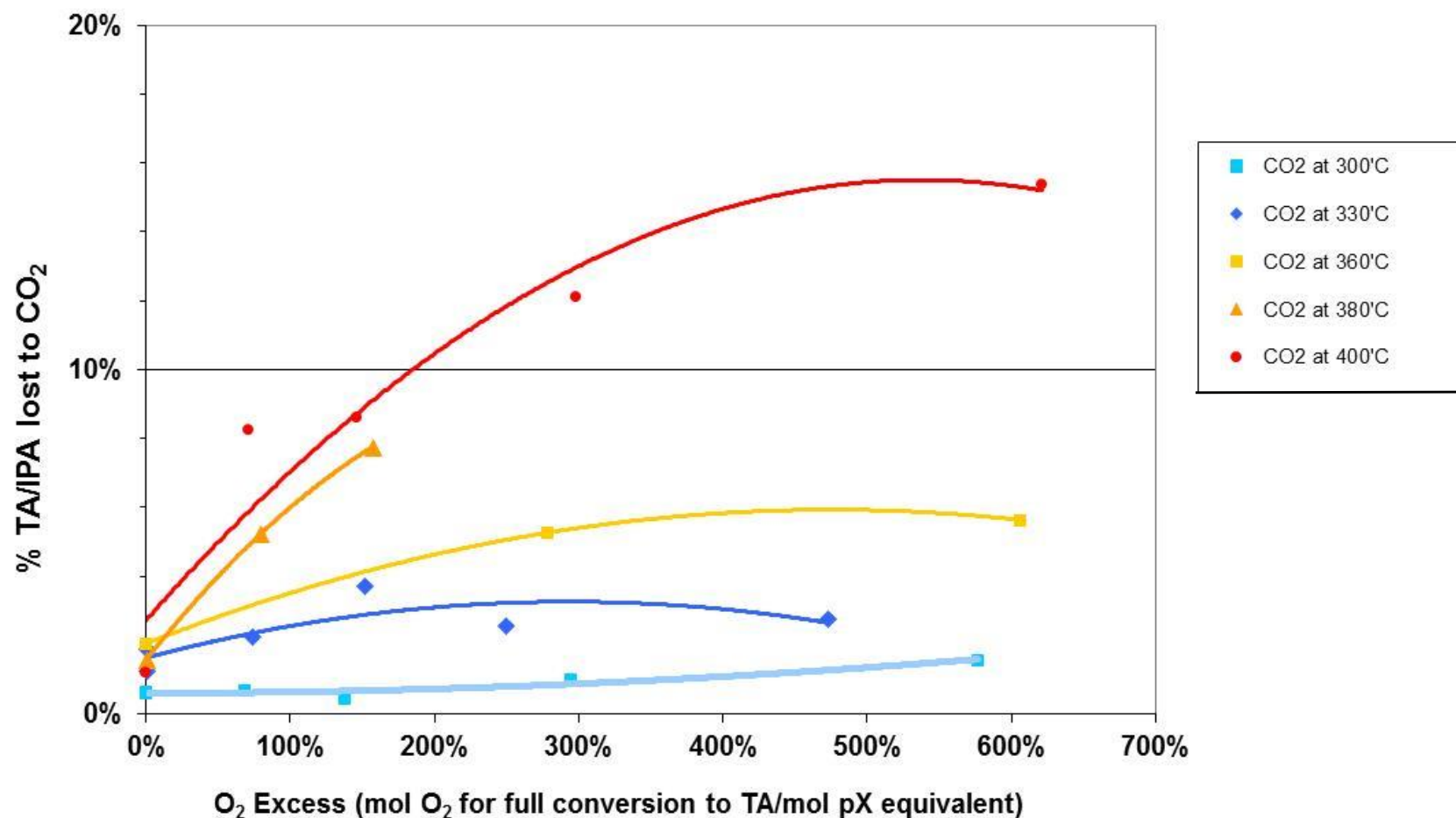


Figure 6-3. The stability of a ~1:1 mixture of TA and *i*PA in water to excess oxygen in the temperature range 300 – 400 °C. The TA/*i*PA mix was produced by the decomposition of a TMA solution at 475 °C. Oxygen is plotted as the amount of oxygen required to fully convert an equivalent amount of *p*X to TA. 100 % corresponds to [O_{2(l)}] of 0.94 M assuming the oxygen is fully in solution.

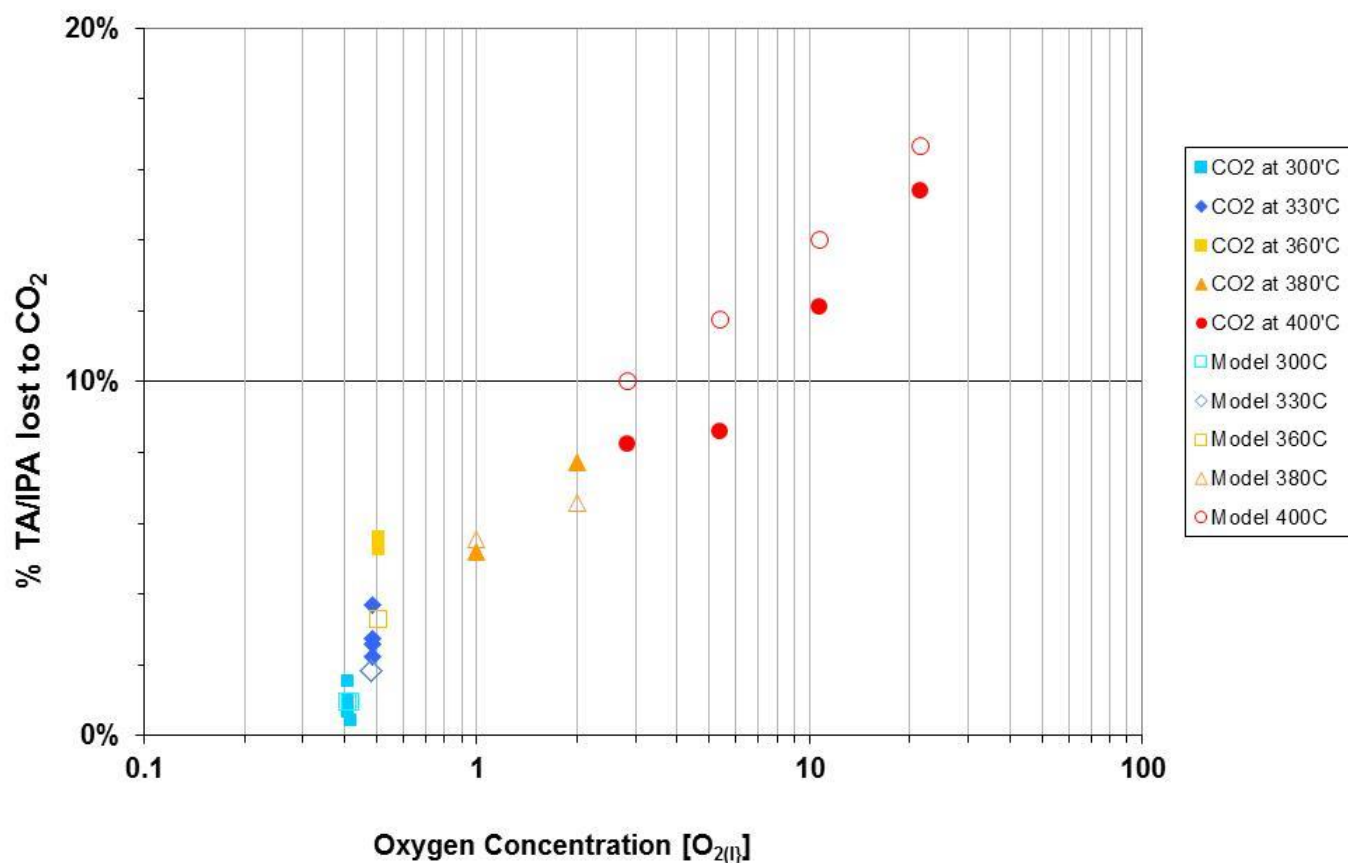


Figure 6-4. The stability of a ~1:1 mixture of TA and *i*PA in water to excess oxygen at in the temperature range 300 – 400 °C. The TA/*i*PA mix was produced by the decomposition of a TMA solution at 475 °C. Oxygen is plotted as the concentration of oxygen in the liquid in M. A concentration of 0.94 M would be required to fully convert an equivalent amount of *p*X to TA. Solid symbols show the experimental results and open symbols show predictions of a model of the form discussed in the main text.

was 0.86 % which is ~0.026 M and an equivalent *pX* concentration would be 0.43 %. The catalyst used was Co/Cu/Br at concentrations typically used for *pX* SCWO in the range 148/28/446 to 591/113/1785 ppm. The temperature of the reactor was varied between 300 – 400 °C.

The results of the oxygen addition experiments are shown in Figure 6-3 and 6-4. The former shows that the exposure of TA to excess residence in the presence of oxygen is damaging particularly at supercritical conditions.

The analysis can be extended further by considering the effect of phase. Oxygen is fully miscible with water above the critical temperature and pressure. At subcritical conditions, oxygen is not fully miscible and its solubility can be estimated using equation 5-11 in Section 5.9. A plot of oxygen concentration in the liquid phase [$O_{2(l)}$] against the loss of TA/IPA to CO_2 is given in Figure 6-4. The oxidation to CO_2 could be fitted to an expression of the form:

$$\frac{d(CO_2)}{dt} = A \exp(-B/RT) [O_{2(l)}]^x \quad (6-1)$$

Where $A \sim 3500$, activation energy $B \sim 60$ kJ/mol and $x \sim 0.25$. The predictions of this expression are also given in the figure.

The experiment showed that Co/Cu/Br catalyst (in the absence of oxygen) has no additional effect on the decomposition of TA/*i*PA beyond that caused by thermal decomposition.

There experiments have some limitations. The methodology is not suitable to study the effect of oxygen and catalyst together because the catalyst will oxidise and precipitate. They study the effect of excessive reagents and residence time but do not consider the effect of an active oxidation on the stability of TA. This would be expected to be worse because the radical flux would give additional decarboxylation mechanisms.

The results suggest that we should seek to minimise residence time and oxygen excess when performing *pX* SCWO. Reactor design and oxygen addition strategies to achieve these aims are considered in Chapter 5.

6.3 *p*-Xylene Concentration

Process intensity is an important parameter in a chemical process because it determines the volume of the reactor needed to perform the process and this has a major influence on the capital cost of the reactor. Conventional TA processes typically operate at TA slurry concentrations of ~30 % w/w which require a *pX* feed concentration of ~20 %.

Process intensity can be measured by the space time yield (STY) which can be defined as the mass of product produced per unit volume per unit of time. The N/SCWO process, when processing a 2 % *pX* stream in a reactor volume of 6.4 mL achieves a STY of ~6340 kg TA/m³/hr; this is an order of magnitude higher than that achieved by the conventional acetic acid process. The conventional process has a relatively poor STY because of the need for a high conversion, back mixed reactor and the large gas hold up, factors that lead to a large reactor size; these aspects were discussed more fully in Section 1.2.

The conventional process feeds a relatively dilute *pX* stream but produces slurry containing ~30 % TA solids. Factors affecting this are the increase in weight of *pX* as it is converted to TA, the water produced, 2 mol/mol of *pX*, and the solvent, *i.e.* acetic acid and water, which is boiled off to remove the heat of reaction; ~80 % of the solvent, fed and produced, is removed. By contrast, the N/SCWO process (as currently envisaged) is non-boiling and the heat produced must either be removed by heat exchange or taken as an adiabatic temperature rise. At an industrial scale, it would be necessary to recycle the water solvent, taking a purge to remove the water of reaction and by-products produced. It is therefore desirable to produce concentrated slurry, of 15 – 30 % TA in water, to limit the size and cost of the recycle stream. It is thus preferable to oxidise a concentrated stream of *pX*, containing 10 – 20 % *pX*.

As the *pX* concentration rises, the adiabatic temperature rise of the reaction will rise and this can be estimated if the heat of reaction and specific heat capacity of the reaction medium are known. It is also possible to estimate the sand bath temperature that would be needed to run the reaction isothermally provided the

Reactor length m	0.877	0.877	0.877	0.877	2.343
Pipe outer diameter "	0.25	0.25	0.25	0.25	0.25
Reactor volume ml	6.399	6.399	6.399	6.399	17.096
Temperature C	300	330	360	380	400
Pressure bar	230	230	230	230	230
Phase	liquid	liquid	liquid	supercritical	supercritical
Ambient flow rate mls/min	24	24	24	24	24
Residence time s	11.8	10.8	9.2	3.3	5.7
Reynolds Number	1836	2092	2519	5443	6088
Flow Regime	Laminar	Transitional	Transitional	Turbulent	Turbulent
[pX] %	2	2	2	2	2
Temp difference (process - sand) C	28	30	29	27	26
Sandbath temperature C	272	300	331	353	374

Figure 6-5a. The cooling requirements for *pX* N/SCWO in tubular reactors on the Kinetics Rig with variation in temperature and phase.

$Q = m_{pX} H$ where Q is heat generated (W) to be transferred, m_{pX} is *pX* mass rate and H is heat of reaction = 12264 kJ/kg *pX*.

Temperature difference ΔT (K) = $Q/H_t A$ where H_t is overall heat transfer coefficient (HTC) ($Wm^{-2}K^{-1}$) and A is heat transfer area (m^2).

$H_t = 1/[(1/H_{sand}) + (1/H_{tube}) + ((1/i)*(D_o/D_i))]$. where H_x is HTC of component x , i is internal film coefficient ($Wm^{-2}K^{-1}$) and D_o and D_i are outer and inner pipe diameters (m) respectively. Tubing wall thickness is 0.065".

Fluidised sand HTC, $H_{sand} = 600 Wm^2K^{-1}$.

Tube HTC = $2W/(D_o \ln(D_o/D_i))$ where W is Hasteloy C-276 thermal conductivity = $15 Wm^{-1}K^{-1}$.

Internal film coefficient $i = N_u S/D_i$ where N_u is Nusselt number and S is fluid specific heat capacity ($kJkg^{-1}K^{-1}$).

$N_u = 1.86 \times (Re/P_r)^{0.33} (D_i/L)^{0.33}$ with a minimum of 3.5 where Re and P_r are Reynolds and Prandtl numbers.

$P_r = S \nu W^{-1}$ where ν is dynamic viscosity (cP) and W is fluid thermal conductivity ($Wm^{-1}K^{-1}$).

Fluid properties are assumed to be those of pure water as obtained from NIST website.

Reactor length m	0.877	0.877	0.877	0.877	0.877	0.877	0.877	0.877
Pipe outer diameter "	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Reactor volume ml	6.399	6.399	6.399	6.399	6.399	6.399	6.399	6.399
Temperature C	300	300	300	300	300	300	300	300
Pressure bar	230	230	230	230	230	230	230	230
Phase	liquid	liquid	liquid	liquid	liquid	liquid	liquid	liquid
Ambient flow rate mls/min	24	24	24	24	124	124	124	124
Residence time s	11.8	11.8	11.8	11.8	2.3	2.3	2.3	2.3
Reynolds Number	1836	1836	1836	1836	9485	9485	9485	9485
Flow Regime	Laminar	Laminar	Laminar	Laminar	Turbulent	Turbulent	Turbulent	Turbulent
[pX] %	2	5	10	20	2	5	10	20
Temp difference (process - sand) C	28	70	139	279	110	276	552	1104
Sandbath temperature C	272	230	161	21	190	24	-252	-804

Figure 6-5b. The cooling requirements for *pX* N/SCWO in tubular reactors on the Kinetics Rig with varying *pX* concentration under laminar and turbulent flow conditions.

$Q = m_{px} H$ where Q is heat generated (W) to be transferred, m_{px} is *pX* mass rate and H is heat of reaction = 12264 kJ/kg *pX*.

Temperature difference ΔT (K) = $Q/H_t A$ where H_t is overall heat transfer coefficient (HTC) ($Wm^{-2}K^{-1}$) and A is heat transfer area (m^2).

$H_t = 1/[(1/H_{sand}) + (1/H_{tube}) + ((1/i)*(D_o/D_i))]$, where H_x is HTC of component x , i is internal film coefficient ($Wm^{-2}K^{-1}$) and D_o and D_i are outer and inner pipe diameters (m) respectively. Tubing wall thickness is 0.065".

Fluidised sand HTC, $H_{sand} = 600 Wm^2K^{-1}$.

Tube HTC = $2W/(D_o \ln(D_o/D_i))$ where W is Hasteloy C-276 thermal conductivity = $15 Wm^{-1}K^{-1}$.

Internal film coefficient $i = N_u S/D_i$ where N_u is Nusselt number and S is fluid specific heat capacity ($kJkg^{-1}K^{-1}$).

$N_u = 1.86 \times (Re/P_r)^{0.33} (D_i/L)^{0.33}$ with a minimum of 3.5 where Re and P_r are Reynolds and Prandtl numbers.

$P_r = S \nu W^{-1}$ where ν is dynamic viscosity (cP) and W is fluid thermal conductivity ($Wm^{-1}K^{-1}$).

Fluid properties are assumed to be those of pure water as obtained from NIST website.

heat transfer coefficients at the process fluid/reactor wall and reactor/sand can be estimated. These calculations are presented in Figure 6-5.

Figure 6-5(a) shows the cooling requirement for typical low throughput (*i.e.* 24 mL/min), low *pX* concentration (*i.e.* 2 %) experiments on the K5 rig. It shows a modest cooling requirement of a delta temperature (between the reactor and the sand bath) of 26 – 30 °C and that this does not vary much with the reactor temperature over the range 300 – 400 °C. Figure 6-5(b) shows the cooling requirement as the *pX* concentration is raised from 2 % to 20 % for low throughput and high throughput (*i.e.* 124 mL/min) experiments. The cooling requirement rises dramatically with increasing *pX* concentration and some conditions are clearly not achievable. Low throughput experiments require an ambient temperature sand bath at 20 % [*pX*] and the maximum attainable [*pX*] is 5 % with an ambient sand bath temperature at high throughput conditions.

It is not possible to start up with an ambient temperature sand bath. Thus, high *pX* concentration conditions must be attained by starting up at lower concentrations and then progressively increasing the *pX* rate while dropping the sand bath temperature to maintain the required reactor temperature.

A further consideration is the phase. Unpublished work with a third party has shown that *pX* and oxygen will spontaneously explode if they are contacted at a temperature of greater than ~260 °C at a pressure of ~230 bar in the absence of diluents such as nitrogen or water. It is therefore an important safety parameter to design to avoid phase separation of either *pX* or oxygen and the precautions to avoid this when working at high *pX* concentrations are discussed in Section 5.9. This analysis shows that at [*pX*] of 10 % and higher, that 30 % H₂O₂ solutions contains insufficient oxygen to perform the reaction and that it is necessary to use O_{2(g)}. The use of 50 % H₂O₂ enables the use of 10 % *pX* at 360 °C and above. This is problematic because the use of H₂O₂ solutions is integral to the rig safety case because peroxide use constrains the O₂:H₂O ratio (*i.e.* oxidant:diluent ratio) that it is possible to achieve. The use of O_{2(g)} therefore requires a major rework of the engineering and safety case of the rig.

The author therefore decided to split work at higher pX concentrations into three phases:

- A study at 1 – 5 % pX using 30 % H_2O_2 .
- A study at 5 – 10 % pX using 50 % H_2O_2 at 360° C and above.
- A study at 10 – 20 % pX using $O_{2(g)}$.

This section describes the first study. The second and third studies are more difficult and were not undertaken because of time constraints.

The study was undertaken using the standard methodologies described in Chapter 3. The experimental conditions were [pX] concentrations of 1 – 5 % wt/wt on total reactor flow of ~ 13 mL/min at ambient, oxygen 115 % of stoichiometric fed in 4 equal shots, temperature 330 °C, pressure 250 bar. The catalyst used was $CoBr_2/CuBr_2/HBr$ with Co:Cu 84:16 by mass. The catalyst to substrate ratio was kept constant at that used in the standard catalyst formulation detailed in Section 3.10.2. The effect of increased concentration of pX on the CO_2 production is shown in Figure 6-6.

The results show that at higher pX concentrations, the oxidation to CO_2 increases compared to lower concentrations. At 5 % pX the CO_2 is approximately twice that attained at lower concentrations. This result is clearly not encouraging for the attainment of commercially viable reactor conditions.

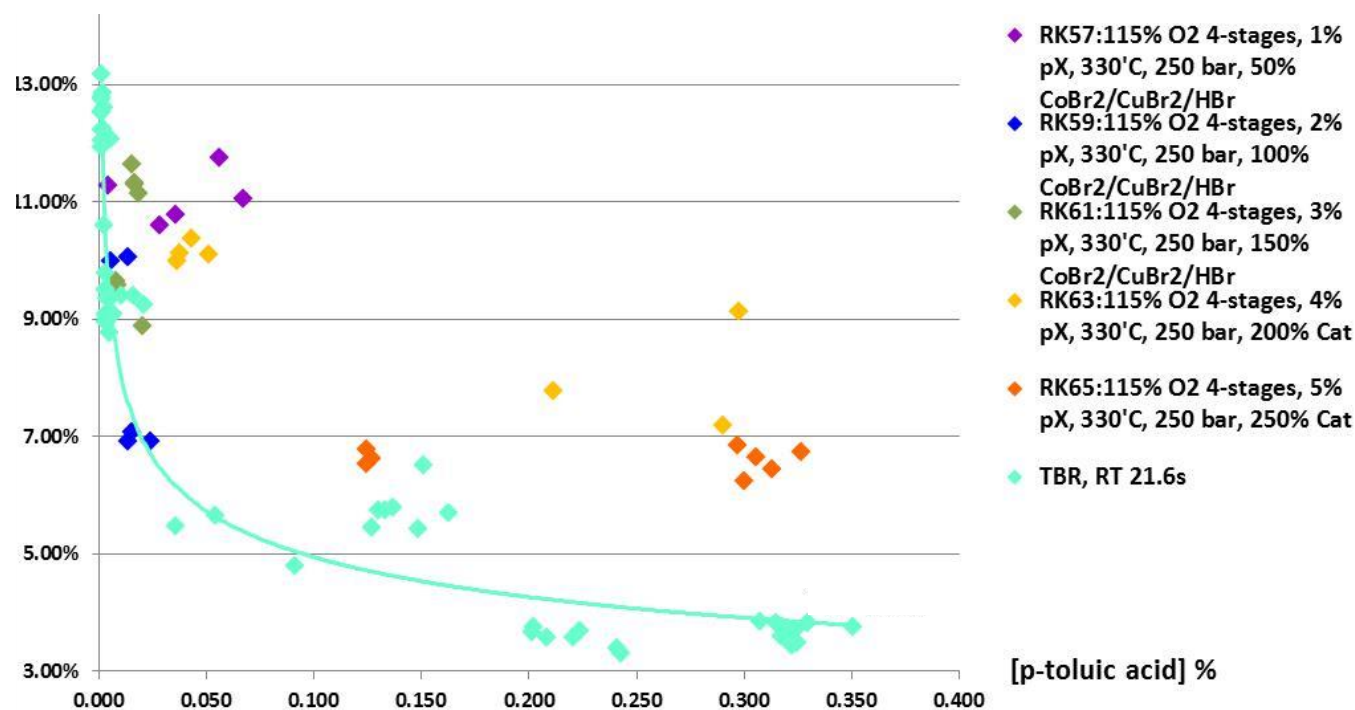


Figure 6-6. The variation of the oxidation of *p*X to CO₂ with the substrate concentration in the feed stream. Conditions for the 1 through 5 % [*p*X] cases were 330 °C, 250 bar, with Co/Cu/Br catalyst. The light blue data and trend line is for a selection of 2 % [*p*X] cases at 330 °C under a variety of oxygen feed and residence time conditions. The blue 2 % [*p*X] data sit on the 2 % trend curve. The 1 -3 % [*p*X] and some 4 % [*p*X] data are reasonably high conversion and generally sit above the trend curve. Conversion is reduced for some 4 % [*p*X] and for the 5 % [*p*X] data and these are well above the trend curve. In the legend, the catalyst concentration used with 2 % *p*X is referred to as 100 % and other catalyst levels have been scaled to keep the catalyst to substrate ratio constant. 100 % catalyst = 1625 ppm Br (from metal bromide salt) and 325 ppm Br (from extra HBr) in the reactor and the Co/Cu ratio was 85/15.

6.4 Other Chemistry Studies

The main conclusions from other chemistry studies undertaken are described briefly in the following sections.

6.4.1 Catalyst Studies

A systematic study of possible catalysts for *p*X SCWO¹ was undertaken by the author and co-workers and a copy of the paper is available in Appendix 1. The elements that were tested are summarised in Figure 6-7.

H																	He
Li	Be											B	C	NH ₄ ⁺	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	C	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Uut					

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 6-7. Summary of all the elements (highlighted in black) plus NH_4^+ used in this study. Most metals were used as the halide salts. Non-redox active metal ions, *e.g.* Na^+ or Ca^{2+} , were used to vary the concentration of Br^- relative to the redox active metals. W, Ti, V were evaluated but, due to the unavailability or instability of their bromide salts in water, NaWO_4 , titanium(IV) bis(ammonium lactate) dihydroxide and NH_4VO_3 were used instead. Combinations of these W, Ti and V salts with different sources of bromide are reported however the results were poor. Some metals such as Bi and Sb could not be evaluated because their bromide salts are not soluble in water. SnBr_2 is soluble in water only at low concentrations. BiBr_3 and SbBr_3 hydrolysed in water to BiOBr or SbOBr and HBr .

These studies found that Cu^{II} in the presence of bromide was a very active N/SCWO catalyst down to very low metal concentrations of a few ppm.

Some other metal bromides were found to have some catalytic activity *e.g.* Fe and Cr. Catalytic activity seemed to be associated with the availability of two oxidation states one electron apart *e.g.* $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$, $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$, $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$, $\text{Cr}^{\text{II}}/\text{Cr}^{\text{III}}$ though curiously Co/Br was a low activity catalyst despite fitting this criteria, and being an important and active catalyst in the acetic acid based process. One can speculate that Hg and U could be N/SCWO catalysts though these were not tested because of toxicity concerns. Eu was found inactive, probably because the $\text{Eu}^{\text{II}}/\text{Eu}^{\text{III}}$ couple occurs at too low an oxidation potential.

The Cu/Br catalyst was implemented on the IP1 and K5 rigs and was a great improvement because it was much less fouling than Mn based catalysts. The new catalyst enabled the stabilisation, using dissolved aromatic acids, to be discontinued with the removal of the hot catalyst feed system and the operational improvements were so great that the use of Mn catalysts was completely discontinued. The oxidation performance was improved by the use of Co/Cu/Br catalysts with the optimum Co:Cu ratio being about 85:15. Oxidation to CO_2 was similar to that that had been achieved with Mn based catalysts. Oxidation to CO_2 was further reduced with high catalyst levels even though this wasn't necessary to get high conversion. Eventually this effect saturated and further catalyst produced no further CO_2 reduction benefit. These effects are illustrated in Figures 6-8(a)-(c).

Remaining challenges for catalysts are the activity and selectivity. The bromide content is undesirable regards corrosion. These aspects are discussed further in Section 9.3.2.

Data Point	Catalyst	Yield of component as % <i>pX</i> fed							Material balance %
		<i>pX</i>	TA	4-CBA	BA	BPTC	<i>pTol</i>	CO ₂	
AV 205	25 % CoBr ₂ /HBr	6	3	3	< 0.5	0	23	28	72
AV 187	25 % CuBr ₂ /HBr	< 0.5	21	4	3	< 0.5	26	32	90
AV 186	25 % MnBr ₂ /HBr	< 0.5	24	3	2	0	20	29	81
AV 204	25 % MnBr ₂ /CuBr ₂ /HBr [Mn:Cu 85:15]	< 0.5	31	4	3	< 0.5	15	29	87
AV 192	25 % CoBr ₂ /CuBr ₂ /HBr [Co:Cu 85:15]	< 0.5	50	13	5	< 0.5	4	27	88

Figure 6-8(a). The application of the Cu/Co based catalysts on the K5 rig and comparison with the Mn based catalysts. The level of catalyst in the standard UoN formulation (detailed in Section 2.4.1) is designated as 100 % and further defined below. 25 % levels are unsaturated catalysts, similar in concentration to those used in the catalyst study.¹ Results show the % of components produced and the % aromatic mass balance (averaged data from ~6 samples collected during the runs). Red highlights the TA yield. Result AV 192 shows that the Co/Cu catalyst is the most active. Oxidation to CO₂ is high and TA yields low because of the use of unsaturated catalysts. Conditions are: K5 rig, ¼" O.D. reactor, 2 % *pX*, 250 bar, 380 °C where 100 % catalyst = 1625 ppm Br (from metal bromide salt) and 325 ppm Br (from extra HBr) in reactor, non-staged 150 % O₂ (stoichiometry for conversion to TA).

Data Point	Catalyst	Yield of component as % <i>pX</i> fed							Material balance %
		<i>pX</i>	TA	4-CBA	BA	BPTC	<i>pTol</i>	CO ₂	
AV 187	25 % CuBr ₂ /HBr	< 0.5	21	4	3	< 0.5	26	31	90
AV 190	50 % CuBr ₂ /HBr	< 0.5	38	4	4	< 0.5	16	28	92
AV 191	100 % CuBr ₂ /HBr	< 0.5	61	< 0.5	3	< 0.5	1	22	88
AV 192	25 % CoBr ₂ /CuBr ₂ /HBr [Co:Cu 85:15]	< 0.5	50	1	5	< 0.5	4	27	88
AV 193	50 % CoBr ₂ /CuBr ₂ /HBr [Co:Cu 85:15]	< 0.5	57	< 0.5	4	< 0.5	1	23	88
AV 194	100 % CoBr ₂ /CuBr ₂ /HBr [Co:Cu 85:15]	< 0.5	62	< 0.5	5	< 0.5	1	21	90

Figure 6-8(b). K5 reactor results, conditions and definitions were as detailed in Figure 6-8(a). Series AV 187 - AV191 and AV 192 – AV194 show that TA yield increases with increasing catalyst concentration and oxidation to CO₂ decreases. Red highlights the lowest CO₂ values obtained.

Data Point	Catalyst	Yield of component as % <i>pX</i> fed							Material balance %
		<i>pX</i>	TA	4-CBA	BA	BPTC	<i>pTol</i>	CO ₂	
AV 217	100 % CuBr ₂ /HBr	0	62	< 0.5	7	< 0.5	3	18	92
AV 195	100 % CoBr ₂ /CuBr ₂ /HBr [Co:Cu 85:15]	< 0.5	66	1	5	< 0.5	2	13	89
AV 196	100 % CoBr ₂ /CuBr ₂ [Co:Cu 85:15]	< 0.5	65	1	4	< 0.5	3	15	90
AV 200	150 % CoBr ₂ /CuBr ₂ /HBr [Co:Cu 85:15]	0	71	< 0.5	4	< 0.5	< 0.5	14	90
AV 197 & 199	150 % CoBr ₂ /CuBr ₂ [Co:Cu 85:15]	0	68	< 0.5	3	< 0.5	< 0.5	14	88
AV 203	200 % CoBr ₂ /CuBr ₂ /HBr [Co:Cu 85:15]	0	75	0	3	< 0.5	0	13	93
AV 201	200 % CoBr ₂ /CuBr ₂ [Co:Cu 85:15]	< 0.5	69	< 0.5	4	1	< 0.5	14	89

Figure 6-8(c). K5 reactor results, conditions and definitions were as detailed in Figure 6-8(a) except runs use 130 % O₂ in 2 stages of 80 % & 50 %. Results show that TA yield continues to increase with increasing catalyst levels. Further increases (beyond 200 % catalyst) produce no further benefit. Catalysts with additional HBr are marginally more active and selective. Co/Cu/Br catalysts are superior to Cu/Br. Red highlights the highest TA yields obtained.

6.4.2 Conversion

It was possible to vary the extent of conversion by feeding varying, sub-stoichiometric amounts of oxygen to the reactor. Early experiments experienced blockages in the cooler, and this was thought to be due to freezing of unreacted *pX*. This problem was solved by using warmed cooling water for the cooler as described in Section 3.7.4. Some results are shown in Figure 6-9.

Total oxidation to CO₂ and CO and by-products were found to increase with conversion. Surprisingly large amounts of toluene were observed at low conversion and this, perhaps, suggests that *p*-toluic acid is more prone to decarboxylation than TA under N/SCWO conditions. The amount of toluene seen was similar to the later amount of BA suggesting that a significant amount of BA may be formed by this route. Kim *et al.*^{3, 4} used uncatalyzed N/SCWO conditions and also noted large amounts of toluene.

6.4.3 Oxygen Addition Strategies

The effect of oxygen concentration was discussed in Section 6.2. Possible oxygen addition strategies such as using a CSTR or staging in a PFR are discussed in Chapter 5 and illustrated in Figure 5-3. Oxygen staging in a tubular reactor was extensively investigated. It was found to be quite effective at reducing oxidation to CO_2 when the mixing of the reaction components was poor. As the mixer designs were improved, as discussed in Chapters 4 and 7, oxygen staging became considerably less effective at reducing oxidation to CO_2 , as illustrated in Figure 6-10.

6.4.4 Residence Time

pX N/SCWO is thought to be an autocatalytic autoxidation with a mechanism similar to that discussed in Section 1.3.1. The reactions are initially rapid but, in a tubular reactor, exhibit a long tail where intermediates persist. It is not possible to achieve high conversions in a back mixed reactor. These characteristics are demonstrated in Figures 5-1 and 5-2. Section 6.2 demonstrated the vulnerability of TA and intermediates to decomposition with excessive residence time, especially in the presence of oxygen. There is thus a trade-off between the degree of conversion that can be achieved and the selectivity to TA.

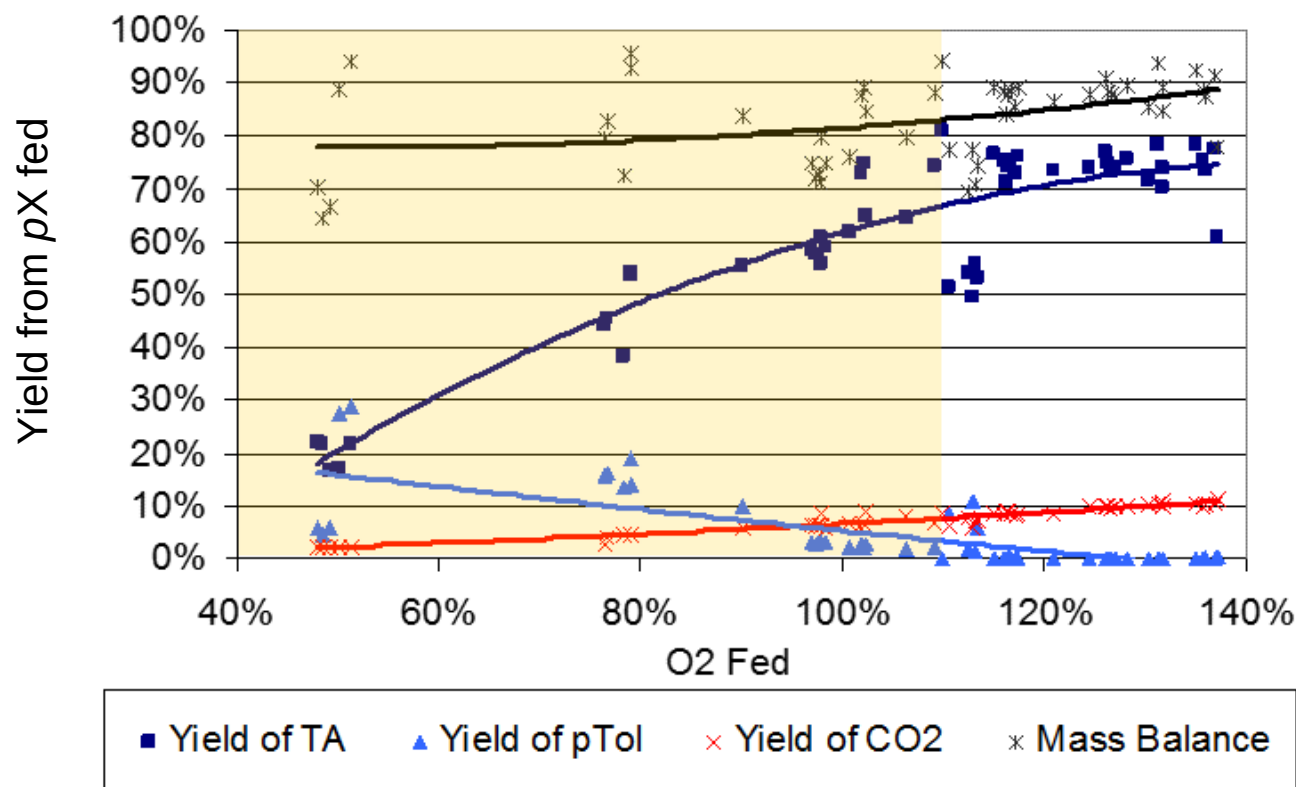


Figure 6-9. The effect of degree of conversion in *pX* NCWO where conversion is controlled by limiting the supply of oxygen. Note that under conversion occurs below ~115 % O₂ in the coloured region. Note that oxidation to CO₂ increases as conversion increases and appears to be back end loaded. Also note that aromatic material balance has less variation at higher conversions, probably because there is less unreacted *pX* which is more difficult to accurately quantify because of its volatility and tendency to solidify in the cooler. Maximum TA yields are ~80 %. Lines are Excel fits (2nd order polynomials) and are provided for guidance of the eye. Conditions are K5 rig, ¼" O.D. reactor, 2 % *pX*, 330 °C, 200 bar, % stoichiometric O₂ in 1 stage, 200 % Co/Cu 85/15 catalyst where 100 % catalyst = 1625 ppm Br (from metal bromide salts) and 325 ppm Br (from extra HBr) in the reactor.

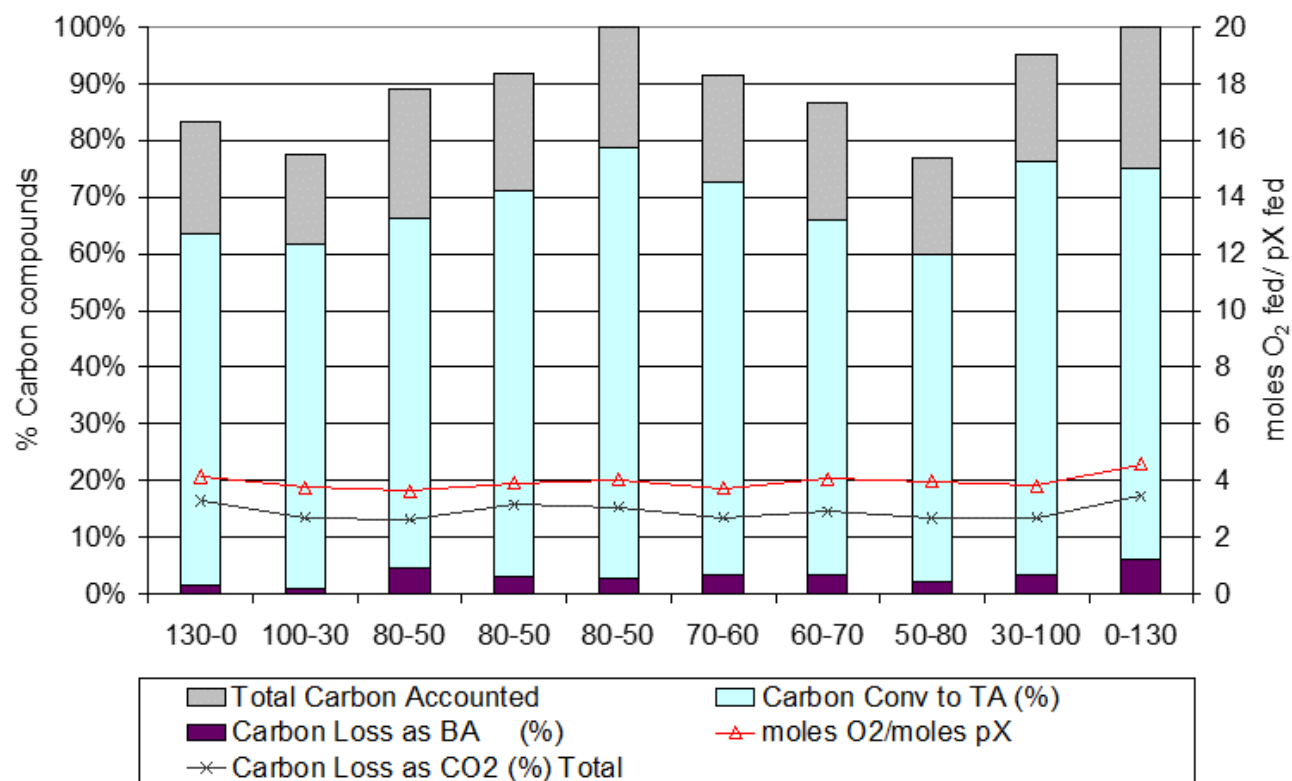


Figure 6-10. The effect of oxygen staging; *pX* SCWO with one or two oxygen stages. The x axis shows the degree of oxygen staging, varied between 130 %/0 % and 0 %/130 %. Note that oxidation to CO₂ is marginally higher for single stage oxygen (*i.e.* the two extremes) but the effects are small. Lines join data points and are provided for guidance of the eye. Reactor conditions: IP1 rig, ¼" O.D. reactor, 5 % *pX*, 380 °C, 250 bar, 130 % stoichiometric O₂ with varying staging, 100 % Mn/Br catalyst where 100 % catalyst = 1625 ppm Br (from MnBr₂ salt) and 325 ppm Br (from extra HBr) in reactor.

6.4.5 Temperature

Dropping the reactor temperature takes the reaction medium into the liquid phase and increases the system density and residence time (for a given reactor volume). Section 6.2 and the study of Savage *et al.*² demonstrated that the TA product is more stable under these conditions. The effect on the *pX* N/SCWO chemistry is shown in Figure 6-11. The oxidation to CO₂ and BA production reduces as the temperature drops from the SCW to the NCW region. The oxidation to CO₂ is invariant below ~340 °C. It is difficult to explain this invariance in CO₂ as the strong activation of oxidation to CO₂ is a dominating feature of the acetic acid based process. *pX* NCWO is probably preferable to *pX* SCWO because of the higher selectivity to TA and lower tendency to foul, though phase separation would be an issue at higher *pX* concentrations as discussed in Section 5.9. It is not desirable to operate between ~260 °C and 280 °C because of phase separation and *pX*/O₂ detonation hazards.

6.4.6 Phase Studies

The advantage of SCW conditions is that *pX*⁵ and O₂⁶ are fully miscible with the water. Phase envelopes under NCW conditions are considered in Section 5.9. The phase diagram of water is given in Figure 1-11(a). From the SCW phase it is possible to drop temperature to enter the NCW liquid phase and to drop pressure to enter the gas phase. The effect of dropping temperature was considered in Section 6.4.5 above. Dropping pressure to enter the gas phase causes the catalyst activity to deteriorate, as shown in Figure 6-12, and the system becomes fouling. This is presumably because the catalyst becomes less soluble. The reaction selectivity marginally improved at the lower pressure while in the liquid phase though this could be a residence time effect. Note the high TA yields of ~85 – 98 % at ~100-105 % material balance in the liquid phase. It is unclear why material balance drops at higher pressures.

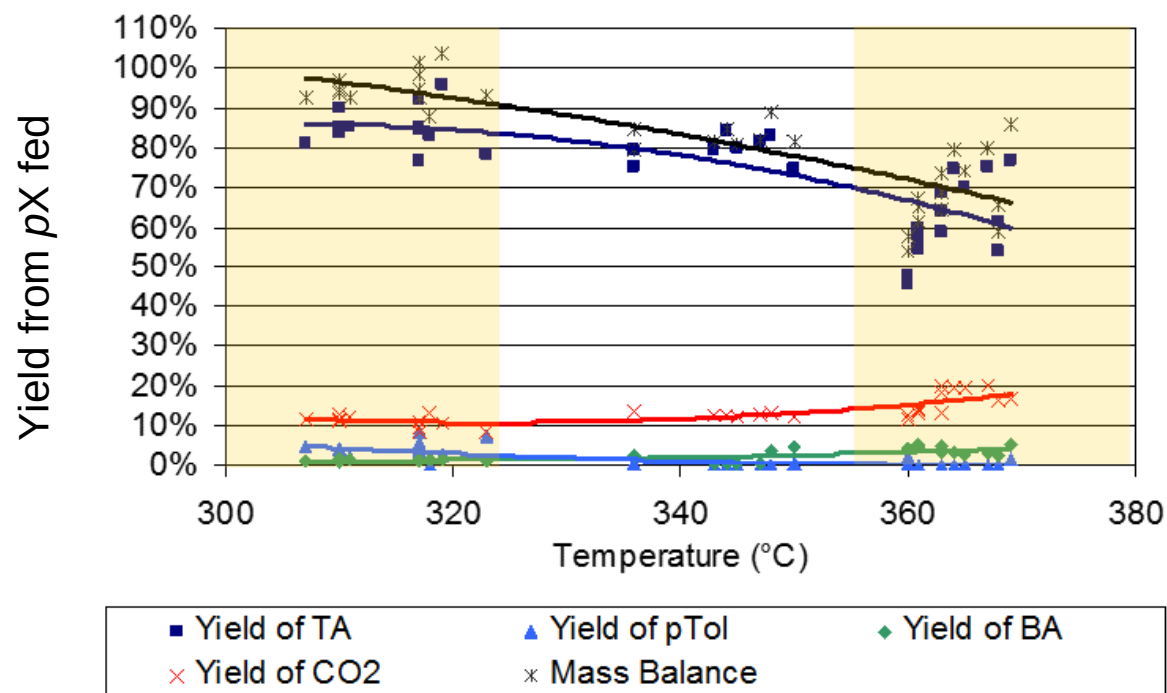


Figure 6-11. The effect of temperature (and hence phase) on the % yields of components and aromatic material balance for *pX* N/SCWO. The liquid/SCW phase transition occurs at ~374 °C with the reactor in the SCW phase above this temperature. Note the TA yields of ~85 % at ~95 % material balance in the lower temperature liquid phase. It is unclear why material balance drops at higher temperatures. Note the zones of under conversion and over conversion shown (approximately) by the coloured areas. Lines are Excel fits (2nd order polynomials) and are provided for guidance of the eye. Reactor conditions: IP1 rig, 1/8" O.D. reactor, 2 % *pX*, 200 or 300bar, 130 % stoichiometric O₂ stages 80 %/50 %, 100 % Co/Cu 85/15 catalyst where 100 % catalyst = 1625 ppm Br (from metal bromide salts) and 325 ppm Br (from extra HBr) in reactor.

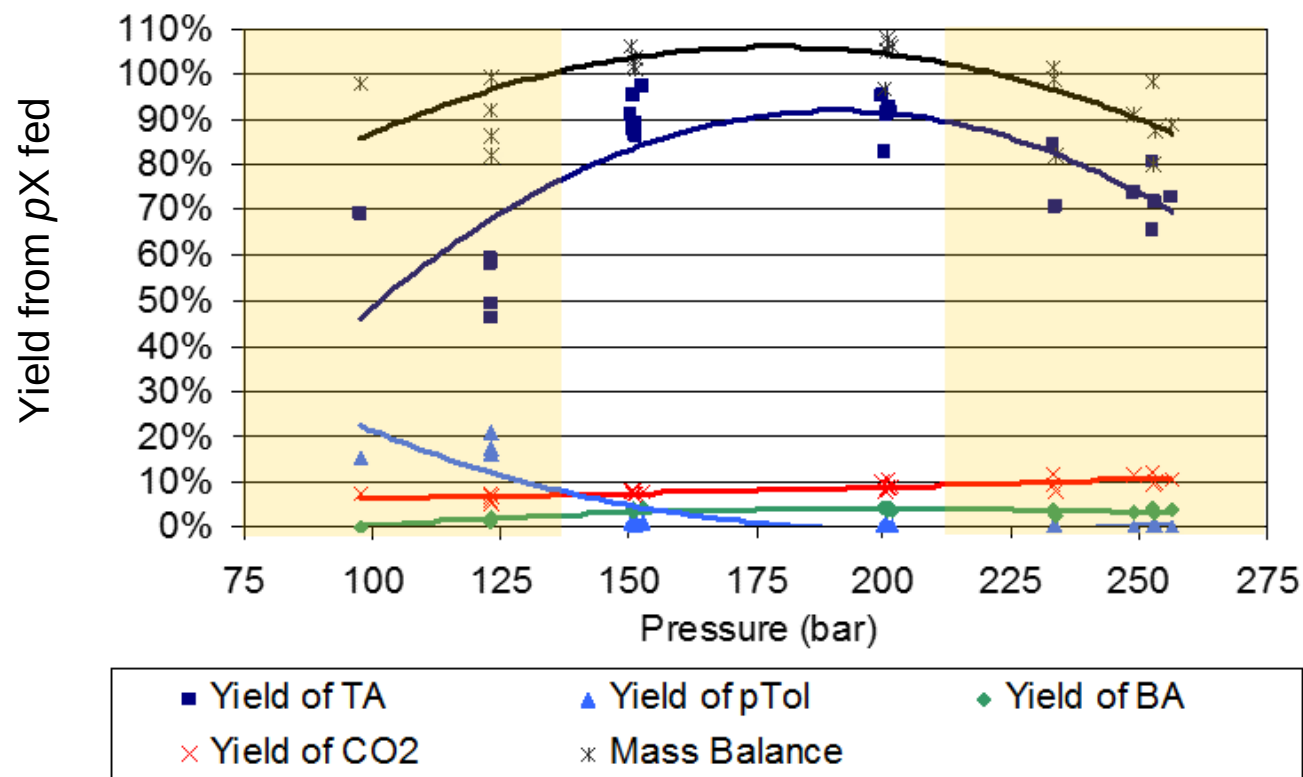


Figure 6-12. The effect of pressure (and hence phase) on % yields of components (from added *pX*) and aromatic material balance for *pX* NCWO. The liquid/gas phase transition occurs at ~130 bar with the reactor in the liquid phase above this pressure. Note the TA yields of ~85 – 98 % at at ~100-105 % material balance in the liquid phase. It is unclear why material balance drops at higher pressures. Note the zones of under conversion and over conversion shown by the coloured areas. Lines are Excel fits (2nd order polynomials) and are provided for guidance of the eye. Reactor conditions: IP1 rig, 1/8" O.D. reactor, 1 % *pX*, 330 °C, 130 % stoichiometric O₂ in 2 stages 80 %/50 %, 100 % Co/Cu 85/15 catalyst where 100 % catalyst = 1625 ppm Br (from metal bromide salts) and 325 ppm Br (from extra HBr) in reactor.

6.4.7 Quench

The effect of the sodium hydroxide quench on the chemistry is covered in Section 7.4. It was found that the back flow of sodium hydroxide into the reactor had no discernible effect on the reaction selectivity. However, the higher pH will initially lower the oxidation potential of the catalyst metals and probably reduce the catalyst activity. A sufficiently high pH will ultimately precipitate the catalyst metals as hydroxides or oxides.

6.4.8 Residual Hydrogen Peroxide

Experiments to determine the level of residual, undissociated hydrogen peroxide exit the pre-heater were described in Section 3.3.3. The study found that 1-2 ppm of undissociated H_2O_2 are slipped from the pre-heater (under normal operation) and enter the reactor. Running the pre-heater at low temperatures ($< 200\text{ }^\circ\text{C}$) slips several hundred to several thousand ppm of peroxide. Figure 6-13 shows the effect of deliberately slipping (several hundred to several thousand ppm of) peroxide into a *pX* NCWO reaction. This produced no discernible effect on the chemistry as shown. The author speculated that H_2O_2 rapidly dissociates to O_2 and water in the presence of metal ions under N/SCW conditions.

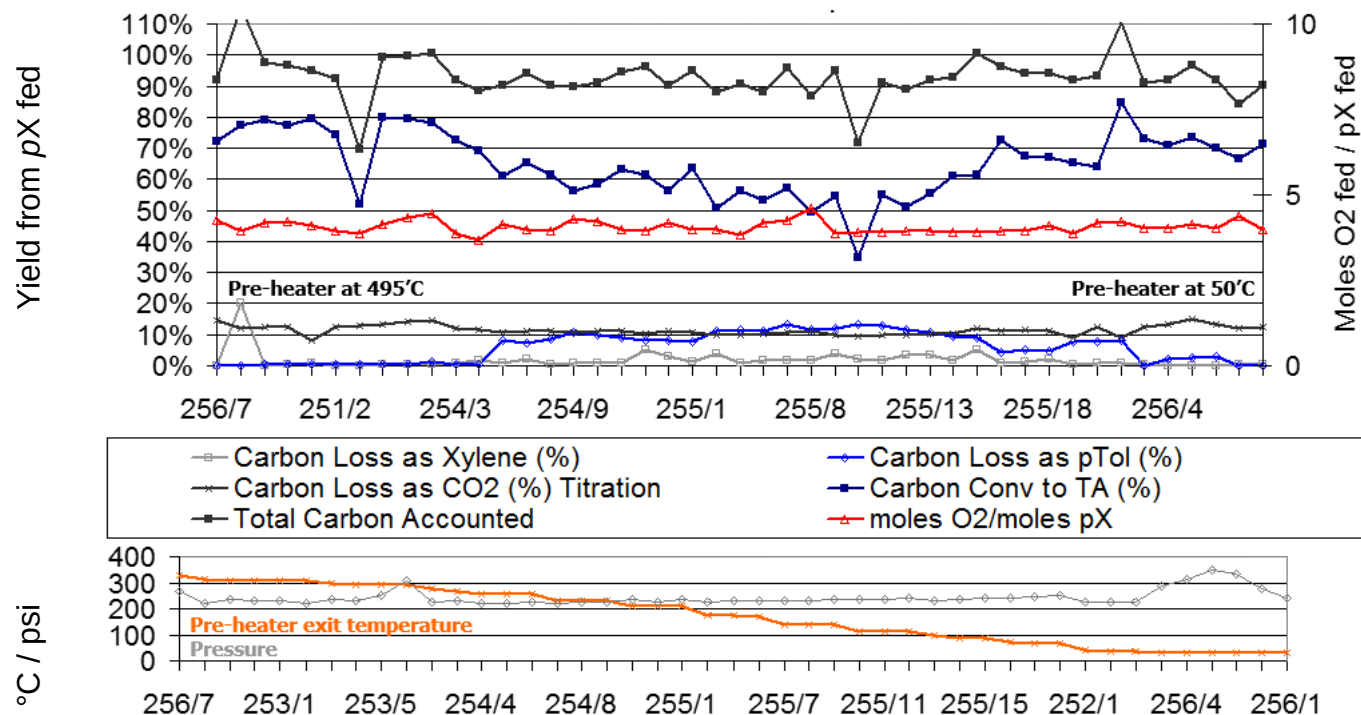


Figure 6-13. The effect of hydrogen peroxide slippage on the reaction chemistry. The x-axis numbering is run/sample numbers *e.g.* 254/3 is the third sample from run 254. The lower graph shows the pre-heater exit conditions with the pre-heater block controlled at a temperature between 495 °C and 50 °C and pressure in psi. The effect of this on peroxide slippage to the main reactor is discussed in Section 3.3.3 shown in Figure 3-6 and concluded that at the lower pre-heater temperature several hundred ppm of undissociated peroxide would likely be slipped into the reactor. The upper graph shows the effect of this on the 5 yields of components and aromatic material balance in pX NCWO chemistry; no discernible effect of the peroxide on the chemistry was apparent. Lines join data points and are provided for guidance of the eye. Reaction conditions were IP1 1/8" O.D. reactor, 360 °C, 230 bar, 140 % stoichiometric O₂ in 1 stage, 2 % pX, 100 % Co/Cu 85/15 catalyst where 100 % catalyst = 1625 ppm Br (from metal bromide salts) and 325 ppm Br (from extra HBr) in reactor.

6.5 References

1. E. Perez, J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, M. L. Thomas, C. Yan, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 2. The discovery of better catalysts, *Green Chem.*, 2011, **13**, 2397-2407.
2. J. B. Dunn, M. L. Burns, S. E. Hunter and P. E. Savage, Hydrothermal stability of aromatic carboxylic acids, *J. Supercrit. Fluids*, 2003, **27**, 263-274.
3. Y. L. Kim, J. D. Kim, J. S. Lim, Y. W. Lee and S. C. Yi, Reaction pathway and kinetics for uncatalyzed partial oxidation of *p*-xylene in sub- and supercritical water, *Ind. Eng. Chem. Res.*, 2002, **41**, 5576-5583.
4. Y. L. Kim, S. J. Chung, J. D. Kim, J. S. Lim, Y. W. Lee and S. C. Yi, Uncatalyzed partial oxidation of *p*-xylene in sub- and supercritical water, *React. Kinet. Catal. Lett.*, 2002, **77**, 35-42.
5. K. G. Knauss and S. A. Copenhaver, The solubility of *p*-xylene in water as a function of temperature and pressure and calculated thermodynamic quantities, *Geochim. Cosmochim. Acta*, 1995, **59**, 2443-2448.
6. H. Weingartner and E. U. Franck, Supercritical water as a solvent, *Angew. Chem., Int. Ed.*, 2005, **44**, 2672-2692.

7 The Evolution of *p*-Xylene Near/Supercritical Water Oxidation

7.1 Introduction

The structure of this thesis is discussed in Section 1.8 and is summarised in Figure 1-14. It shows how Chapters 4, 5 and 6 provide supporting studies in hydrodynamics and chemistry that are brought together in this chapter that charts the development of *p*X N/SCWO technology through the twin strands of reactor evolution and chemistry evolution. These are then related back to the project aims set out in Chapters 1 and 2 and feed forward to an assessment of the process economics in Chapter 8.

This chapter first describes the commissioning of *p*X N/SCWO on the IP1 rig and describes improvements that were made, particularly the introduction of buoyancy mixers as described and characterised in Chapter 4. It next describes the commissioning of the K5 reactor and describes its problems and the improvements to the reactor designs that were made. It finally charts the evolution of the TA yield and the material balances that were achieved (on the K5 rig) and relates improvements to key developments in reactor design and chemistry development.

7.2 The Commissioning of and Improvements to the IP1 Rig

7.2.1 Commissioning of the IP1 Rig

The IP1 rig is described in Section 2.3.2. The rig was initially commissioned for SCWO using *o*X as feedstock. *o*X SCWO is operationally easier than *p*X SCWO because *o*X does not freeze at ambient temperatures at the pumping pressure and because the product, *o*PA has a higher water solubility than TA.

Three main problems were found with the initial IP1 reactor design when undertaking xylene SCWO:

- Rapid reactor corrosion occurred.
- There were subcritical regions within the reactor.
- The mixer fouled and blocked.

The original reactor was constructed with 316L stainless steel tubing and stainless steel compression fittings. The tubing was corroded very rapidly, lasting at best a few days and on occasions failing within a few hours.

Heating of the IP1 reactor was achieved in two ways. Heat was convected into the reactor with the water/oxygen stream that had been heated in the pre-heater coil. Heat was also provided by the electrical heaters in the reactor block. The mixer was laid against the reactor coils and wrapped into the lagging of the reactor but despite this, it proved impossible to raise the mixer temperature (as measured by the thermocouple within one of the arms of the mixer cross) to supercritical temperatures. The mixer could only be got to a temperature of about 300 - 330 °C by these methods, well below the critical temperature of ~372 °C. Sub-critical regions are problematic because they have longer residence times than supercritical regions (by a factor of ~3 to 4 for a given volume) due to their higher densities and lower velocities as seen in Figure 2-10. Thus, the residence time in the reactor was dominated by the sub-critical regions and the relative performance of sub and supercritical regions was difficult to assess.

The catalyst in use during the commissioning was manganese bromide. This catalyst was very prone to precipitation¹ and the oxides formed (*e.g.* MnO₂, Mn₂O₃) were highly fouling. Thus, the reactor and especially the mixing cross, were highly prone to blockage. This manifested itself in a tendency for the delivery pressures of the feed pumps (for water/oxygen, catalyst solution and *pX*) to increase over time and to eventually trip the pumps out on high pressure. The original mixer cross design is shown in Figure 2-6. The idea of this design was to premix *pX* and oxygen and delay contacting catalyst with oxygen (which tends to precipitate the catalyst).

7.2.2 Improvements to the IP1 Rig

Owing to the rapid corrosion of stainless steel 316L, the tubing material was changed to Hastelloy C276. $\frac{1}{8}$ " Hastelloy tubing would typically last for 60-80 hours of *pX* N/SCWO operation. Stainless steel compression fittings could last for a few tens of hours. They were often used as a stop gap while waiting for deliveries of Hastelloy fittings. The latter were much more corrosion resistant and very rarely failed – they were however very expensive. Usually the Hastelloy fittings had to be retired when their attached tubing failed as it was often not possible to get them to reseal once their joints had been disassembled.

Lester *et al.*²⁻⁴ had developed a ‘buoyancy mixer’ for the mixing of metal salt solutions with supercritical water for the production of nano-particles. Chapter 4 and the authors papers^{5, 6} (copies in Appendix 1) describe how this concept was adapted for use in *pX* N/SCWO.

It was decided to trial these mixers on the IP1 rig. Two possible ways of engineering such mixers using compression fittings are shown in Figures 7-2(a) and 7-2(b). Designs could be engineered using $\frac{1}{8}$ " or $\frac{1}{16}$ " tubing inside $\frac{1}{4}$ " fittings with the use of suitable reducers. However, mixers could not be engineered using $\frac{1}{8}$ " fittings as the insertion of $\frac{1}{16}$ " O.D. tubing into this size of fitting allowed no space for an annular gap.

These mixer arrangements were trialled on the IP1 rig as shown in Figure 7-1. Each feed line to the mixer had a pressure transducer and Figures 7-2(a) and 7-2(b) show the pressure traces obtained during operation for the two designs. These traces provided a good means of assessing whether and where blockages were occurring within the rig and clearly show the design with the larger tubing was less prone to blockage. However, the good performance shown was intermittent and, in general, this reactor design was prone to blockage when using Mn based catalysts. It was therefore concluded that $\frac{1}{8}$ " tubing was not very suitable for *pX* N/SCWO while using manganese based catalysts and that $\frac{1}{4}$ " tubing should be trialled.

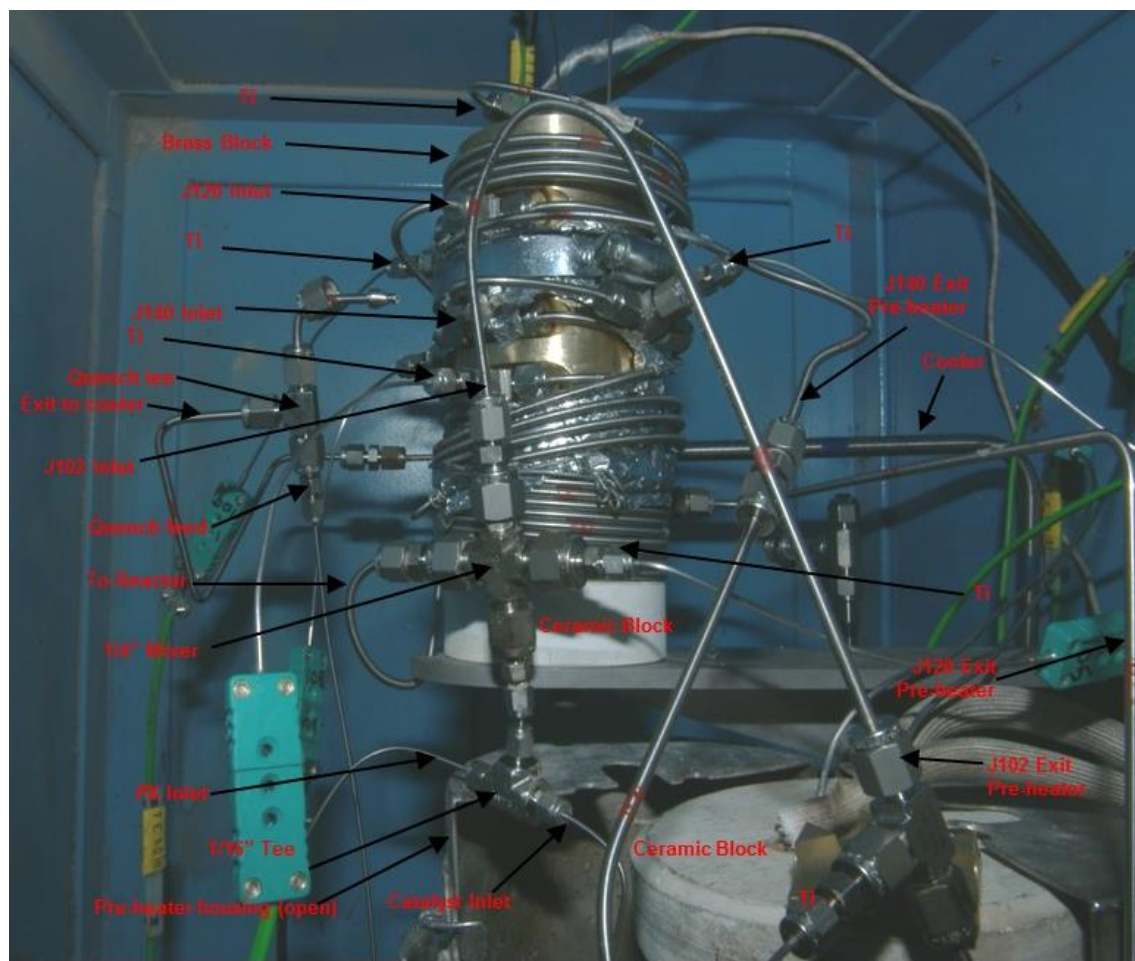


Figure 7-1. The IP1 reactor modified with the buoyancy mixer illustrated in Figure 7-2(b). Pump J102 pumps O_2/H_2O into the top of the buoyancy mixer where it mixes with pX and catalyst solution that mix in a tee piece and then enter the mixing cross from below. Ti is temperature indication provided by thermocouples in tee pieces. J120 and J140 are additional O_2/H_2O feed lines to provide staged O_2 feed.

The method of reactor construction of wrapping $\frac{1}{8}$ " O.D. tubing around a heated brass block is clear. The ends of the brass block are insulated with ceramic blocks and the assembly is lagged and enclosed in a metal housing (not present in picture) though the housing for the pre-heater block can be seen. Figure 3-5 further illustrates the assembly (but at an earlier stage in the project).

The quench tee is clearly visible (though is disconnected from the reactor for maintenance in the picture) as is the cooler that is behind the reactor.

The whole assembly is inside a steel cabinet (painted blue) and is viewed from the open side that is closed off with a polycarbonate door during operation.

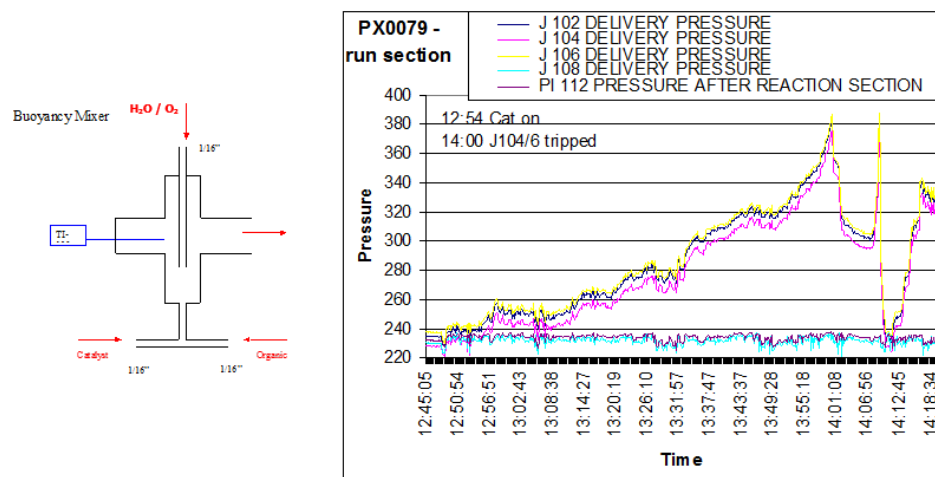


Figure 7-2(a). The performance of a buoyancy mixer with a $\frac{1}{16}$ " dip pipe in a $\frac{1}{4}$ " fitting. The trace shows the delivery pressure (in bar_g) of the four feed pumps J102 H₂O₂/water, J104 catalyst solution, J106 pX, J108 quench and the PI 112 pressure transducer after the quench. The pressure of three pumps feeding the mixer rises throughout the experimental period indicating that a progressive blockage is occurring. The delivery pressure of the quench pump does not rise thus indicating that blockage must be in the mixer cross or reactor sections though the former is the more likely. The unit trips at a pressure of 380 bar_g after 1:06 hrs:mins of operation.

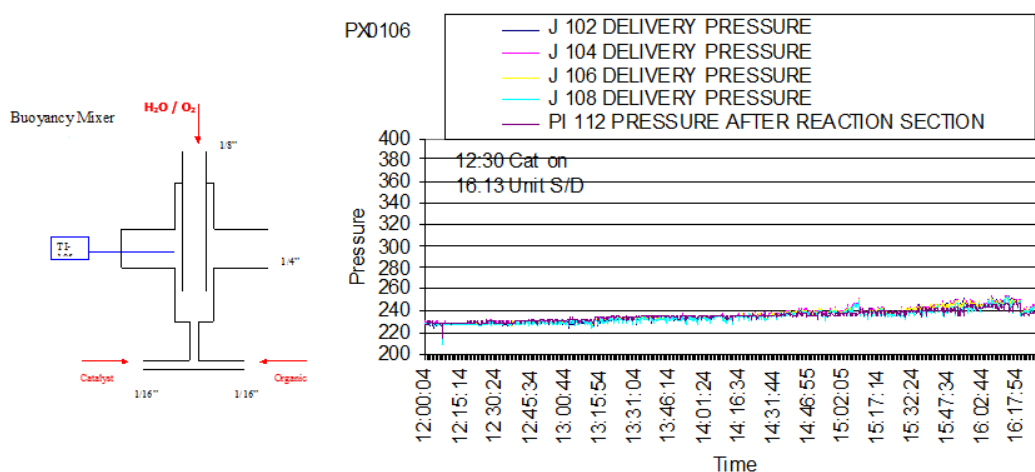


Figure 7-2(b). The performance of a buoyancy mixer with a $\frac{1}{8}$ " dip pipe in a $\frac{1}{4}$ " fitting. See caption for 7-1 for descriptions. The trace shows that the delivery pressure (in bar_g) of all four feed pumps and the downstream pressure transducer rises slightly throughout the experimental period. It is likely that the pressure rise is occurring due to progressive build up on the filters upstream of the BPR. Performance is much improved compared to the design in Figure 7-1.

7.3 The Commissioning of the Kinetics Rig

The Kinetics (K5) rig, as it was first installed, is described in Section 2.3.2. This rig and its reactor was commissioned using a standard, one oxygen-feed formulation that had been developed on the IP1 rig (and is described in Section 3.10.2). The reactor was found to give poor aromatics material balance and oxidation to carbon dioxide compared to those obtained on the IP1 rig with the equivalent formulation; more detail is available in Section 7.5. It was also prone to fouling and blockage and to having a cool, sub-critical mixer.

Clearly these problems were attributable to one or more aspects of the difference between the IP1 and K5 rigs. These differences were:

- Use of a differing detailed geometry in the mixer.
- Use of an ISCO pump in place of a Gilson pump to feed *pX*.
- Use of Jasco pumps rather than Gilson pumps on the other feeds.
- Use of a Thar BPR rather than Tescom or Pressure Tech BPRs.
- Use of sand bath for heating rather than tubing wrapped around metal blocks heated by cartridge heaters.
- Use of ¼" reactor tubing rather than ⅛" tubing.

These differences were investigated systematically as described in the next section.

7.4 Evolution of the Kinetics Rig and Reactor

The design of the K5 rig was investigated and (where appropriate) was modified to address the issues identified in the preceding section. The modifications undertaken are described chronologically in the following sections. The effect of the changes on the performance of the unit are described in Section 7.5.

The original mixer design installed on the K5 rig is detailed in Figure 2-8. This was a buoyancy mixer but differed from that used on the IP1 rig (shown in Figure 7-2) in that the catalyst solution and *pX* were fed and mixed in ¼" tubing and fittings rather than ⅛". The mixer was modified to that used on the IP1 rig with

pX and catalyst being fed in $\frac{1}{16}$ " O.D. tubing and mixed in a $\frac{1}{16}$ " tee-piece and then fed into a buoyancy mixer constructed with $\frac{1}{8}$ " O.D. down flow dip pipe in a $\frac{1}{4}$ " mixing cross. This arrangement is illustrated in Figures 7-2(b) and 7-3.

The original mixer arrangement was initially installed outside the sand bath as shown in Figure 2-8. Its only means of heating was from sensible heat in the SCW conveyed from the pre-heater. This was insufficient to attain supercritical conditions in the mixer. The mixer arrangement was therefore relocated into the sand bath so it could achieve supercritical conditions if required. It was thought that this might also help fouling though it was later learned that sub-critical is the less fouling condition.

The high degree of mixer fouling ceased after a reactor rebuild and was thought to have been caused by an incorrectly configured mixer dip pipe.

The original reactor was installed with one stage of oxygen feed as shown in Figure 2-8. This was subsequently increased to two and later four stages. The first stage was introduced through a buoyancy mixer and the subsequent stages through tee-pieces. The configuration of the reactor after these changes is shown in Figure 7-3.

The installation of a thermal mass flow meter on the *pX* line revealed that the ISCO pump fed *pX* erratically at low flow rates, details are in Section 3.5.2. Also, the complex valve mechanism on the ISCO pump, to enable switching between the two feed cylinders, was not robust and would periodically mis-sequence and allow back flow into the pump chambers which caused pump damage. The pump was therefore (eventually) removed from the rig and replaced with a twin headed Jasco pump.

A thermal mass flow meter was installed on the catalyst line and demonstrated that the Jasco pump was pumping reliably. Details are in Section 3.4.3.

The Thar BPR proved to be difficult to configure and unreliable in the *pX* N/SCWO duty and was replaced by a Tescom BPR. A detailed description of BPR operation and issues is available in Section 3.8.1.



Figure 7-3. Kinetics rig (K5) reactor (Ref. 3 in Figure 7-7) with modified mixer design and 4 oxygen stages. Catalyst solution and *pX* were fed in (a) $\frac{1}{8}$ " and (b) $\frac{1}{16}$ " tubing respectively to a $\frac{1}{16}$ " Swagelok tee-piece mixer (c). The mixture flowed upwards into a buoyancy mixer (d) constructed from a $\frac{1}{4}$ " cross piece and containing a downwards oxygen/water feed through an $\frac{1}{8}$ " tubing dip-pipe (e) and with a thermocouple inserted through an $\frac{1}{8}$ " line (f). There were thermocouple points on the *pX* feed line (g) and air/O₂ line (h). There were three additional oxygen/water $\frac{1}{4}$ " tee-piece (i),(j),(k) mixing points in the reactor, fed by $\frac{1}{8}$ " tubing. The first of these (i) had a thermocouple both immediately up (l) and down (m) stream of the mixing point. The other two had thermocouples downstream of the mixing point (n), (o). The reactor flow then passed through a high point (p) and flowed downwards where an up-flow quench (q) was added from an $\frac{1}{8}$ " line. There was a final thermocouple (r) on the line downstream of the quench mixing point. The reactor was attached to supports (s).

The manganese bromide based catalysts were replaced by cobalt and copper bromide based catalysts, the development of which is described in Section 6.4.1 and in the author's paper ⁷ available in Appendix 1. This switch was made because these new catalysts were much less fouling than the manganese based catalysts and this improved the operability of the rigs.

It was noted that compression joints did not last long in the sand bath having to be replaced after a few uses because they failed in pressure testing. It was postulated that joints could be leaking under operational conditions due to the high temperatures combined with the vibration and abrasion of the sand. However, it was thought that the joints might be able to reseal during cooling such that it appeared (during subsequent pressure testing) that the joints were still sound. To test this hypothesis, it was decided to construct a welded reactor in which all the compression fittings inside the sand bath were replaced with welded joints. The detailed design of this reactor is described in the next section.

The design for a welded reactor is shown in Figure 7-4 and the detail of the construction of the mixers in Figure 7-5. The author provided the conceptual design; this kept many of the internal dimensions the same as those that had been proven in the mixers fabricated from Swagelok fittings. This included the sizing of the mixing point for catalyst solution and pX , the sizing of the SCW/O₂ dip pipe and the annular gap mixing clearances in the buoyancy mixing chamber. The fabrication methods used were developed by the Project Mechanical Engineer. A photograph of the finished unit is shown in Figure 7-6.

The all welded reactors gave much improved mass balance (details are given in Section 7.5) and had longer lifetimes than the reactors made from Swagelok fittings. They would eventually fail because of corrosion of the Hastelloy and a reactor constructed of ¼" O.D. tubing with 0.065" wall thickness was found to have a lifetime of ~100 hours of operation under reacting conditions. Thus, there was a constant need and opportunity to construct new reactors and to evolve the design. The changes to and versions of the reactor are summarised in Figure 7-7.

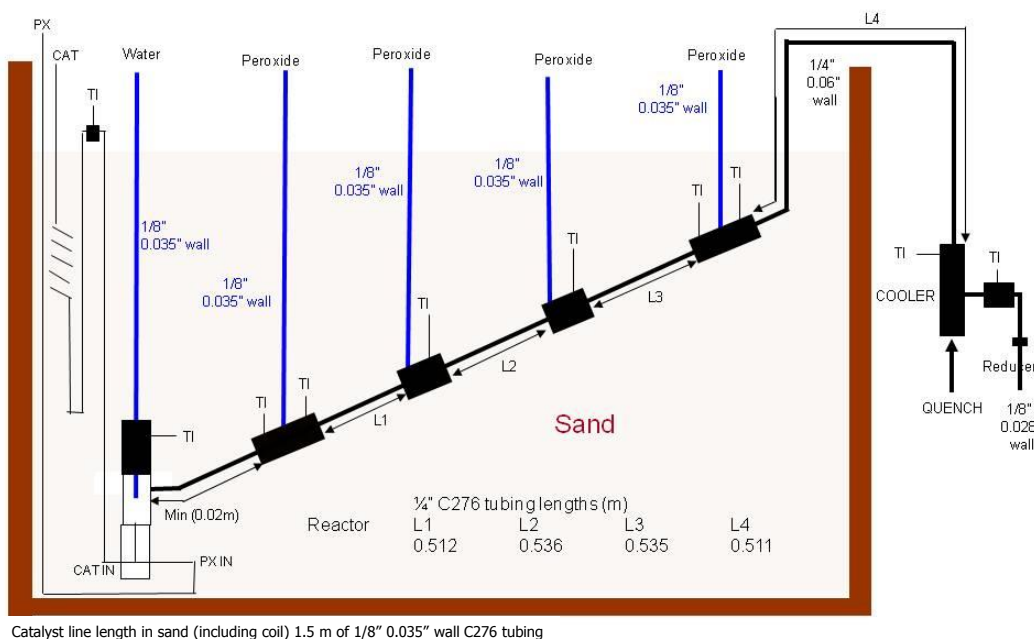


Figure 7-4. The design of welded reactor (Ref. 6 in Figure 7-7) on the K5 rig. Catalyst solution was pre-heated in a coil in the hot sand and was mixed in a tee-piece with the *pX*. This combined stream was mixed with SCW in a buoyancy mixer. O₂ is introduced in 4 stages in down flow injection tee-piece mixers by (low volumetric flow) O₂/SCW injections within the heated sand bath. Thermocouples gave temperature indication (TI) around each mixing operation. After the last O₂ injection, the flow exited the sand bath and passed through a lute (a high point) designed to prevent back flow of quench. At the quench point, caustic quench was injected in an up-flow tee-piece. There was a final thermocouple prior to a pipe size reducer. The detailed design and sizing of the mixing components is given in Figure 7-5 and a photo in Figure 7-6.

During this period, an important discovery was made, though completely by accident. It was clear that Hastelloy would not be a suitable material for a commercial reactor because of its corrosion rate. It was therefore decided to test the corrosion resistance of titanium by threading a thin titanium wire through the reactor during fabrication. This proved to be successful and did not compromise the performance of the reactor through additional fouling (though the less fouling Co/Cu/Br formulations were in use by this time). At the end of the reactor's life time, it was cut up for corrosion inspection and the titanium wire was removed and examined. Surprisingly the wire showed no corrosion at the start of the reactor but progressively increasing damage towards the end of the reactor. This was attributed to back flow of caustic into the reactor from the quench point; hot

caustic is known to damage titanium. The insertion of Ti wire thus constitutes a test for back flow of caustic. There was a lute at the quench point which was designed to prevent back flow of quench liquor but which had clearly been ineffective. The lute was therefore redesigned, compare the design in Figure 7-3 with the redesign shown in Figures 7-4 and 7-6. It was planned to use this method to check the design of the new lute (against backflow) but unfortunately, this is a slow test (taking 4 months from wire installation to inspection) and the project ended before a conclusion could be reached.

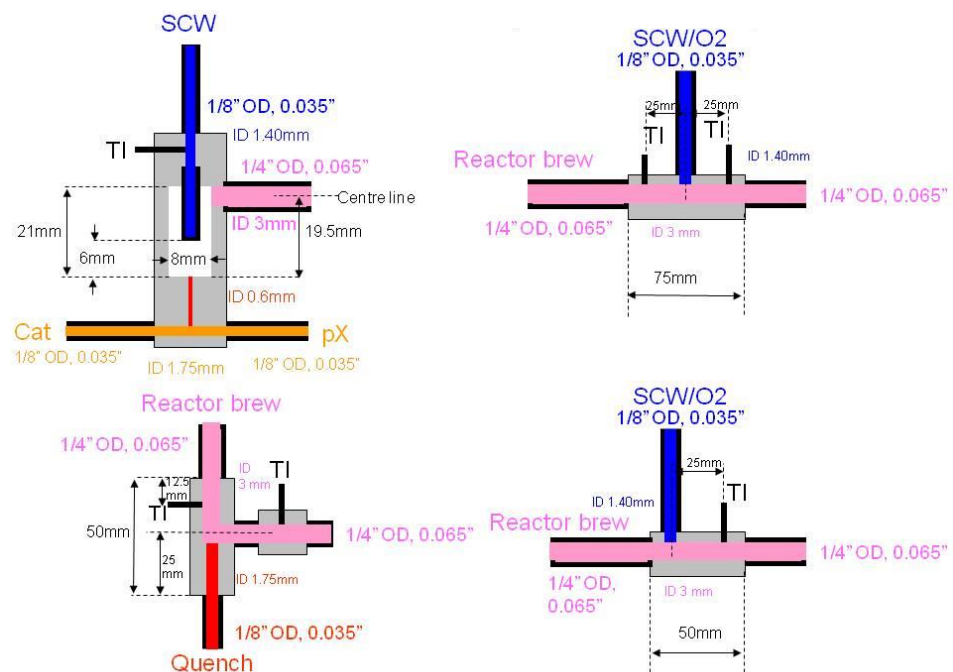


Figure 7-5. The detailed design and sizing of the mixing components in the welded reactor. The mixing components were a combined tee-piece and buoyancy mixer (top left) for mixing catalyst, *pX* and O₂/SCW, tee-piece mixers (top and bottom right) for introducing O₂/SCW and quench mixer (bottom left). The mixers were constructed from pipe and drilled rod which were subsequently welded together. Thermocouples (for temperature indication (TI)) were subsequently pushed into the guide/retaining pipes. The material of construction was Hastelloy.



Figure 7-6. The welded reactor (Ref. 6 in Figure 7-7) on the K5 rig. The detail of components can be seen in Figures 7-5. The initial buoyancy mixer is bottom right and has a vertical orientation. Feeds and thermocouples to this mixer enter through the vertical $\frac{1}{8}$ " tubing. The exit from this mixer is to the left through $\frac{1}{4}$ " tubing and immediately enters a tee-piece mixer with a close to horizontal but rising orientation with a O_2/SCW feed and 2 thermocouples entering through vertical $\frac{1}{8}$ " tubing. This is the start of the reaction section. The reactor continues in an upwards spiral of $\frac{1}{4}$ " tubing with 3 further O_2/SCW tee-pieces, feed and thermocouples points and is arranged in this spiral fashion so that it will fit into a sand bath. After the final injection point, the tubing rises vertically to exit the sand bath and then passes through a lute with a high point, designed to prevent back flow of quench into the reactor. It then passes to a quench addition point (seen to the left), that has a vertical orientation, where the caustic quench stream enters through $\frac{1}{8}$ " tubing from below. The exit from the quench mixer is horizontal and passes to a final thermocouple point. Note that all the joints in this assembly that are within the sand bath are welded and all Swaged joint points to this assembly fall outside of the bath.

The reactor had to be rebuilt periodically because of corrosion failures. A summary of the K5 reactors employed during the project is given in Figure 7-7.

Rx Type	Tubular	Tubular	Tubular	Tubular	Tubular	Tubular	Tubular
Reference	1	2	3	4	5	6	7
Tube OD "	1/4	1/4	1/4	1/4	1/4	1/4	1/4
Wall "	0.065	0.065	0.065	0.065	0.065	0.065	0.065
Flow ml/min	12-24	12-24	12-24	12-24	12-24	50-124	50-124
Volume ml	11.6	13.7	12.1	6.4	6.4	17.1	17.1
Re 380 °C	2720-5440					11340-28120	
Re 330 °C	1050-2090					4360-10810	
RT(s) 380 °C	6.1-12.1	7.2-14.3	6.3-12.6	3.3-6.7		1.7-4.3	
330 °C	19.6-39.2	23.1-46.3	20.4-40.9	10.8-21.6		5.6-13.9	
O ₂ stages	2	2	4	4	4	4	4
Mixers	1 x Buoyancy	1 x Buoyancy	1 x Buoyancy	1 x Buoyancy	1 x Buoyancy	1 x Buoyancy	4 x Buoyancy
	1 x Tee-piece	1 x Tee-piece	3 x Tee-piece	3 x Tee-piece	3 x Tee-piece	4 x Tee-piece	
Construction	Fittings	Fittings	Fittings	Fittings	Welded	Welded	Welded

Figure 7-7. The evolution of tubular reactors that were deployed on the K5 Kinetics rig. Rx Type gives the reactor type which was tubular. Tube OD gives the tubing outer diameter which was 1/4" with a wall thickness of 0.065". Ambient flow rates (as pumped by the HPLC pumps) were low for reactors 1-5 but were latterly increased for reactors 6-7 by, the use of larger pumps. The effect on Reynolds numbers (Re) and residence time (RT) at supercritical conditions (temperature 380 °C) and subcritical conditions (330 °C) is given. O₂ stages gives the number of injections of oxygen and mixers indicate how the initial mixing (of *p*X, catalyst and oxygen) and subsequent injection of further oxygen was undertaken. Construction indicates how the reactor was constructed either with Swagelok compression fittings or by the welding together of components machined from bar stock.

The residence time of the reactors was roughly halved over the course of the project (from Reactor 1 to Reactor 5). This was because the early reactors were found to be oversized; the chemistry of this is discussed in Section 6.4.4.

For Reactor 6, the pumps on the reactor were uprated by the addition of two Gilson HPLC pumps capable of pumping 50 mL/min as detailed in Section 3.3.2. This enabled a total flow of up to ~124 mL/min (comprising 2 x 50 mL/min water/oxygen pumps, 1 x 20 mL/min catalyst solution pump, and 4 x 1 mL/min water/oxygen pumps) to enable increased flow rates. This enabled a Reynolds number of $\sim 10^4$ to be obtained at subcritical conditions and thus enabled an investigation of the laminar ($Re < 2000$) to turbulent ($Re > 2000$) transition to be made as detailed in Section 5.8.3. The size of the reactor had to be increased in order, to maintain adequate residence time. However, there were constraints on the size of reactor that could be fitted into the sand bath and so a decrease of residence time compared to Reactor 5 was necessary. A plug flow reactor undertaking a free radical reaction tends to have a conversion profile with a long tail out (where the last bit of conversion requires a disproportionate amount of residence time and reactor volume) as illustrated in Figure 5.2. Reactors 6 and 7 thus tended to be short of residence time for this reaction tail out and gave under conversion as seen in Figure 5-11.

The final reactor, Reactor 7, was built using four buoyancy mixers in place of one buoyancy mixer and three or four tee-piece mixers. This reactor is shown in Figure 7-8.



Figure 7-8. The final K5 reactor (Ref. 7 in Figure 7-7), with 4 buoyancy mixers, the first to mix *p*X, catalyst solution and SCW/O₂ and the other three for further SCW/O₂ staged addition.

7.5 The Progression of Aromatic Material Balance and TA Yield

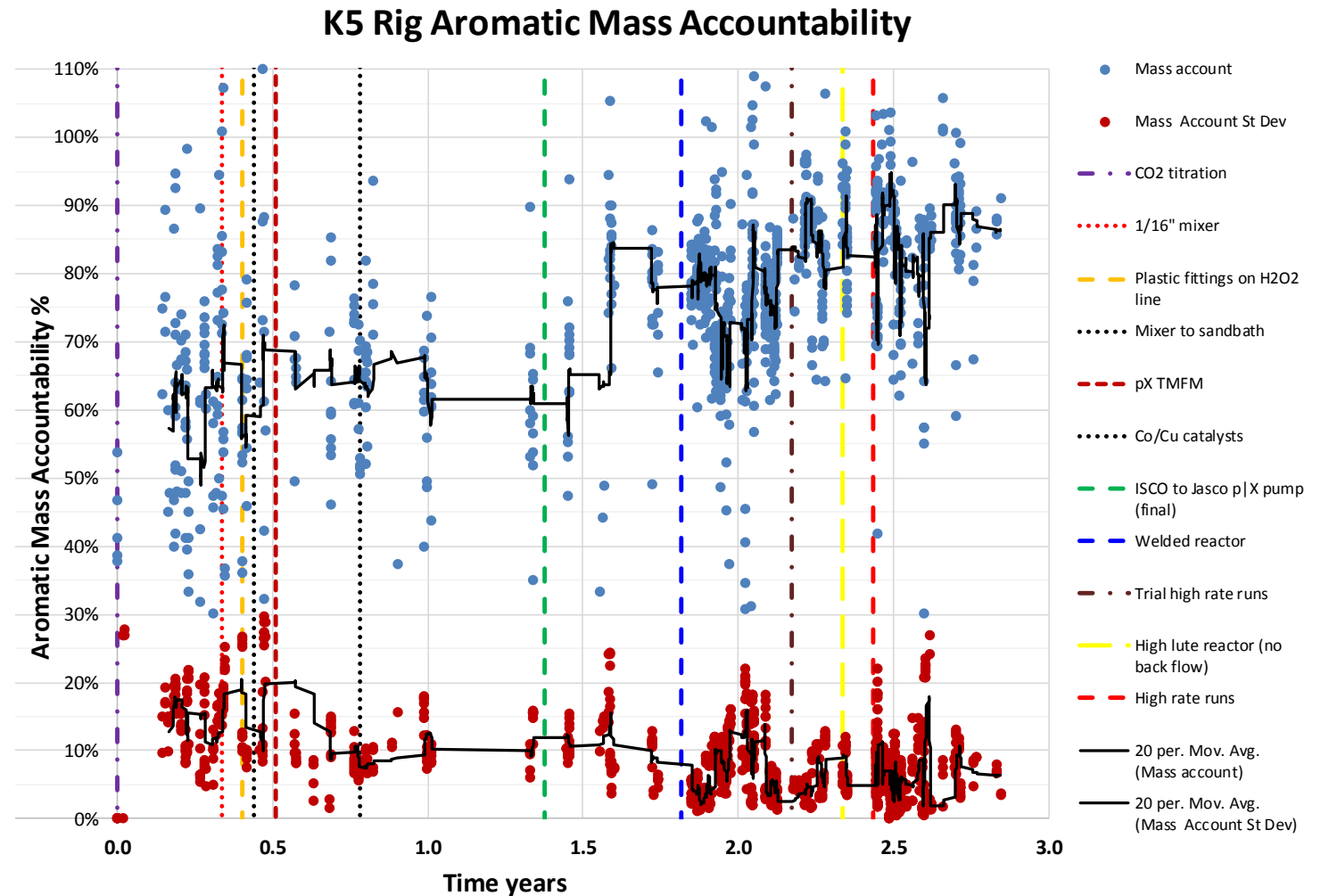
The ambition for the aromatic material balance of the Kinetics (K5) rig was set out in Section 2.5.1 as at least 99 % $\pm$ 1 %. This section examines how this balance progressed over the project and the extent to which this ambition was realised.

The evolution of the aromatic material balance, with the timing of major rig improvements, is given in Figure 7-9. Note that this analysis does not include the STR as this reactor was implemented on the IP1 rig. The analysis shows that when the unit was first started up, the aromatic material balance was around 55 – 65 % with a standard deviation (σ) of around 15 %. This was clearly not good

and was poorer than that being achieved on the IP1 rig of around 80 %. The first wave of improvements raised the balance to ~65 % and reduced σ to ~10 %. The *pX* thermal mass flow meter was probably the most significant improvement. Another major improvement was the replacement of the ISCO *pX* pump with a Jasco pump which caused the material balance to jump to ~80 % and σ to drop below 10 %. The introduction of welded reactors led to a large increase in rig occupancy, *i.e.* the number of runs per unit time. This was because of a large reduction in the number of rig rebuilds and repairs that were necessary. The reactor failures of the early reactors (built with compression fittings) also led to many electrical failures in the sand bath because of the leak of reactor fluid onto the electric heating components. The high rate trials led to average material balance of around 90 % with σ of around 2 – 5 % with some runs achieving close to 100 % material balance.

There are several conclusions that can be drawn from these experiences. Firstly, the K5 rig did not get close to the ‘kinetics quality’ ambitions that were articulated at the project outset. The four most important elements in achieving improvements were the use of a thermal mass flow meter for *pX*, the use of (twin headed) Jasco pumps for *pX* pumping, the use of all welded reactors and the use of higher reactor flow rates. The nature of the missing mass is unclear. The author’s view is that the issue was not the presence of a ‘mystery component’ or the mis-measurement of a known product component but poor measurement of the *pX* flow rate combined with possible hold up of TA within the unit; the main evidence to support this view was the ability to achieve 100 % material balance on occasions though this is not conclusive. Section 3.5.3 discusses how the *pX* thermal mass flow meter was probably oversized which contributed to the problems.

Figure 7-9. The progression of the K5 rig aromatic material balance with time. The blue points show the aromatic material balances obtained for all K5 rig experiments over time from the start-up of the rig to the project closure. Material balances of < 40 % and > 110 % were omitted from the analysis. The red points show the standard deviation of the aromatic material balance for the previous 10 runs. Both of these datasets have a 20 point moving average trendline. The vertical lines show the timing of the implementation of key developments on the rig as follows: the titration to measure CO₂ (discussed in Section 2.5.1), mixing *pX* and catalyst solution with 1/16" mixer immediately prior to buoyancy mixer (Section 7.4), use of plastic fittings on peroxide lines (Section 3.3.1), moving the buoyancy mixer assembly into the sand bath (Section 7.4), adding a thermal mass flow meter (TMFM) to the *pX* line (Section 3.5.3), Co/Cu based catalysts (Section 6.4.1), replacing the ISCO pump with a Jasco pump (Section 3.5.2), using all welded reactors (Section 7.4), trialling high rate runs (Sections 3.3.2 & 5.8.3), high lute to eliminate caustic backflow into the reactor (Section 7.4), further high rate runs.



Recommendations for any future work would be to use a lower range thermal mass flow meter, high flow rates and to consider if the quench mixing is adequate. However, the attainment of ‘kinetics quality’ data for *pX* N/SCWO at small scale remains a challenging problem.

The time progression of the maximum TA yield obtained is harder to assess because of the aromatic material balance issues and plots of the TA yield tend to simply track the material balance trend seen in Figure 7-9 with the best yields obtained towards the project end. The TA yields obtained at the start of the project were around 55 - 60 % and increased as the rig improvements were made. Applying the criteria that the yield must be consistent over a run with high material balance (which is ~100 %) then the highest repeatable yield of TA obtained was ~90 % with reactor conditions 2 % *pX*, high reactor flow, 300 °C, 230 bar, 115 % O₂ in 1 stage, 200 % Co/Cu 85/15 catalyst, where 100 % catalyst = 1625 ppm Br (from the metal bromide salts) and 325 ppm Br (from extra HBr) in reactor obtained on a mass balance of ~100 %. By products were ~7.5 % CO₂, ~1.5 % BA and ~ 1 % others. This is consistent with the chemistry discussions in Section 6.4 which suggest high yields at low [*pX*], high optimised [catalyst], low temperature and low but adequate [O₂]. The implications of this level of TA yield are considered in Chapter 8.

7.6 References

1. J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, E. Perez, I. Pearson, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Prevention of Manganese Precipitation during the Continuous Selective Partial Oxidation of Methyl Aromatics with Molecular Oxygen in Supercritical Water, *Adv. Synth. Catal.*, 2009, **351**, 1866-1876.
2. P. J. Blood, J. P. Denyer, B. J. Azzopardi, M. Poliakoff and E. Lester, A versatile flow visualisation technique for quantifying mixing in a binary system: application to continuous supercritical water hydrothermal synthesis (SWHS), *Chem. Eng. Sci.*, 2004, **59**, 2853-2861.
3. E. Lester, P. J. Blood, J. P. Denyer, B. J. Azzopardi, J. Li and M. Poliakoff, Impact of reactor geometry on continuous hydrothermal synthesis mixing, *Mater. Res. Innovations*, 2010, **14**, 19-26.
4. E. Lester, P. J. Blood, J. P. Denyer, D. Giddings, B. Azzopardi and M. Poliakoff, Reaction engineering: The supercritical water hydrothermal synthesis of nano-particles, *J. Supercrit. Fluids*, 2006, **37**, 209-214.
5. E. Perez, M. L. Thomas, D. Housley, P. A. Hamley, J. Fraga-Dubreuil, J. Li, E. Lester and M. Poliakoff, Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 3: effects of geometry and mixing in laboratory scale continuous reactors, *RSC Adv.*, 2016, **6**, 11289-11294.
6. D. Housley, T. Huddle, E. Lester and M. Poliakoff, The use of dimensionless groups to analyse the mixing of streams with large density differences in sub- and supercritical water, *Chem. Eng. J.*, 2016, **287**, 350-358.
7. E. Perez, J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, M. L. Thomas, C. Yan, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 2. The discovery of better catalysts, *Green Chem.*, 2011, **13**, 2397-2407.

8 The Economics of *p*X N/SCWO

8.1 Introduction

An assessment of the economics of *p*X N/SCWO oxidation needs to consider capital and variable costs as these are the two major economic metrics which determine the likely take up and economic success of a technology. Other aspects include pollutant intensity, energy intensity and inherent process safety; these factors impact the economic decision making by their costs (which may be needed to achieve required regulatory or self-imposed standards) and are thus dealt with, within the major cost metrics. However, clearly a process that is inherently safe will (tend to) be preferred.

Assessments of the capital and variable costs of the acetic based *p*X oxidation process are published by the market analysis consultancies SRI/IHS ^{1, 2, 3} and Nexant.⁴ The only published assessment of the economics of *p*X N/SCWO is by Dunn and Savage ⁵ who present a capital cost, pollution intensity and energy intensity analysis of NCW and SCW processes with air and oxygen as alternative oxidants. They do not attempt a variable cost analysis.

To undertake rigorous capital and variable cost analyses is a sizeable task that requires access to proprietary data which is not available to the author. Within this limitation, this chapter will assess the impact of the findings of this PhD study on the capital and variable costs of *p*X N/SCWO and assess the prospects of this technology displacing the conventional, acetic acid based process.

8.2 Review of Process Economics Literature

There is only one published paper on *p*X N/SCWO economics which is by Dunn and Savage.⁵ They considered four cases which are NCW and SCW (at 300 °C and 380 °C respectively), using air or oxygen as oxidant and MnBr₂ as catalyst. They considered a TA rate of 80 te/hr with a *p*X concentration of 1 M which is 10.6 % w/w which gives a TA slurry of 16.6 % rising to 20 % with liquid vapour removal. Current PTA plants produce up to 140 te/hr of PTA, processing TA

slurry concentrations (ex the oxidation reactor) of 30 – 38 %. A commercial *pX* N/SCWO process would likely need a TA slurry strength of at least 20 % and preferably 30 %. The oxygen stoichiometry considered was 3.5 : 1 which (the work in Chapter 6 suggests) is a little high. The reactor residence times were 30 mins and 12 seconds for NCWO and SCWO respectively, again these are probably higher than necessary. The analysis assumed a boiling reactor for air cases; this has not been tested experimentally. The TA and 4-CBA yields were assumed to be 99 % and 1 % respectively, and they cited Hamley *et al.*⁶ as justification for this. The analysis in Table 2-2(c) of this thesis shows that this TA yield is much too optimistic; the author suspects that Savage *et al.* have interpreted Hamley *et al.*'s quoted selectivities as yields. The work in Chapter 6 of this thesis suggest that maximum TA yields of ~90 % are more realistic. It is unclear the extent of heat integration considered by Savage *et al.* in their Aspen models and to what extent they captured and reused the heat of the oxidation reaction. They included the purification process and assumed that one can use oxidation reactor liquor, containing 20 % TA, in the hydrogenation process. They did not consider that the oxidation metal catalysts are likely to be a poison for the Pd/C purification catalyst and would need to be removed and recovered first. The materials of construction quoted include Hastelloy for the reactor – the data in Section 7.2.2 shows that this is not suitable and titanium would be necessary.

Savage *et al.* do not provide a variable cost analysis but they give 'energy intensities' for the various processes as a 'proxy' for variable cost. The energy intensity and capital cost estimates for the air based plants are over twice the equivalent figures for an acetic acid technology plant and these figures are dominated by the high cost of air compressors and compression; a clear conclusion is that N/SCWO technology must use oxygen (separated from nitrogen) as the oxidant. The capital cost of oxygen fed NCWO and SCWO plants are estimated at 112 % and 124 % of an acetic acid based technology plant respectively and the energy intensities are 89 % and 121 % respectively. The error of the analysis is given as ± 20 % and they therefore conclude that the capital and energy costs of an oxygen fed NCWO plant are similar to those of a conventional, acetic acid based process.

8.3 Capital Cost Aspects

This section considers the ways in which capital costs can be built up. It undertakes a high-level process synthesis for a *pX* N/SCWO process and assesses the likely impact on the process capital cost compared to the conventional, acetic acid based technology. It only considers oxygen fed N/SCWO as Savage *et al.*'s analysis demonstrated the prohibitive cost of air fed options.

Capital cost assessments of a new process technology are usually undertaken in one of two ways:

- A build-up of cost based on an equipment list of main plant items with specifications for sizing and materials of construction. A formula is then applied to estimate design and piping costs.
- By difference from similar existing technology for which the capital cost is known and applying a factor to account for differences in scale.

Clearly both approaches require some knowledge of equipment costs and how these vary with throughput, size and materials. This requires access to considerable data, much of which comes from detailed discussions with equipment vendors and which is treated as proprietary by technology vendors.

The most recent market report is by IHS ³ from 2015 and gives the ISBL and OSBL capital costs of a world class Asia based PTA plant as approximately \$300 million and \$400 million respectively; prices are in US dollars. ISBL and OSBL bases roughly equate to excluding and including utilities (such as water treatment and effluent treatment) respectively. Savage ⁵ estimated that the ISBL cost is split ~50:50 between the oxidation and purification plants though it is likely the oxidation plant is more expensive because of the extensive use of titanium materials.

Using the current state of the *pX* N/SCWO technology (as assessed in this thesis), the author has undertaken a high-level process synthesis and assessed the differences from the conventional acetic acid based technology; this analysis is summarised in Table 8-1. This analysis should be viewed referencing the process description given in Section 1.2.

Table 8-1. The differences in equipment for unit operations between current *pX* N/SCWO and conventional acetic acid based technology.

Unit Operation	Conventional acetic acid PTA technology	N/SCW PTA technology
Oxidation Reactor	Large titanium clad STR	Small titanium clad TBR
Oxidant Supply	Air, large compressor	Smaller O ₂ system
Off gas treatment	Large	Small
CTA Crystallisers	Several large STRs	As conventional
CTA Separators	Centrifuges and/or filters	As conventional
Solvent recovery	Acetic/water separation by distillation	Water purification system
Catalyst and by-products handling	Liquor recycle. Purge stream with catalyst and solvent recovery and optional by-product recovery.	Similar to conventional
Purification reactor	Large Pd/C bed hydrogenation reactor	As conventional
PTA Crystallisers	Several large STRs	As conventional
PTA Separators	Centrifuges and/or filters	As conventional
Driers	Hot air	As conventional
PTA Storage	Silos	As conventional

The conventional process has a very large titanium lined carbon steel STR. *pX* N/SCWO would have a much smaller but higher pressure PFR with a shorter liquid residence time of less than 5 minutes; data in Section 6.3 suggest N/SCWO's STY is higher by an order of magnitude compared to the conventional process; the reactor would probably be titanium lined carbon steel because of the need for a catalyst containing bromide. *pX* N/SCWO eliminates a large compressor and spent air handling system but requires an oxygen supply system. *pX* N/SCWO eliminates the solvent dehydration system which requires and energy intensive acetic acid and water distillation. However, many PTA facilities are sited in regions where water is scarce and it would be necessary to recycle water. This water reclamation would be unlikely to use distillation because this is too energy intensive (due to the high heat capacity of water) so would probably need a membrane technology such as reverse osmosis; however, this has a large electricity requirement. *pX* N/SCWO would require catalyst and

by-products handling which would be similar to conventional though differing in the detail.

Chapter 1 describes the twin role of the purification plant of:

- converting 4-CBA to *p*-toluic acid to reduce the 4-CBA incorporation into TA in the subsequent PTA recrystallisation
- hydrogenating highly coloured by-product species into less coloured forms.

The data presented in Chapter 6 shows that *pX* N/SCWO can eliminate the first issue provided the PFR has sufficient residence time to enable the 4-CBA to react away to a low level. However, the data in Chapter 5 showed that in *pX* N/SCWO, the levels of coloured by-product species are higher than in the conventional acetic based process. Thus, the *pX* N/SCWO technology is currently unable to remove the need for the purification plant; such a plant would be similar to that deployed in the conventional acetic based technology.

Overall, we can see that sizeable proportions of the plant remain unchanged, and that though some equipment in the conventional process is eliminated, in every case alternative equipment is needed.

Savage *et al.*⁵ estimated that the cost of a *pX* NCWO plant would be within ± 20 % of that of a plant using conventional, acetic acid based technology. The analysis in this section suggests that this is probably a reasonable conclusion.

8.4 Variable Cost Aspects

Sources of variable cost for *pX* N/SCWO and conventional acetic acid based PTA technology are given in Table 8-2. Some of these items are quantified later in this section. In the oxidation reactor, the most significant variable cost contributions are the oxidation of the *pX* feedstock and acetic acid solvent to CO₂ and CO. There is a sizeable energy credit from steam raising from the heat of the oxidation reaction. In the N/SCWO process there is no acetic acid oxidation but the *pX* oxidation (to CO₂ and CO) is greater. The energy credit is greater because the reaction is performed at a greater temperature (300 – 400 °C for N/SCWO versus

Table 8-2. Sources of variable cost in unit operations in *pX* N/SCWO and conventional acetic acid based technology. The most significant items are highlighted in red.

Unit Operation	Variable Costs	
	Conventional acetic acid PTA technology	N/SCW PTA technology
Oxidation Reactor	CSTR motor Acetic acid oxidation <i>pX</i> oxidation (to CO ₂ & CO) Catalyst make up Steam raising	Pumps No acetic acid oxidation Increased <i>pX</i> oxidation (to CO ₂ & CO) Catalyst make up Higher grade steam
Oxidant Supply	Air compression	Cost of O ₂
Off gas treatment	Large power recovery	Small power recovery
CTA Crystallisers	CSTR motors Energy recovery from flash in overheads	As conventional
CTA Separators	Centrifuge and/or filter motors	As conventional
Solvent recovery	Heat for acetic/water separation by distillation	Power for reverse osmosis
Catalyst and by-products handling	Heat for solvent recovery Oxalate for catalyst recovery	Power for reverse osmosis. Oxalate as conventional
Purification reactor	Heating water Pd/C catalyst Hydrogen	As conventional
PTA Crystallisers	CSTR motors Energy recovery from flash in overheads	As conventional
PTA Separators	Centrifuge and/or filter motors	As conventional
Driers	Hot air	As conventional
PTA Storage	Air pneumatic conveying	As conventional

160 - 200 °C for acetic acid technology) which enables raising of a higher grade of steam which is more thermodynamically useful. The conventional technology requires the compression of large quantities of air though significant energy can be recovered from the expansion of the spent air. The N/SCWO technology requires the provision of oxygen and has less opportunity for energy recovery from spent gas. Significant energy is recovered from the condensing overheads in the progressive flashing to lower temperatures in the crystallisers. The acetic acid/water separation is by an energy intensive distillation. N/SCWO technology

would need to recover and recycle water because it is often a scarce resource. The use of distillation would not be cost effective because of the high heat capacity of water. The use of a membrane technology, such as reverse osmosis, would probably be required, however, this is energy intensive. The purification plant requires the heating of large quantities of water to high temperatures and this requires significant energy. Some of this energy is recovered in the subsequent flashing in the crystalliser vessels. The energy needed for the purification plant is roughly equal to the energy credit from the oxidation plant (from the oxidation reaction exotherm) so overall a conventional technology plant is close to neutral on energy though modern plants have a small energy export. A N/SCWO plant would have a larger net energy export because the oxidation reactor raises steam at a higher temperature which is more thermodynamically useful. The value of this extra energy export would be very location dependent. On an integrated chemical complex, the plant could export steam to a main that feeds other plants, otherwise the steam could be converted to electricity for export to a grid though this is only about 30 % efficient. However, if the necessary infrastructure (or market mechanisms) are lacking then this energy credit may be of little value. The remaining variable cost items in Table 8-2 (that have not been discussed) are relatively minor to the overall process economics.

The build-up of a comparative variable cost model for conventional and N/SCWO PTA technologies is a sizeable task requiring access to proprietary information and is beyond the scope of this PhD study. Savage *et al.*⁵ did not attempt a variable cost analysis. However, using publicly available data sources, it is possible to make a high-level assessment of some of the variable cost trade-offs of conventional and N/SCWO technologies. Section 1.7 discussed the vital importance of process yield in determining the economic viability of a commodity chemical process. Thus, the key trade-off of conventional versus N/SCWO PTA technologies is between PTA yield, acetic acid oxidation and the enhanced energy value of higher grade (*i.e.* higher temperature and pressure) steam. This analysis is undertaken in Table 8-3.

Table 8-3. Variable cost trade-off for *pX* oxidation in acetic acid and N/SCW.

	Acetic process	N/SCW process						Source
<i>pX</i> losses %								
<i>pX</i> burn	1	1	3	5	7.6	10	15	
<i>pX</i> physical losses	2	2	2	2	2	2	2	
Total <i>pX</i> losses	3	3	5	7	9.6	12	17	
Relative variable costs \$/te								
Acetic loss	0	-36.5	-36.5	-36.5	-36.5	-36.5	-36.5	Kingsley <i>et al.</i> , Sunsirs
<i>pX</i> loss	0	0	11	22	36	49	77	
Heat credit	0	-7	-7	-7	-7	-7	-7	Forbes/US DoE
Total (exc. heat credit)	0	-37	-26	-15	0	13	40	
Total (inc. heat credit)	0	-44	-33	-22	-7	6	33	

The table considers differences in the variable costs of the acetic based and N/SCW based TA process. Acetic losses comprise chemical oxidation to CO₂ and CO (the major chemical loss) and physical losses. Kingsley *et al.*⁷ suggest a chemical acetic acid loss of ~0.03 te/te TA, physical losses are assumed to be twice chemical losses, using an Asian spot acetic acid price (Sunsirs)⁸ of \$406/te and an exchange rate of 6.9 RMB/US\$; no acetic is lost in the N/SCW based process. Chapter 1 discussed the yield of the PTA process as ~99 % chemical (with ~1 % to *pX* oxidation to CO₂ and CO) and 97 % overall (with 2 % physical losses). The same physical losses are assumed for the N/SCW process and several levels of *pX* oxidation to CO₂ And CO are considered. The *pX* loss variable cost is calculated from these losses using an Asian spot *pX* price⁸ of \$855/te at the above exchange rate. The fuel credit for the oxidation process is based on the heat of reaction, an energy price of 0.142 \$/MJ,⁹ and an assumed energy efficiency of 70 %. The costing of steam raising¹⁰⁻¹² is not trivial and the detail of this is beyond the scope of this thesis. However, the US Department of Energy data¹³ suggests that the extra value of steam raising at higher temperature is ~9 % and this reduction in costs represents the heat credit.

The analysis shows that (on these oxidation metrics) the N/SCWO process matches the variable cost of the acetic based process with a *pX* chemical oxidation (to CO₂ and CO) of ~7.5 %, *i.e.* a TA chemical yield of 92.5 %. At a *pX* oxidation (to CO₂ and CO) of 1 %, the variable cost advantage is about \$44/te (of TA) and at the current yield of ~90 % the variable cost penalty is about \$6/te.

Another major difference between the technologies is the use of compressed air versus an oxygen feed. The author has insufficient information to make a variable cost comparison for these oxidants.

8.5 Assessing the Commercial Viability of *p*-Xylene N/SCWO Technology

Section 1.5 of this thesis discussed why it is very difficult to displace established, capital intensive, incumbent technology with new technology unless there are large capital and/or variable (preferably both) cost reductions. This is because of the risk to capital inherent in novel technology. The cost reductions required are ultimately determined by the appetite of the market for change. In the author's opinion, it is likely that a capital reduction of 30 – 40 % and a variable cost advantage of \$30 – 40/te over the conventional technology would be required for a novel technology to be considered for commercial deployment. The analysis presented in the preceding sections suggests that the current *pX* N/SCWO technology has no capital and a negative variable cost compared to acetic acid based technology. There is thus little prospect that this technology would be commercially deployed in its current form.

If *pX* N/SCWO could achieve a 99 % yield then it would have a variable cost advantage of ~\$44/te which would give it borderline investment case on the above criteria.

If *pX* N/SCWO could either:

- combine the oxidation and purification plants, or
- enable the elimination of the purification plant

then the process would obtain a 30-40% capital advantage (*i.e.* the approximate cost of the purification plant) and a proportion of the heat credit (estimate at ~\$78/te) from the oxidation plant as this would no longer have to be used to heat water in the purification plant. The proportion of this heat credit that could be realised would depend on the local circumstances for taking advantage of that extra energy. For situations where the energy value is realisable, a *pX* N/SCWO plant would likely meet the potential investment criteria set out above.

Combining the oxidation and purification plant would involve passing the output stream of the oxidation plant to a hydrogenation reactor without the need to flash crystallise the TA, solvent exchange and reheat to redissolve the TA. The

oxidation catalyst metals would likely poison the Pd/C catalyst and the bromide would be highly corrosive so both would need to be removed, probably by precipitation and filtration processes using *e.g.* metal carbonates and silver bromide respectively. There would also be a process safety issue of preventing the slippage of excess oxygen into a hydrogen containing environment. None of these aspects are currently developed, though all are conceptually possible. They should be targets in any future development.

Section 8.3 discussed the criteria for eliminating the purification plant. The *pX* N/SCWO process can obtain the low level of 4-CBA required but currently produces too many coloured by-products. Another target for future developments could be the reduction of minor components to a level at which they could be dealt with by the crystallisation in the oxidation plant without the need for a subsequent purification plant, *i.e.* to produce the PTA specification from the oxidation plant. However, there is at present, no obvious means but which this could be achieved.

8.6 References

1. M. Cesar, *SRI Report No. 9F, Terephthalic Acid*, SRI Consulting, Menlo Park, CA, 2005.
2. *SRI Report 9E. Terephthalic acid and dimethyl terephthalate*, SRI Consulting, Menlo Park, CA, 1997.
3. *IHS Chemical World Analysis, PTA/DMT*, IHS Chemical Consulting, London, 2015.
4. *Terephthalic Acid 05/06 - 6 PERP Report.*, Nexant Chem Systems, White Plains, NY, 2006.
5. J. B. Dunn and P. E. Savage, Economic and environmental assessment of high-temperature water as a medium for terephthalic acid synthesis, *Green Chem.*, 2003, **5**, 649-655.
6. P. J. Hamley, T. Ilkenhans, J. M. Webster, E. Garcia-Verdugo, E. Venardou, M. J. Clarke, R. Auerbach, W. B. Thomas, K. Whiston and M. Poliakoff, Selective partial oxidation in supercritical water: the continuous generation of terephthalic acid from *para*-xylene in high yield, *Green Chem.*, 2002, **4**, 235-238.
7. J. P. Kingsley, A. K. Roby and L. M. Litz, Terephthalic acid production, US Pat., 5,371,283, 1993.
8. Sunsirs China Commodity Data Group. Spot Price: Daily, <http://www.sunsirs.com>, (Accessed April, 2017).

9. R. Rapier, The price of energy,
<https://www.forbes.com/sites/energysource/2010/01/26/the-price-of-energy>, (Accessed April 2017).
10. D. Cooper Do you value your steam correctly?, *Hydrocarbon Process.*, July 1989.
11. K. Nelson A Practical Guide to Energy Accounting, *Chemical Engineering*, September 1994.
12. R. Smith, Chemical Process Design, in *Chemical Process Design*, McGraw-Hill Inc., NY, 1995, ch. 6.
13. How to Calculate the True Cost of Steam, *U.S. Department of Energy*, DOE/GO-102003-1736, September 2003.

9 Conclusions and Recommendations

9.1 Introductory Remarks

The fundamental question to be addressed in this PhD was whether *pX* N/SCWO to produce PTA is economically viable when compared to the conventional acetic acid based process currently in use in the industry.

The technical requirements to achieve a commercial process for *pX* N/SCWO were set out in Chapter 1. There were four key areas that required development to potentially achieve a commercial technology basis:

- Obtain a high yield of TA.
- Obtain a product specification suitable for sales.
- Develop an oxidation reactor design with a suitable basis of safety.
- Identify suitable materials of construction for the reactor and wider process.

In addition, the chapter discussed the difficulties in displacing an established, capital intensive technology with a new technology and the need for a substantial capital and/or variable cost advantage to justify the risk to new capital. Chapter 8 attempted to quantify the advantages that would be necessary and the extent to which the process performance could achieve this.

Obtaining the required yield of TA was identified as the most important objective because without a commercially viable yield all other considerations (such as product quality) are rendered unimportant. It is also the requirement requiring the largest chemistry input and it was therefore selected as the major focus of this project. High material balance was also identified as an important target because of the importance of both accurately establishing the yield of TA and of determining the nature and level of by-products and the ability of the process to deal with them.

Chapter 2 set out a series of detailed questions that, if answered, would address these issues and this PhD project aimed to address as many of these questions as was possible.

This final chapter reviews the work undertaken, determines the extent to which the questions were addressed and answered, draws conclusions about the technical and commercial viability of a *pX* N/SCWO process and identifies further work that could be undertaken.

9.2 Review of Project and Thesis

As described in the previous section, obtaining high TA yield at high material balance was the major focus of this PhD project.

Chapter 7 assesses the carbon material balances and terephthalic acid yields obtained in this project. The project did not achieve its target aromatic material balance of > 99 % and the reasons for this are discussed in that chapter; they are mostly related to the scale of the experimentation. This section concludes that the highest TA yield obtained during these studies was probably ~ 90 % which was obtained at a *pX* concentration of ~ 2 % with an aromatic material balance of ~100 %.

Chapter 8 discusses the TA yield required to obtain a commercial process. The analysis shows that a yield of ~92.5 % would be required to match the variable cost of the current acetic acid based process and that a yield of 99 % would be required to give a variable cost advantage that would approach the investment criteria. These yields would need to be demonstrated at a mass balance of > 99 % and at a *pX* concentration of at least 10 % and preferably 20 %. In addition, Section 5.8.5 considers the formation rate of minor by-products and finds that this is several times higher than in the conventional, acetic acid based process. This leads to some unwelcome conclusions, particularly that:

- The combination of high temperature and a solution based processes for TA leads to:
 - high levels of *pX* oxidation to CO₂ and CO.
 - high production of undesirable by products.

- The latter means that a conventional technology purification plant, based on hydrogenation and progressive recrystallisation from high temperature water would be required.

The analysis in Chapter 8 demonstrated that both the level of TA yield and the need for a purification plant are investment killers against the *pX* N/SCWO technology investment criteria.

Section 6.3 and particularly Figure 6-6 give data on the variation of *pX* oxidation to CO₂ as the *pX* concentration is raised from 2 % to 5 %. This shows that CO₂ increases significantly over this concentration range by a factor of 50 – 100 %. This work requires extension to *pX* concentrations of at least 10 % and preferably 20 %. These studies have not, to date, been undertaken and represent a critical area of further work. There are some major challenges with such studies due to the high heat generation and this aspect is discussed in Section 6.3. However, in view of the adverse CO₂ trend observed in the work to date, it would seem likely that the performance will deteriorate further at *pX* concentrations above 5 %.

Chapters 4 described improvements in the mixing of the three feed streams, aqueous catalyst, water/oxygen and *pX*. The application of these improvements to reactor design and its effect on key process metrics of CO₂, CO and by-product formation was discussed in Chapter 7. Chapter 5 described the effect of the residence time distribution in the reactor on the key process metrics and the likely effects of process scale up from laboratory to industrial scale. These studies showed that the process performance was unlikely to be improved further through scale up despite the increase in turbulence that this would bring.

Thus, the required improvement in process yield would need to be obtained through improved catalyst selectivity. The author's supporting publication ¹ considered a broad range of possible catalytic metals and combinations of metals and identified the Co/Cu/Br combination as the most promising combination, however, this catalyst does not currently deliver the required selectivity.

Section 2.6 considered in detail the questions that need to be addressed for a technology and economic assessment of the *pX* N/SCWO process compared to the conventional acetic acid based process. Tables 9-1 to 9-4 summarise the

questions identified, the progress that has been made in answering them and the relevant sections of this thesis where they have been considered.

9.3 Conclusion and Recommendations

9.3.1 Technical Perspective

Having reviewed the key questions regarding the industrial deployment of *pX* N/SCWO technology and the progress that has been made in addressing them, there clearly remain unresolved technical issues:

- The lower than required TA yields obtained.
- The high production of coloured by-products (greater than in the conventional process) and whether these can be removed cost effectively, to produce material of PTA specification.
- The phase separation of *pX* and oxygen from HTW below a certain temperature, the consequent risk of explosion and determining a suitable basis of safety at industrial scale.
- The unsuitability of Hastelloy C-276 as a material of construction for the reactor.

These issues compromise all the major process success requirements and prevent the industrial scale deployment of this technology at the current time. They would require substantial further effort to resolve.

9.3.2 Areas for Further Work

As discussed in Chapter 8, the minimum TA yield required for a commercial process is ~99 % at a reactor concentration of 10 – 20 % *pX*. Obtaining this yield is the priority because without this, all other criteria are rendered unimportant. Therefore, other aspects of the technology should be afforded lower priority until the required yield can be demonstrated.

Table 9-1. The status of the mixing and reactor design questions identified for the development of *pX* N/SCWO technology.

Mixing Questions	Status at Project Close	Thesis section
What order should the component streams be mixed in?	Issues discussed & literature reviewed. Catalyst hydrolysis quantified. <i>pX</i> oxidation to CO ₂ observed and mixing optimised to minimise this.	4.2
What is the effect of oxygen excess on <i>pX</i> , catalyst and product stability?	Effect oxygen on <i>pX</i> feedstock, TA product stability and catalyst investigated.	4.2, 6.2
Is staging of oxygen/catalyst/ <i>pX</i> beneficial?	Staging of the various components investigated. Oxygen staging shown to be beneficial but catalyst and <i>pX</i> staging shown to be not beneficial	6.4.3, 6.4.1
What's the most effective method to mix streams with large density differences?	Extensively investigated by experimental study. Paper published. ²	4.4 A1
What is the effect of pre-heating the catalyst stream prior to mixing and how much catalyst hydrolysis then occurs?	Catalyst hydrolysis prior to the reaction studied and quantified.	3.4.2
What is the effect of the idealised RTDs of plug flow and back mixed on reaction yield and selectivity? How do these affect the distribution of by-products?	Extensively investigated by experimental study and by-products quantified.	5.8
How can these RTDs be engineered for <i>pX</i> SCWO at laboratory scale?	Plug flow and back mixed reactors engineered and characterised.	5.5, 5.6
What is the optimum RTD?	Experimental studies undertaken and optimum configuration identified.	5.10
How can quench solution be efficiently mixed with the process fluid?	Quench point design optimised.	3.7, 7.4
What is the best quench material to use? What is the effect of quenching on the reaction chemistry?	Water and sodium hydroxide quench studied and optimised. Effect of quench on reaction chemistry determined.	3.3.2, 6.4.7, 7.4
How does mixing scale up to full plant scale? What would be a suitable reactor design for the larger scale?	Scale up factors investigated and initial assessment of industrial scale reactors undertaken.	4.5. 5.9, 5.10
What are the major hazards of the process and what is the safe operating envelope? How could these hazards be mitigated for a full-scale process?	Initial assessment of industrial scale issues. Much more to do.	3.1, 5.9, 5.10

Table 9-2. The status of the chemistry questions identified for the development of *pX* N/SCWO technology.

Chemistry Questions	Status at Project Close	Thesis section
What material balances can be achieved?	Material balances quantified and substantially improved. However, 'kinetics' standard material balances were not achieved.	7.5
What is the optimised yield of TA for this chemistry and is this yield sufficient to enable an economic industrial process?	Optimised reactor and chemistry to maximise TA yield. Assessed resulting process economics.	7.5, 8.5
What is the effect of phase? What are the chemistry effects of working in the supercritical, liquid and gas phases?	Phase effects were assessed.	6.4.5, 6.4.6
What are the effects of process conditions, specifically temperature, pressure, catalyst nature and concentration, substrate concentration <i>etc.</i> on the intermediates and product yields? What are the optimum conditions?	Experimental studies undertaken on temperature, pressure, catalyst composition and concentration, substrate concentration, oxygen, residence time. Optimum conditions determined.	6, 7.5
What by-products are produced? Do these differ (in nature and quantity) from those produced in the acetic acid process? What are the production rates of these by-products? Can these be effectively separated from the desired product?	Review of by-products in acetic process. Nature of by-products in N/SCWO process determined and quantified. Separation methods discussed.	1.3.2 – 1.3.4 5.8 8
What is the extent of total oxidation to CO ₂ and CO?	Oxidation to CO ₂ and CO quantified.	5.8, 8
What catalyst components (<i>e.g.</i> metals) are effective? How can the catalyst be optimised?	Extensive studies of catalyst composition. Paper published. ¹	6.4.1, A1
How can the catalyst be stabilised against hydrolysis and precipitation?	Hydrolysis quantified. Previous publication on catalyst stabilisation, Fraga-Dubreuil <i>et al</i> ³	3.4.2
What is the role of the reaction quench and how does this affect the chemistry? What is the effect of the quench pH on the reaction course, <i>e.g.</i> does aromatic acid decarboxylation occur?	Effect of quench quantified.	6.4.7
Does the use of H ₂ O ₂ as the oxygen source affect or compromise the chemistry?	Effect of H ₂ O ₂ on reaction chemistry determined.	3.3.3, 6.4.8
What are the reaction mechanisms? How do these differ from those observed in the acetic acid based process?	Initial observations made. Systematic mechanistic studies not undertaken. More to do.	1.3

Table 9-3. The status of the materials questions identified for the development of *pX* N/SCWO technology.

Materials Questions	Status at Project Close	Thesis section
What would be suitable materials of construction for a <i>pX</i> N/SCWO reactor and what would be the corrosion rates?	Some initial observations and discussion. Initial quantification of Hastelloy corrosion rates in the reactor. Much more to do.	2.5, 3.3.3, 3.4, 7.2.2, 7.4

Table 9-4. The status of the process synthesis questions identified for the development of *pX* N/SCWO technology.

Process Synthesis Questions	Status at Project Close	Thesis section
How can individual unit operations be integrated into an overall process?	Discussion in Chapter 8. Much more to do.	8

The residence time studies, described in Chapter 5, were reasonably thorough and achieved high levels of turbulence in both a plug flow tubular reactor and in a STR. The turbulence was sufficient to eliminate 90 % of the axial dispersion in the tubular reactor and to achieve a mixing time of < 1 s in the STR. The mixing studies, described in Chapter 4, also demonstrated highly effective mixing designs by utilising both the kinetic and potential energy of the streams to achieve rapid mixing. It thus seems unlikely that yield can be much improved by further improvements and optimisation of residence time and/or mixing.

The catalyst studies reported in the author's supporting paper ¹ and summarised in Section 6.4.1 made a fairly thorough study of possible catalyst metals, especially those with suitable oxidation states, and while they were not totally exhaustive, it is unlikely that there is a better metal catalyst than those identified. The greatest remaining opportunity may therefore be in the further improvement of the Co/Cu/Br catalyst system and this is an area requiring further studies. This could include further catalyst mechanistic studies *e.g.* further extensions to the work of Fulton *et al.* ⁴⁻⁹ and also the addition of modifying ligands. However, the choice of ligands is restricted by the harsh N/SCW oxidative environment as ligands would need to have some stability to radical attack, to thermal decomposition and to hydrolysis. Thus, aromatic nitrogen heterocycles and aromatic amines that have no labile groups, extractable hydrogens or groupings that can be oxidised would seem possible candidates. Groupings such as aliphatic branches, phenols, carboxylic acids and phosphorus or sulphur containing should be avoided. Some guidance can be obtained from ligands that have been tried in the acetic acid based process *e.g.* guanidine,¹⁰ pyridine ¹¹⁻¹⁴ and amines.¹⁵ Possible ligands could be screened for their stability in N/SCW and for their coordination with catalyst metals. UV visible spectroscopy could be a suitable technique with absorptions changing if metal to ligand coordination is occurring.

None of the reactors investigated were capable of producing PTA product purity. The current best *pX* N/SCWO technology produces a CTA with a lower level of 4-CBA but higher level of minor colour components such as 2,6-DCF than the conventional acetic based process. There is therefore a need for a purification

process and this would most likely remain the current process of hydrogenation in and crystallisation from high temperature water. There is a need to demonstrate that this process could handle the increased level of minor components in the CTA. There is also the possibility that the oxidation and purification (hydrogenation) processes could be performed sequentially using the same water solvent. This would require the development of (metal bromide) catalyst removal technologies probably based on the hot precipitation and filtration of metal carbonates and silver bromide and a basis of safety to prevent the formation of explosive hydrogen/oxygen mixtures.

The work in this thesis has demonstrated that Hastelloy C276 is not a suitable material of construction for a *pX* N/SCWO reactor due to its excessive corrosion rate in that environment. Initial work on alternatives has identified titanium as the most promising material that is economic but there are safety concerns regarding the risk of its combustion in the presence of oxygen. Other materials that are economic and are not combustible have not yet been identified. There is thus a need for more work on the suitability of titanium in the *pX* N/SCWO environment.

Commercialisation of this technology will require a robust basis of safety. There is an economic need to use oxygen, rather than hydrogen peroxide, as the oxygen source at large scale and this presents the risk of obtaining incorrect oxygen : water stoichiometries. It is known that *pX* will spontaneously explode in the presence of oxygen at elevated pressures at temperatures above $\sim 265^{\circ}\text{C}$ if there is insufficient water to provide inerting. Such conditions can occur where there is phase separation of *pX*/water and O_2 /water and this can happen in process cold spots or where there is an incorrect stoichiometry. There is thus a need to map the flammability envelope more systematically, to establish a basis of safety for contacting *pX* and oxygen at industrial scale and develop a suitable large-scale reactor design.

9.3.3 Commercial Perspective

Finally, here are some commercial perspectives on the *pX* N/SCWO technology.

The most likely commercialisation route would be to deploy the technology as an owner-operated TA plant. Integrating the plant with owner-operated PET polymer plants would reduce the technical risks around achieving a PTA quality material in a first deployment, however it could increase the capital requirement.

The PTA market is currently long (*i.e.* has over-capacity) and this has squeezed margins; this is unlikely to change in the next few years. This provides a mixed landscape for the technology as a long market reduces the incentive to invest but favours lower cost technology. Section 1.5 discussed the challenges of introducing radical new technology into a mature, commodity and capital-intensive process and the need for a large cost advantage to overcome the considerable risk involved. There have been no recent announcements by any of the major technology developers in the industry of the deployment of such new technology.

The high temperature in the N/SCWO environment is challenging for obtaining high yields because of the thermodynamic tendency for reactions to become less selective with increasing temperature. Without a good yield, it is not possible to obtain the significant cost advantage that this technology needs to overcome the risk of commercialising it against the existing, incumbent technology. Based on the work undertaken to date and presented in this thesis, the author has concluded that, without a further significant technical breakthrough on TA yields, it is unlikely that *pX* N/SCWO will be commercially deployed at an industrial scale.

9.4 References

1. E. Perez, J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, M. L. Thomas, C. Yan, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 2. The discovery of better catalysts, *Green Chem.*, 2011, **13**, 2397-2407.
2. D. Housley, T. Huddle, E. Lester and M. Poliakoff, The use of dimensionless groups to analyse the mixing of streams with large density differences in sub- and supercritical water, *Chem. Eng. J.*, 2016, **287**, 350-358.
3. J. Fraga-Dubreuil, E. Garcia-Verdugo, P. A. Hamley, E. Perez, I. Pearson, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Prevention of Manganese Precipitation during the Continuous Selective

- Partial Oxidation of Methyl Aromatics with Molecular Oxygen in Supercritical Water, *Adv. Synth. Catal.*, 2009, **351**, 1866-1876.
4. Y. S. Chen, J. L. Fulton and W. Partenheimer, The structure of the homogeneous oxidation catalyst, $\text{Mn(II)(Br}^{-1}\text{)}(x)$, in supercritical water: An X-ray absorption fine-structure study, *J. Am. Chem. Soc.*, 2005, **127**, 14085-14093.
 5. Y. S. Chen, J. L. Fulton and W. Partenheimer, A XANES and EXAFS study of hydration and ion pairing in ambient aqueous MnBr_2 solutions, *J. Solution Chem.*, 2005, **34**, 993-1007.
 6. J. L. Fulton, M. M. Hoffmann and J. G. Darab, An X-ray absorption fine structure study of copper(I) chloride coordination structure in water up to 325 degrees C, *Chem. Phys. Lett.*, 2000, **330**, 300-308.
 7. J. L. Fulton, M. M. Hoffmann, J. G. Darab, B. J. Palmer and E. A. Stern, Copper(I) and copper(II) coordination structure under hydrothermal conditions at 325 degrees C: An X-ray absorption fine structure and molecular dynamics study, *J. Phys. Chem. A*, 2000, **104**, 11651-11663.
 8. M. M. Hoffmann, J. G. Darab and J. L. Fulton, High-pressure, high-temperature XAFS and IR spectroscopic studies of reacting hydrothermal systems, *Abstr. Pap., Am. Chem. Soc.*, 2000, **219**, 348-348.
 9. M. M. Hoffmann, J. G. Darab, S. M. Heald, C. R. Yonker and J. L. Fulton, New experimental developments for in situ XAFS studies of chemical reactions under hydrothermal conditions, *Chem. Geol.*, 2000, **167**, 89-103.
 10. Y. W. Cheng, X. Li, Q. B. Wang and L. J. Wang, Effects of guanidine on the liquid-phase catalytic oxidation of *p*-xylene to terephthalic acid, *Ind. Eng. Chem. Res.*, 2005, **44**, 7756-7760.
 11. Z. Cvengrosova, M. Hronec, J. Kizlink, L. Malik and J. Ilavsky, Study of *p*-xylene reaction with Co-Br-pyridine catalyst .2. Reaction in aqueous system, *J. Mol. Catal.*, 1987, **40**, 235-242.
 12. Z. Cvengrosova, M. Hronec, J. Kizlink, T. Pasternakova, S. Holotik and J. Ilavsky, Study of *p*-xylene reaction with Co-Br-pyridine catalyst .1. Reaction in acetic-acid, *J. Mol. Catal.*, 1986, **37**, 349-358.
 13. M. Hronec and J. Ilavsky, Effect of pyridine on cobalt bromide catalyzed oxidation of *p*-xylene in various solvents, *Oxid. Commun.*, 1983, **3**, 303.
 14. A. Kaszonyi, M. Hronec, L. Lauko and J. Ilavsky, Study of the activity of Co-Br-py catalysts during oxidation of *p*-xylene in acetic-acid, *J. Mol. Catal.*, 1989, **57**, 105-112.
 15. G. R. Steinmetz and C. E. Sumner, Role of amine promoters in cobalt bromide catalysed oxidations, *J. Catal.*, 1986, **100**, 549-551.

Appendix 1

Appendix 1 Papers – Copyrighted material removed.

Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 1: comparison with *ortho*-xylene and the role of the catalyst.

Eduardo Pérez, Joan Fraga-Dubreuil, Eduardo Garcia Verdugo, Paul A Hamley, W Barry Thomas, Duncan Housley, Walt Partenheimer and Martyn Poliakoff.
Green Chem., 2011, **13**, 2389-2396.

Selective aerobic oxidation of *para*-xylene in sub and supercritical water. Part 2: the discovery of better catalysts.

Eduardo Pérez, Joan Fraga-Dubreuil, Eduardo Garcia Verdugo, Paul A Hamley, Morgan L Thomas, Yan Chong, W Barry Thomas, Duncan Housley, Walt Partenheimer and Martyn Poliakoff.
Green Chem., 2011, **13**, 2397-2407.

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, Morgan L Thomas, Duncan Housley, Paul A Hamley, Joan Fraga-Dubreuil, Jun Li, Edward Lester and Martyn Poliakoff.
RSC Adv., 2016, **6**, 11289-11294.

The use of dimensionless groups to analyse the mixing of streams with large density differences in sub- and supercritical water.

Duncan Housley, Thomas Huddle, Edward Lester and Martyn Poliakoff.
Chem. Eng. J., 2016, **287**, 350-358.