Design and Development of Microreactors

Kay Kin Yeong

November 2003

A thesis submitted for the degree of Doctor of Philosophy
of the University of London
Summary

The study of microreactors involves the miniaturisation of entire reactor systems on to structures ranging from several millimetres to several centimetres in length and height. Their large surface area to volume ratio results in efficient heat and mass transfer. As such, they allow better control of processes and quick quenching, which can lead to improved selectivity and conversion. Safety is improved as their flame trap dimensions prevent flame propagation. Also, previously unfeasible reaction routes may be opened up. Because of the way they are put together, there will be shorter lag time between R&D and industrial application. This is because scale-up is unnecessary. Instead, numbering-up of reactors can be used to increase production capacities.

The first step in fabricating a microreactor is to appreciate the varied methods available. The most important and applicable methods are: photolithography, wet bulk machining, dry etching, chemical vapour deposition (CVD), LIGA, laser machining, ultraprecision machining, soft lithography and glass microfabrication. Combinations of these techniques will allow the fabrication of most reactors. In addition, since microfluidic systems typically take the form of thin fabricated sheets carrying different unit operations which can be stacked to form a complete reaction system, bonding techniques are also very important. Examples include anodic bonding, fusion bonding, eutectic bonding and adhesive bonding.

A T-microreactor was designed for the gas phase partial oxidation of methanol to formaldehyde over a silver catalyst. It consists of a T-channel etched in silicon with the top of the channel sealed by a piece of glass. While simple, it served to demonstrate the main procedures involved in microfabrication: CVD,
photolithography, wet and dry etching, and anodic bonding. Since methanol is a liquid at room temperature, the reactor had to incorporate a pre-heating section to vaporise methanol prior to it entering the reaction section. Three reactor designs (channel width 600 \(\mu\)m and depth 300 \(\mu\)m) were made with differing reaction channel lengths (15, 104 and 207 mm). This was done to widen the range of residence times. Catalyst deposition methods used included evaporation, manual placement of silver wires/foils, electrodeposition and an in-situ chemical reaction, all of which proved inadequate due to combinations of poor adhesion, activity and stability. The sealing of the reactor and the development of suitable interfacing with external equipment proved to be major challenges too, mostly due to the high temperature operation of the reactor. The final product was a silicon microreactor fabricated using Deep Reactive Ion Etching or KOH etching, with silver catalyst deposited through sputtering and sealed by a Pyrex plate through anodic bonding. High conversion was achieved using a mixture of 8.0 - 8.6 % methanol and balance oxygen, without any helium to quench the reaction.

A micro-falling film reactor (\(\mu\)-FFR) was used to study the gas-liquid hydrogenation of nitrobenzene over a solid palladium catalyst. A robust catalyst had to be developed that was compatible with the reactor system, in terms of incorporation, suitability for continuous use, longevity and reproducibility. Several different catalyst incorporation methods were tested (sputtering, UV-decomposition of palladium acetate, wet impregnation on \(\gamma\)-alumina, incipient wetness on \(\gamma\)-alumina) with the final method satisfying all of these requirements. It was also shown that there were negligible external or internal mass transfer limitations. A batch reactor (3 \(m^3\), 0.4 mol nitrobenzene/l ethanol, 20 bar \(H_2\) pressure, 125 °C, 7.89 \(x\) \(10^5\) g cat/ml, 85 %
conversion, Farrauto, et al (1997)) was estimated to produce 204 kmol aniline/m$^3$ reactor daily (assuming no downtime). In comparison, the µ-FFR using the incipient wetness catalyst (0.1 mol nitrobenzene/l ethanol, 0.5 ml/min., 1 bar H$_2$ pressure, 60 °C, 5.4 g Pd/ml, 82 % conversion) would have a daily production rate of 394 kmol aniline/m$^3$ reactor. While a larger amount of catalyst was used, the process conditions were significantly milder and the catalyst was unoptimised, proving that the µ-FFR could enhance gas-liquid reactions that were mass transfer limited in practice.

The liquid film thickness obtained in the µ-FFR at a range of flowrates (0.5-2.0 ml/min) was studied using confocal microscopy. It was found that the Nusselt equation greatly underpredicted film thicknesses. The temperature profile µ-FFR was measured using an IR-camera under non-reacting conditions by passing hot water through its heat exchanger (30-60 °C). The temperature distribution was reasonably uniform. However, the uniformity decreased slightly as the temperature increased (3 % at 30 °C, 5 % at 60 °C), with the central area of the plate cooler than the sides, and the top and bottom being the warmest.

A simple model of nitrobenzene hydrogenation in the µ-FFR was made using gPROMS. Three Langmuir-Hinselwood-type kinetic expressions were used to fit the experimental data. No close matches were found and the model appeared to underpredict nitrobenzene conversions at high flowrates. This was likely due to inaccuracies in extrapolating liquid film thicknesses (i.e. the thicknesses were too large). In addition, mass transfer enhancement factors (e.g. the Marangoni effect, hydrodynamic instability, wave formation), which were not taken into account in the
The μ-FFR was also used to perform the asymmetric transfer hydrogenation of acetophenone to (S)-phenylethanol catalysed by a homogeneous rhodium complex that was activated by sodium isopropoxide, with isopropanol as the hydrogen source. The aim was to use the μ-FFR as an evaporator-reactor to remove acetone in order to drive the equilibrium forward. It was shown that the μ-FFR was much more efficient at evaporating acetone than a batch reactor (31 % at a theoretical residence time of 9.3 s vs. 50 % in 60 min for a batch reactor with nitrogen bubbling through). However, when the reaction was performed, the μ-FFR was found to have no impact on the conversion. This was most likely because the reactants had been pre-mixed in a flask (with nitrogen bubbling through), had reacted within it and the acetone produced had been evaporated within the flask itself. This is an example of a reaction system where a batch reactor was perfectly capable of driving the reaction to its limits, thus making a microreactor unnecessary.

Based on the knowledge gained in this project, a general design algorithm was proposed in order to bring some structure to the discipline of microreactor engineering. It represents a summary and guide to the microreactor design route. A key aspect of this route is the use of modelling to aid in designing microreactors.
Acknowledgements

I would like to thank the UCL Graduate School and the Overseas Research Students Awards Scheme for financial support, without which this project would not have proceeded.

My deepest gratitude to Dr. Asterios Gavriilidis for his constant guidance and advice throughout the length of this project. I would also like to thank Dr. Enhong Cao for all the advice he has given me and the many discussions we had whenever problems turned up. Many thanks also to Dr. Panagiota Angeli, Professor Ian Boyd, Professor and Dr. Motherwell, Dr. Zheng Cui, Professor Alan Boyde and Dr. Monica Zanfir for the advice they offered.

The greater part of this project was made possible by the Institut für Mikrotechnik Mainz and its staff, most notably Dr. Volker Hessel and Dr. Ralf Zapf. I would also like to offer my appreciation to all the technical staff at various institutions for their aid: Julian Perfect, Ghulam Warsi, Kevin Reeves and Derek Jenkins.

Last but not least, a big ‘Thank You’ to all my colleagues and friends for the support, discussions and fun we’ve had.
# Table of Contents

## 1. Introduction

## 2. Literature Survey

### 2.1 Characteristics of Microfluidic Systems

#### 2.1.1 Surface Tension

#### 2.1.2 Fluid Flow

##### 2.1.2.1 Single-phase Flow

##### 2.1.2.2 Two-phase Flow

##### 2.1.2.3 Fluid delivery

#### 2.1.3 Thermal Characteristics

#### 2.1.4 Structural Characteristics

### 2.2 Fabrication Methods

#### 2.2.1 Photolithography and Etching Techniques

#### 2.2.2 Chemical Vapour Deposition (CVD)

#### 2.2.3 LIGA

#### 2.2.4 Laser Machining

#### 2.2.5 Ultraprecision Machining

#### 2.2.6 Electrodisscharge Machining (EDM)

#### 2.2.7 Soft Lithography

#### 2.2.8 Glass Microfabrication

#### 2.2.9 Microstereolithography

#### 2.2.10 Mass fabrication techniques

#### 2.2.11 Bonding Techniques

### 2.3 Catalyst Incorporation Techniques

### 2.4 Microdevices

#### 2.4.1 Heat Transfer Devices

#### 2.4.2 Mixing Devices

#### 2.4.3 Chemical Analysis Devices

### 2.5 Integration of Microdevices

#### 2.5.1 Vertical integration

#### 2.5.2 Horizontal integration

#### 2.5.3 Integration of heating and catalytic reaction

#### 2.5.4 Integration of mixing and catalytic reaction

#### 2.5.5 Integration of mixing, heating, catalytic reaction and sensing

#### 2.5.6 Integration of heating, sensing and separation

### 2.6 Applications of Microengineered Reactors

#### 2.6.1 Chemical Analysis

#### 2.6.2 High Throughput Screening and Experimentation

#### 2.6.3 Access to New Chemistry and Operating Conditions

##### 2.6.3.1 Systems with efficient heat exchange

##### 2.6.3.1 Systems with good residence time control

##### 2.6.3.1 Systems with efficient mass transfer and heat exchange

#### 2.6.4 Process Development

#### 2.6.5 Distributed and Mobile Processing

#### 2.6.6 Process Intensification

#### 2.6.7 Extraterrestrial Processing

#### 2.6.8 Scale-out

### 2.7 Modelling
3. **T-Microreactor**

3.1 Design Basis and Rationale

3.1.1 Reaction

3.1.2 Materials

3.2 Design Considerations

3.2.1 Flowrate Calculations

3.2.2 Pre-heat Channels

3.2.3 Reactor Configuration

3.3 Reactor Fabrication

3.3.1 Mask

3.3.2 Choice of Etching Route

3.3.3 Wet Etching (Small Depths)

3.3.3.1 First Attempt

3.3.3.2 Second Attempt

3.3.3.3 Third Attempt

3.3.3.4 Optimisation of Etching Parameters

3.3.4 Wet Etching (Large Depths)

3.3.5 Finalised Etching Procedure

3.3.5.1 Wet Etching using KOH

3.3.5.2 Dry Etching using DRIE

3.4 Anodic Bonding

3.4.1 Initial Attempt

3.4.2 Further Exploratory Work

3.4.3 Development Work

3.4.4 Simple Anodic Bonder

3.5 Silicon Fusion Bonding

3.6 Catalyst Deposition

3.6.1 Evaporation

3.6.2 Manual Placement

3.6.3 Electrodeposition

3.6.4 Silver Deposition using an In-situ Chemical Reaction

3.7 Experimental Set-up

3.7.1 Method of Heating

3.7.2 Input/output Interface

3.7.3 Testing of the Set-up

3.8 Reaction Experiments

3.8.1 Silver Foil and Wire Reactor

3.8.2 Silver Mirror Reactor (I)

3.8.3 Silver Mirror Reactor (II)

3.8.4 Summary of Further Experimental Work Carried Out

3.9 Conclusion

4. **Falling Film Reactor: Nitrobenzene Hydrogenation**

4.1 Reactor Configuration

4.1.1 Falling Film Systems
Appendices

Appendix 3-1: Estimation of First Order Reaction Kinetics for Methanol Oxidation
Appendix 3-2: Calculations for the Pre-Heat Channels
Appendix 3-3: Mask Design for the Basic T-Microreactor
Appendix 3-4: Mask Design for the T-Microreactor
Appendix 3-5: Empirical Etch Rate Chart for KOH Etching
Appendix 3-6: Schematic of the Reactor Rig
Appendix 3-7: Schematic of the Second Reactor Rig
Appendix 4-1: Estimation of Reactant Concentration
Appendix 4-2: Analysis Recipe for the Rtx-5 Capillary Column
Appendix 4-3: Calibration Data for the Rtx-5 Capillary Column
Appendix 4-4: GC traces and MS spectrograms of side products for the SP1 catalyst
Appendix 4-5: Analysis Recipe for the Rtx-5 Capillary Column (Comparison Analysis of Side Products)
Appendix 4-6: Raman Spectroscopy Analysis of the UV-decomposed Palladium Acetate Catalyst
Appendix 4-7: Analysis Recipe for the PTA-5 Capillary Column
Appendix 4-8: Calibration Method for the PTA-5 Capillary Column
Appendix 4-9: Method of Correcting Nitrobenzene Conversion for Deactivation
Appendix 4-10: Calculation of the Weisz-Prater Criterion
Appendix 4-11: Calculations for Surface Coverage by Carbon/Organic Deposits
Appendix 6-1: Estimation of the Diffusivity of Gases in Low Viscosity Liquids
Appendix 6-2: Estimation of the Diffusivity of Liquids in Liquids
Appendix 6-3: gPROMS Program
Appendix 6-4: Optimisation of $K_{NB}$ and $K_{HZ}$ for Model (I)
Appendix 7-1: Analysis Recipe for the Cyclodex-B Capillary Column
Appendix 7-2: Analysis Recipe for the DB-624 Capillary Column
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>Photolithography and the etching process</td>
<td>16</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Example of a micromixer utilising the multilamination concept</td>
<td>36</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Example of an interdigital micromixer utilising the multilamination concept</td>
<td>36</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Laminated micro-combustor/reactor for hydrogen production</td>
<td>62</td>
</tr>
<tr>
<td>Figure 2.5</td>
<td>Gas-liquid micro-packed bed with catalyst restrainer</td>
<td>64</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Schematic of the T-reactor</td>
<td>75</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Relationship between channel length, width and height (methanol flowrate 24.4 mg/min)</td>
<td>82</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>Relationship between pressure drop, width and height (methanol flowrate 24.4 mg/min)</td>
<td>82</td>
</tr>
<tr>
<td>Figure 3.4</td>
<td>Schematic of the reactor</td>
<td>83</td>
</tr>
<tr>
<td>Figure 3.5</td>
<td>Channel dimensions of the basic test reactor</td>
<td>86</td>
</tr>
<tr>
<td>Figure 3.6</td>
<td>Baffle designs in the microchannels</td>
<td>87</td>
</tr>
<tr>
<td>Figure 3.7</td>
<td>Summary of the fabrication procedure using HF</td>
<td>88</td>
</tr>
<tr>
<td>Figure 3.8</td>
<td>Summary of the fabrication procedure using dry etching</td>
<td>89</td>
</tr>
<tr>
<td>Figure 3.9</td>
<td>Sketch of the resulting baffles in Case 3 (not to scale)</td>
<td>91</td>
</tr>
<tr>
<td>Figure 3.10</td>
<td>Estimation of the etch rate of 20 wt % KOH at 74 °C</td>
<td>92</td>
</tr>
<tr>
<td>Figure 3.11</td>
<td>Graph of etch depth against temperature</td>
<td>95</td>
</tr>
<tr>
<td>Figure 3.12</td>
<td>Etching vessel used at UCL</td>
<td>99</td>
</tr>
<tr>
<td>Figure 3.13</td>
<td>T-microreactor fabricated via anisotropic wet etching</td>
<td>100</td>
</tr>
<tr>
<td>Figure 3.14</td>
<td>Close-up view of DRIE reactor</td>
<td>102</td>
</tr>
<tr>
<td>Figure 3.15</td>
<td>T-microreactor sealed using anodic bonding</td>
<td>108</td>
</tr>
<tr>
<td>Figure 3.16</td>
<td>Schematic of the experimental set-up</td>
<td>124</td>
</tr>
<tr>
<td>Figure 3.17</td>
<td>Heating block</td>
<td>126</td>
</tr>
<tr>
<td>Figure 3.18</td>
<td>Temperature profile of heating block</td>
<td>126</td>
</tr>
<tr>
<td>Figure 3.19</td>
<td>Schematic of the reactor block assembly</td>
<td>127</td>
</tr>
<tr>
<td>Figure 3.20</td>
<td>Assembled reactor and housing</td>
<td>132</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>Falling film plate</td>
<td>141</td>
</tr>
<tr>
<td>Figure 4.2</td>
<td>Components and schematic of the microstructured falling film reactor</td>
<td>142</td>
</tr>
<tr>
<td>Figure 4.3</td>
<td>Assembled falling film reactor</td>
<td>143</td>
</tr>
<tr>
<td>Figure 4.4</td>
<td>Theoretical liquid film thickness and residence time at various flowrates</td>
<td>144</td>
</tr>
<tr>
<td>Figure 4.5</td>
<td>Reaction scheme for nitrobenzene hydrogenation to aniline times</td>
<td>153</td>
</tr>
<tr>
<td>Figure 4.6</td>
<td>Schematic of the experimental set-up</td>
<td>157</td>
</tr>
<tr>
<td>Figure 4.7</td>
<td>Nitrobenzene conversion as a function of flowrate at various temperatures for the sputtered palladium catalyst (1 mol NB/l, 4 bar)</td>
<td>162</td>
</tr>
<tr>
<td>Figure 4.8</td>
<td>Falling film reactor plate after oxidisation</td>
<td>163</td>
</tr>
<tr>
<td>Figure 4.9</td>
<td>Nitrobenzene conversion as a function of time for the sputtered palladium catalyst (0.4 mol NB/l, 60 °C, 4 bar, 0.2 ml/min)</td>
<td>165</td>
</tr>
<tr>
<td>Figure 4.10</td>
<td>Aniline selectivity as a function of time for the sputtered palladium catalyst (0.4 mol NB/l, 60 °C, 4 bar, 0.2 ml/min)</td>
<td>166</td>
</tr>
<tr>
<td>Figure 4.11</td>
<td>Absorption isotherm for hydrogen on palladium</td>
<td>168</td>
</tr>
</tbody>
</table>
Figure 4.12 Chromatogram for nitrosobenzene 171
Figure 4.13 Chromatogram for N-ethylaniline 171
Figure 4.14 Chromatogram for 4-aminophenol 171
Figure 4.15 Chromatogram for 1,3-dinitrobenzene 171
Figure 4.16 Chromatogram for azobenzene 171
Figure 4.17 Chromatogram for hydrazobenzene 172
Figure 4.18 Chromatogram for the mixture of compounds 172
Figure 4.19 Chromatogram for the reaction product 172
Figure 4.20 Chromatogram for the reaction product after 3 days 172
Figure 4.21 Nitrobenzene conversion and aniline selectivity as a function of
time for the UV-decomposed palladium acetate catalyst
(0.04 mol NB/l, 60 °C, 4 bar, 0.2 ml/min) 176
Figure 4.22 SEM image of UV-deposited palladium plate (magnification: 50x) 178
Figure 4.23 SEM image of UV-deposited palladium plate (magnification: 500x) 178
Figure 4.24 Chromatogram for the reaction product using the PTA-5 column 179
Figure 4.25 Nitrobenzene conversion as a function of time for the sputtered
palladium catalyst SP2 (0.04 mol NB/l, 60 °C, 4 bar, 0.35 ml/min) 180
Figure 4.26 Nitrobenzene conversion as a function of time for the sputtered
palladium catalyst SP2, after regeneration (0.04 mol NB/l, 60 °C,
4 bar, 0.35 ml/min) 180
Figure 4.27 Optical microscope image of unused sputtered palladium plate SP2
(magnification 160x) 181
Figure 4.28 Image of sputtered palladium plate after reaction
(confocal microscope, 200x) 181
Figure 4.29 Optical microscope image of flaking sputtered palladium plate SP2 181
Figure 4.30 Nitrobenzene conversion and aniline selectivity as a function of
time for the impregnated palladium catalyst IP1
(0.04 mol NB/l, 60 °C, 4 bar, 0.35 ml/min) 183
Figure 4.31 Nitrobenzene conversion as a function of flowrate at various
pressures for the impregnated palladium catalyst IP1
(0.04 mol NB/l, 60 °C) 184
Figure 4.32 Nitrobenzene conversion as a function of flowrate at various
pressures for the impregnated palladium catalyst IP1
(0.04 mol NB/l, 70 °C) 184
Figure 4.33 Nitrobenzene conversion as a function of time for the
impregnated palladium catalyst after different reactivation
procedures (0.04 mol NB/l, 60 °C, 1 bar, 0.35 ml/min):
IP1A - dichloromethane wash and oxidation (note: 4 bar pressure
used for first 3.5 h), IP1B - dichloromethane wash, IP1C -
dichloromethane wash, IP1D - oxidation 186
Figure 4.34 Nitrobenzene conversion as a function of time for the
impregnated palladium catalyst after baking
(IP1E, 0.05 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) 188
Figure 4.35 Nitrobenzene conversion as a function of time for the
impregnated palladium catalyst after baking
(IP1F, 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) 188
Figure 4.36 Nitrobenzene conversion as a function of time for the
impregnated palladium catalyst, base case results during
parametric studies (IP1H, 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) 190
Figure 4.37 Nitrobenzene conversion as a function of flowrate at various pressures for the impregnated palladium catalyst (IP1H, 0.1 mol NB/l, 60 °C) 190

Figure 4.38 Nitrobenzene conversion as a function of pressure at various flowrates for the impregnated palladium catalyst (IP1H, 0.1 mol NB/l, 60 °C) 191

Figure 4.39 Aniline selectivity as a function of time for the impregnated palladium catalyst, base case results during parametric studies (IP1H, 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) 191

Figure 4.40 Aniline selectivity as a function of flowrate at various pressures (IP1H) for the impregnated palladium catalyst, base case results during parametric studies (IP1H, 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) 192

Figure 4.41 Nitrobenzene conversion and aniline selectivity as a function of time for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) 194

Figure 4.42 Nitrobenzene conversion as a function of flowrate at various pressures for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C) 195

Figure 4.43 Nitrobenzene conversion as a function of flowrate at various pressures for the incipient wetness catalyst IW1 (0.1 mol NB/l, 70 °C) 195

Figure 4.44 Aniline selectivity as a function of flowrate at various pressures for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C) 196

Figure 4.45 Aniline selectivity as a function of pressure at various flowrates for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C) 196

Figure 4.46 Aniline selectivity as a function of flowrate at various pressures for the incipient wetness catalyst IW1 (0.1 mol NB/l, 70 °C) 196

Figure 4.47 Aniline selectivity as a function of pressure at various flowrates for the incipient wetness catalyst IW1 (0.1 mol NB/l, 70 °C) 196

Figure 4.48 EDX analysis of IW1 plate after reactivation to remove carbonaceous particles, (a) map view, (b) alumina content, (c) palladium content, (d) iron content. Magnification 180x 201

Figure 4.49 EDX analysis of IW1 plate after reactivation to remove carbonaceous particles, (a) map view, (b) alumina content, (c) palladium content, (d) iron content. Magnification 270x 202

Figure 4.48 Nitrobenzene conversion and aniline selectivity as a function of time for the impregnated palladium catalyst IP2 (0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) 203

Figure 4.49 Nitrobenzene conversion as a function of time for the impregnated palladium catalyst IP2, after reduction (IP2C, 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) 204

Figure 4.50 Nitrobenzene conversion as a function of time for the impregnated palladium catalyst IP2, after reduction (IP2D, 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) (note: parametric studies performed after 6.5 h) 205

Figure 4.51 Nitrobenzene conversion as a function of flowrate at various pressures for the impregnated palladium catalyst IP2, after reduction (IP2D, 0.1 mol NB/l, 60 °C) 205
Figure 4.52 Comparison of nitrobenzene conversion as a function of time for the incipient wetness catalysts IW1 and IW2 (0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) 207

Figure 4.53 Comparison of aniline selectivity as a function of time for the incipient wetness catalysts IW1 and IW2 (0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) 207

Figure 4.54 Nitrobenzene conversion as a function of flowrate at various pressures for the incipient wetness catalyst IW2 (0.1 mol NB/l, 60 °C) 208

Figure 4.55 Aniline selectivity as a function of flowrate at various pressures for the incipient wetness catalyst IW2 (0.1 mol NB/l, 60 °C) 208

Figure 4.56 Aniline selectivity as a function of pressures at various flowrate for the incipient wetness catalyst IW2 (0.1 mol NB/l, 60 °C) 209

Figure 4.57 Nitrobenzene conversion and aniline selectivity as a function of time for the incipient wetness catalyst IW2 (1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) 209

Figure 4.58 Comparison of catalyst life 212

Figure 4.59 Comparison of catalyst selectivity 213

Figure 4.60 Selectivity of the UV catalyst 213

Figure 4.61 Nitrobenzene conversion as a function of liquid film thickness at various pressures for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C) 218

Figure 4.62 Nitrobenzene conversion as a function of residence time at various pressures for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C) 219

Figure 4.63 Nitrobenzene conversion as a function of Reynolds number at various pressures for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C) 219

Figure 4.64 Nitrobenzene conversion as a function of Reynolds number and hydrogen pressure for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C) 220

Figure 5.1 Principle of the confocal microscope 223

Figure 5.2 Confocal microscopy images of the UV-decomposed palladium acetate catalyst plate. a) Visual view from above b) View using analysis software (channel depth 100 μm, width 300 μm) 224

Figure 5.3 Confocal microscopy images of the tilted catalyst plate (bottom of image is tilted up). a) Visual view from above b) View using analysis software 225

Figure 5.4 Confocal microscopy images of the catalyst plate with a thin film of water 225

Figure 5.5 Software processed confocal microscopy images of the catalyst plate a) with a thin film of water b) after drying out. Colour code (highest to lowest): white, brown, yellow, green, dark blue, light blue 226

Figure 5.6 Confocal microscope image of water on stainless steel plate (magnification 40x). Yellow line on right figure depicts height data of the liquid film in the middle channel (bottom to top) 227

Figure 5.7 Confocal microscope image of dry stainless steel plate (magnification 40x) 227
Figure 5.8  Resulting image from the subtraction of dry plate from wet plate. Colour code (highest to lowest): brown, yellow, green.

Figure 5.9  Resulting image from the subtraction of dry plate from wet plate, wireframe figure on right. Colour code (highest to lowest): brown, yellow, green

Figure 5.10  Microscope stage with a horizontal focusing mechanism (to and away from the confocal beam) controlled using a screw micrometer (for depth measurements), and a secondary horizontal axis of motion perpendicular to the confocal beam.

Figure 5.11  Average liquid film thickness profile across a channel at various flowrates.

Figure 5.12  Temperature profile of the falling film plate at 30 °C

Figure 5.13  Temperature profile of the falling film plate at 40 °C

Figure 5.14  Temperature profile of the falling film plate at 50 °C

Figure 5.15  Temperature profile of the falling film plate at 60 °C

Figure 6.1  Geometry of the model.

Figure 6.2  Extrapolation of liquid film thicknesses at different flowrates.

Figure 6.3  Base case comparison of model with experimental results (Langmuir-Hinselwood (I), laminar flow, $k = 0.0021$, $K_{NB} = 1.72$, $K_{H2} = 0.3$)

Figure 6.4  Base case comparison of model with experimental results (Langmuir-Hinselwood (I), plug flow, $k = 0.013$, $K_{NB} = 1.72$, $K_{H2} = 0.3$)

Figure 6.5  Effect of varying $K_{H2}$ (Langmuir-Hinselwood (I), laminar flow, $K_{NB} = 1.72$, 1 bar)

Figure 6.6  Effect of varying $K_{H2}$ (Langmuir-Hinselwood (I), laminar flow, $K_{NB} = 1.72$, 4 bar)

Figure 6.7  Effect of varying $K_{H2}$ (Langmuir-Hinselwood (I), laminar flow, $K_{NB} = 1.72$, 6 bar)

Figure 6.8  Final comparison of model with experimental results (Langmuir-Hinselwood (I), laminar flow, $k = 0.0042$, $K_{NB} = 0.01$, $K_{H2} = 1$)

Figure 6.9  Final comparison of model with experimental results (Langmuir-Hinselwood (I), plug flow, $k = 0.02$, $K_{NB} = 0.01$, $K_{H2} = 1$)

Figure 6.10  Comparison of laminar and plug flow using first order reaction kinetics ($r = kC_A$)

Figure 6.11  Comparison of laminar and plug flow using zero order reaction kinetics ($r = k$)

Figure 6.12  Comparison of laminar and plug flow wall hydrogen concentration using first and zero order kinetics (2 ml/min flowrate)

Figure 6.13  Effect of varying $K_{H2}$ at 1 bar (Langmuir-Hinselwood (II), laminar flow, $K_{NB} = 0.01$)

Figure 6.14  Effect of varying $K_{H2}$ at 4 bar (Langmuir-Hinselwood (II), laminar flow, $K_{NB} = 0.01$)

Figure 6.15  Effect of varying $K_{H2}$ at 6 bar (Langmuir-Hinselwood (II), laminar flow, $K_{NB} = 0.01$)

Figure 6.16  Final comparison of model with experimental results (Langmuir-Hinselwood (II), laminar flow, $k = 0.036$, $K_{NB} = 0.01$, $K_{H2} = 0.3$)

Figure 6.17  Final comparison of model with experimental results (Langmuir-Hinselwood (II), plug flow, $k = 0.2$, $K_{NB} = 0.01$, $K_{H2} = 0.3$)
Figure 6.18 Final comparison of model with experimental results (Langmuir-Hinselwood (III), laminar flow, $k = 0.00034$, $K_{NB} = 0.01$, $K_{H_2} = 15$)  

Figure 6.19 Final comparison of model with experimental results (Langmuir-Hinselwood (III), laminar flow, $k = 0.0012$, $K_{NB} = 0.01$, $K_{H_2} = 15$)  

Figure 6.20 Comparison of all models with experimental results (1 bar)  

Figure 6.21 Comparison of all models with experimental results (4 bar)  

Figure 6.22 Comparison of all models with experimental results (6 bar)  

Figure 6.23 Comparison of model (I) with experimental results, matched to the experimental value at 0.5 ml/min and 6 bar (laminar flow, $k = 0.00305$, $K_{NB} = 0.01$, $K_{H_2} = 1$)  

Figure 6.24 Comparison of model (II) with experimental results, matched to the experimental value at 0.5 ml/min and 6 bar (laminar flow, $k = 0.02$, $K_{NB} = 0.01$, $K_{H_2} = 0.3$)  

Figure 6.25 Comparison of model (III) with experimental results, matched to the experimental value at 0.5 ml/min and 6 bar (laminar flow, $k = 0.00024$, $K_{NB} = 0.01$, $K_{H_2} = 15$)  

Figure 7.1 Schematic of the experimental set-up  

Figure 7.2 Acetone evaporation as a function of nitrogen flowrate at various liquid flowrates  

Figure 7.3 Acetone evaporation as a function of liquid flowrate at various nitrogen flowrates  

Figure 7.4 Conversion and selectivity as a function of total reaction time (P1A, flask temperature 0 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min, nitrogen flowrate 50 ml/min)  

Figure 7.5 Conversion and selectivity as a function of total reaction time for the second experiment (P1B, flask temperature 0 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min, nitrogen flowrate 50 ml/min)  

Figure 7.6 Conversion and selectivity as a function of total reaction time for the third experiment (P1C, flask temperature 0 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min, nitrogen flowrate 150 ml/min)  

Figure 7.7 Conversion and selectivity as a function of total reaction time (P2A, flask temperature 0 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min, nitrogen flowrate 150 ml/min)  

Figure 8.1 Microsystem design algorithm
List of Tables

<table>
<thead>
<tr>
<th>Table Reference</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.1</td>
<td>Surface area to volume ratio</td>
<td>3</td>
</tr>
<tr>
<td>Table 2.1</td>
<td>Comparison of isotropic and anisotropic etchants</td>
<td>17</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Calculation data for the estimation of reaction kinetics for methanol oxidation</td>
<td>80</td>
</tr>
<tr>
<td>Table 3.2</td>
<td>Residence times to achieve a range conversions for methanol oxidation</td>
<td>80</td>
</tr>
<tr>
<td>Table 3.3</td>
<td>Results of the second attempt at microfabrication</td>
<td>90</td>
</tr>
<tr>
<td>Table 3.4</td>
<td>Effect of KOH concentration on etching</td>
<td>94</td>
</tr>
<tr>
<td>Table 3.5</td>
<td>Effect of temperature on etching</td>
<td>94</td>
</tr>
<tr>
<td>Table 3.6</td>
<td>Effects of agitation speed on etching</td>
<td>95</td>
</tr>
<tr>
<td>Table 3.7</td>
<td>Effect of etch depth on smoothness of channel surface</td>
<td>95</td>
</tr>
<tr>
<td>Table 3.8</td>
<td>Electroplating experiments</td>
<td>115</td>
</tr>
<tr>
<td>Table 3.9</td>
<td>Results of silver mirror experiment</td>
<td>120</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Selected types of hydrogenation reactions and the preferred catalysts</td>
<td>146</td>
</tr>
<tr>
<td>Table 4.2</td>
<td>Comparison of reactor sizes for processing 11360 l/day of DNB</td>
<td>148</td>
</tr>
<tr>
<td>Table 4.3</td>
<td>Enthalpies of hydrogenation for selected organic functional group</td>
<td>150</td>
</tr>
<tr>
<td>Table 4.4</td>
<td>Effect of catalyst, solvent and operating conditions on the hydrogenation product of nitrobenzene</td>
<td>152</td>
</tr>
<tr>
<td>Table 4.5</td>
<td>Minimum flowrates before dryout at various temperatures at 4 bar</td>
<td>159</td>
</tr>
<tr>
<td>Table 4.6</td>
<td>Falling film calculation parameters</td>
<td>160</td>
</tr>
<tr>
<td>Table 4.7</td>
<td>Operating conditions for deactivation experiments</td>
<td>164</td>
</tr>
<tr>
<td>Table 4.8</td>
<td>Detected compounds in the GCMS</td>
<td>169</td>
</tr>
<tr>
<td>Table 4.9</td>
<td>Weisz-Prater calculations for the reaction system</td>
<td>199</td>
</tr>
<tr>
<td>Table 4.10</td>
<td>Comparison of diffusion time for hydrogen across the liquid film and the residence time in the reactor</td>
<td>200</td>
</tr>
<tr>
<td>Table 4.11</td>
<td>Experimental conditions for the various catalysts</td>
<td>212</td>
</tr>
<tr>
<td>Table 4.12</td>
<td>Discrepancy between carbon moles entering and leaving the reactor for the various catalysts</td>
<td>214</td>
</tr>
<tr>
<td>Table 4.13</td>
<td>Time required for the formation of a monolayer</td>
<td>215</td>
</tr>
<tr>
<td>Table 5.1</td>
<td>Comparison of measured and calculated liquid film thickness at various flowrates</td>
<td>232</td>
</tr>
<tr>
<td>Table 5.2</td>
<td>Maximum, minimum and average plate temperature at various water bath temperatures</td>
<td>234</td>
</tr>
<tr>
<td>Table 6.1</td>
<td>Parameters used in the reactor model</td>
<td>241</td>
</tr>
<tr>
<td>Table 6.2</td>
<td>Effect of the number of points used on nitrobenzene conversion and modelling time (Langmuir-Hinselwood (I), laminar flow, k = 0.0021, K_{NB} = 1.72, K_{H2} = 0.3, 1 bar, 0.5 ml/min)</td>
<td>242</td>
</tr>
<tr>
<td>Table 6.3</td>
<td>Calculated liquid film thicknesses</td>
<td>243</td>
</tr>
<tr>
<td>Table 7.1</td>
<td>Conversion and selectivity in reproducibility experiments (P2D, flask temperature 0 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min, nitrogen flowrate 150)</td>
<td>268</td>
</tr>
<tr>
<td>Table 7.2</td>
<td>Conversion and selectivity in deactivation experiments (P2N, flask temperature 30 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min, nitrogen flowrate 150 ml/min)</td>
<td>270</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------------------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>a</td>
<td>channel width</td>
<td>m</td>
</tr>
<tr>
<td>A</td>
<td>cross-sectional area for flow</td>
<td>m²</td>
</tr>
<tr>
<td>b</td>
<td>channel height</td>
<td>m</td>
</tr>
<tr>
<td>C</td>
<td>concentration</td>
<td>mol/m³</td>
</tr>
<tr>
<td>Cₐ</td>
<td>concentration of reactant a</td>
<td>mol/m³</td>
</tr>
<tr>
<td>Cₐ(0)</td>
<td>initial concentration of reactant a</td>
<td>mol/m³</td>
</tr>
<tr>
<td>Cₐₛ</td>
<td>concentration of A at the surface of the catalyst</td>
<td>mol/m³</td>
</tr>
<tr>
<td>C_f</td>
<td>friction factor in a pipe</td>
<td></td>
</tr>
<tr>
<td>C_p</td>
<td>specific heat capacity of reactant</td>
<td>J/kg K</td>
</tr>
<tr>
<td>D</td>
<td>molecular diffusivity</td>
<td>m²/s</td>
</tr>
<tr>
<td>DₑA</td>
<td>effective diffusivity of A</td>
<td>m²/s</td>
</tr>
<tr>
<td>Da</td>
<td>Damkohler number</td>
<td></td>
</tr>
<tr>
<td>D_H</td>
<td>Hydraulic diameter</td>
<td>m</td>
</tr>
<tr>
<td>F</td>
<td>feed flow rate</td>
<td>m³/min</td>
</tr>
<tr>
<td>fₑ</td>
<td>convective boiling factor</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>mass flow rate of inlet liquid per unit area of flow</td>
<td>kg/m² s</td>
</tr>
<tr>
<td>g</td>
<td>gravitational acceleration</td>
<td>m³/s</td>
</tr>
<tr>
<td>h</td>
<td>distance between plates, liquid film thickness</td>
<td>m</td>
</tr>
<tr>
<td>hₑvap</td>
<td>latent heat of vaporisation</td>
<td>J/kg</td>
</tr>
<tr>
<td>k</td>
<td>thermal conductivity of reactant</td>
<td>W/m K</td>
</tr>
<tr>
<td>K</td>
<td>absolute response factor of compound i</td>
<td></td>
</tr>
<tr>
<td>k₁</td>
<td>first order reaction rate constant</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>K_H₂</td>
<td>adsorption coefficient for hydrogen</td>
<td>m³/mol</td>
</tr>
<tr>
<td>K_NB</td>
<td>adsorption coefficient for nitrobenzene</td>
<td>m³/mol</td>
</tr>
<tr>
<td>k_w</td>
<td>channel wall thermal conductivity</td>
<td>W/m K</td>
</tr>
<tr>
<td>L</td>
<td>total length</td>
<td>m</td>
</tr>
<tr>
<td>l</td>
<td>channel length</td>
<td>m</td>
</tr>
<tr>
<td>m</td>
<td>gradient of a straight line</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>mass flow rate of reactant</td>
<td>kg/s</td>
</tr>
<tr>
<td>M</td>
<td>relative molecular mass</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>number of channels</td>
<td></td>
</tr>
<tr>
<td>N_Bₐｃｔ</td>
<td>corrected nitrobenzene conversion</td>
<td></td>
</tr>
<tr>
<td>N_Bₑₓᵖ</td>
<td>experimental conversion</td>
<td></td>
</tr>
<tr>
<td>Nu</td>
<td>Nusselt number</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>pressure</td>
<td>bar</td>
</tr>
<tr>
<td>P</td>
<td>perimeter</td>
<td>m</td>
</tr>
</tbody>
</table>
\( \varepsilon_s \) void fraction
\( \varepsilon_s \) void fraction
\( \Phi \) Thiele modulus
\( \phi_B \) association factor for B
\( \gamma_g \) friction surface tension parameter
\( \gamma_{lg} \) gas-liquid surface tension
\( \eta \) dimensionless distance
\( \lambda \) dimensionless distance
\( \lambda_a \) concentration decay constant
\( \mu \) liquid viscosity
\( \Theta \) contact angle
\( \Theta \) dimensionless concentration
\( \rho \) density
\( \rho_s \) density of catalyst
\( \sigma \) stoichiometric coefficient
\( \tau \) Residence time
tortuosity
\( \tau_d \) Diffusion time
\( \zeta \) dimensionless distance

Subscripts
AN subscript denoting aniline
g subscript denoting gas
H2 subscript denoting hydrogen
i subscript denoting nitrobenzene, hydrogen and aniline
L subscript denoting liquid
l subscript denoting liquid
NB subscript denoting nitrobenzene
V subscript denoting vapour
1. Introduction

Environment and economics; these are the major concerns in Chemical Engineering today. Processes need to make increasingly more product and profit using less and less resources and cash expenditure to be economically viable. At the same time, environmental laws get more stringent each year. Generally, being environmentally friendly requires processes to operate at less extreme conditions. However, this often leads to a decrease in reaction rate. While this is likely to reduce the amount of by-products, fuel and heat, a corresponding decrease in production is likely to occur. As such, these two factors are usually in opposition.

Enter the microreactor - reactors in the size range of several centimetres in length and thickness. Using techniques originally developed in the microchip manufacturing industry and refinements in general workshop equipment, they are now readily realisable. Once commercialised, these reactors will become affordable, mirroring the integrated circuit industry where the economies of mass production allow low cost manufacturing.

But why is the chemical industry only just beginning to examine the prospects of microreactors? Most important is the resistance to new ideas. The first microsystem applicable to industry, a chromatography column, was fabricated in the early 80s. Some interest was shown, but it did not cause much impact. Later, a microchannel crossflow heat exchanger was patented (Swift, 1985). Again, nothing. Even now, when such systems have been demonstrated and are in use in some companies, many chemical engineers have either never heard of them or display open scepticism.
Another reason is lack of expertise. Producing these systems requires knowledge of microfabrication, which is used in manufacturing small, electronic components. Chemical engineers in general tend to concentrate on bulk chemical manufacture and bulk structural characteristics of materials. More importantly, there is the thought that bigger, centralised production centres minimise waste, pollution and costs. In addition, the thought of the difficulties involved in developing a knowledge-base in an entirely different field of expertise may have imposed a barrier that was difficult to surmount.

However, in the last decade, the gap between the two realms has been bridged. Microfabrication technology has now become accessible enough to be taken advantage of. The development of microfluidic devices can now be performed in microfabrication foundries/research centres. Alternatively, some microfabrication technology is cheap enough to be set-up in research laboratories. In addition, conventional bulk machining methods (i.e. the traditional workshop toolkit) have been refined to the stage where they can be used on the sub-millimetre level. Together, these factors have resulted in a burst of research determined to put microchemical systems into general use.

Microreactors have the potential to offer improvements to a major problem: by-product formation, which are usually made due to inefficiencies in processes. This is mainly due to the large size of industrial reactors. Large volumes result in uneven mixing and thermal distribution. Control actions take longer to effect while the desired product(s) take longer to be removed from the reactor system. In many systems, a combination of these factors results in low yields of the product and
undesirable amounts of by-products.

With channels one or more orders smaller in magnitude, the ratio of surface area \( (L^2) \) to volume \( (L^3) \) increases dramatically, leading to more efficient heat and mass transfer. As such control is better and quicker, which leads to less by products. Using microreactors could see an increase in production, profits and a decrease in pollution.

<table>
<thead>
<tr>
<th>Dimensions (m)</th>
<th>( L^2 : L^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>0.1</td>
<td>10</td>
</tr>
<tr>
<td>0.01</td>
<td>100</td>
</tr>
<tr>
<td>0.001</td>
<td>1000</td>
</tr>
</tbody>
</table>

Table 1.1: Surface area to volume ratio

Other improvements microreactors can bring include:

a) improved safety due to the smaller amount of reaction material used and the quicker response time of control measures. In addition, the dimensions of the systems prevent the propagation of flames thus causing them to act as natural flame traps.

b) the ability to exploit previously unfeasible reaction routes due to safety restrictions and/or operational limitations.

c) shorter lag time between R&D and actual production. Production volumes can be increased by increasing the number of systems working in parallel.

However, the path ahead does have several bumps in it. The behaviour of fluids at the microscale can be different from that in the macroscale which chemical engineers have traditionally dealt with. There is also the problem of interfacing and integrating these smaller systems to larger distribution and collection systems, which is currently
proving to be the largest stumbling block affecting microchemical systems. As such, much work is being done to further understanding in these areas.

This thesis is divided into several chapters, each dealing with different areas in microreaction engineering. A comprehensive literature survey of microfabrication methods and microfluidic devices is presented in Chapter 2. Chapter 3 details the process of fabricating and testing a silicon-based catalytic microreactor for the silver-catalysed gas phase partial oxidation of methanol to formaldehyde. The application of a micro-falling film reactor for the gas-liquid hydrogenation of nitrobenzene to aniline over a solid palladium catalyst is explored in detail in Chapter 4 while investigations into the hydrodynamics and thermal characteristics of the microreactor are presented in Chapter 5. A simple model of the reaction system was developed in Chapter 6. In Chapter 7, the micro-falling film reactor was utilised as an evaporator-reactor for the asymmetric transfer hydrogenation of acetophenone to (S)-phenylethanol catalysed by a rhodium complex that was activated by sodium isopropoxide, in order to explore alternative uses of the reactor. Chapter 8 brings together the experience gained in this project in the form of a microreactor design algorithm. Finally, the conclusions of this project are presented in Chapter 9, together with avenues of potential future work.
2. Literature Survey

In order to design and fabricate microreactors, research was carried out on the topic of microfabrication to determine the most suitable methods. With microreactors being such a new field, there was no on-hand expertise. Therefore, a comprehensive survey of literature relating to microfluidic systems (covering characteristics, fabrication, applications and modelling) was carried out.

2.1 Characteristics of Microfluidic Systems

Microsystems behave differently from macrosystems because surface area-dependent effects are dominant. A brief review of the most important differences follows.

2.1.1 Surface Tension

At sub-millimetre scales, surface tension is important and can render the flow characteristics independent of the channel configuration with respect to gravity. Brauner and Moalem-Maron (1992) suggested that surface tension would be dominant when the tube diameter $D$ satisfied the following correlation:

$$\frac{(2\pi)^2 \sigma}{(\rho_1 - \rho_g)D^2g} > 1$$

where $\sigma$ = surface tension
$\rho_1$ = density (subscripts g and l denoting gas and liquid respectively)
g = gravitational acceleration

Filling channels with liquids can be problematic, especially during start-up when bubbles of gas may be trapped. The pressure drop across a liquid gas interface of a gas bubble in a capillary tube and the pressure difference required to move the gas bubble are, respectively,
\[ \Delta P = \frac{2\gamma_{lg} \cos \theta}{r} \quad \text{and} \quad \frac{P_f}{r} = \frac{2\gamma_g}{r} \]

where \( r = \) channel radius
\( \gamma_{lg} = \) gas-liquid surface tension
\( \gamma_g = \) friction surface tension parameter
\( \theta = \) contact angle

When the bubble is within the tube, the pressure drops at both interfaces cancel out. However, when there is a change in channel radius, the net resulting force creates a blocking pressure. It was found that the pressure required to discharge a bubble from a 1 \( \mu \)m capillary tube filled with water was about 1.4 bar (Matsumoto, et al, 1990, Gravesen, et al, 1993). As such, surfaces with good wetting properties should be used to promote flow. When pumping is required, channels should not be made too small. On the other hand, capillary forces will fill even small channels (Söderkvist, 1997).

### 2.1.2 Fluid Flow

The growing body of work in this area shows that the application of conventional approaches to fluidics can be rather much a case of hit-or-miss. While general predictions tend to hold true, a more specific understanding of the fluid mechanics at the microscale is required.

#### 2.1.2.1 Single phase Flow

Fluid flow in microchannels has been found to behave differently than in macrochannel flow. A number of phenomena which are usually not significant in large scale flows can contribute to this: surface tension, formation of an electrical double layer and the relative magnitude of roughness compared to the channel dimensions. In many cases friction factors different from those predicted for large channels are measured in microchannels. In laminar flow, the common expression for the friction
factor in tubes is $64/\text{Re}$ while in non-circular channels the value of the friction factor will depend on the geometric characteristics. Often the friction coefficient ($f^*\text{Re}$), which is independent of the Reynolds number for a given channel geometry, is used for comparisons.

A number of investigators have attempted to measure friction factors in microchannels with contradicting results. Wu and Little (1983), using gas flow in trapezoidal test sections (hydraulic diameter 45-83 μm), found that in both laminar and turbulent flow, the friction factors for rough channels were higher than the theoretical ones. Peng, et al (1994), experimenting with liquids, also found that laminar flow in rectangular channels (hydraulic diameters 133-367 μm) resulted in larger than predicted friction coefficients. In contrast to large channels where this parameter decreases with the channel aspect ratio, they found the opposite trend. In turbulent flow, deviations from the classical theory were attributed to small flow passages that can suppress the fluctuations and vorticity of the flow. Pfahler, et al (1990) found that experimental data in channels with hydraulic diameters 76.1 μm and 3.34 μm were in reasonable agreement with theoretical predictions. However, in the smallest channels (hydraulic diameter 1.6 μm) the friction coefficient was up to 3 orders of magnitude higher than predicted. Contrary to this, Pfahler, et al, (1991) observed friction factors lower than theoretical values for channels with hydraulic diameters 0.96-40 μm. During liquid flow, the friction coefficient for alcohol (polar liquid) showed a dependency on the channel size but not on Re, while for oil (non-polar liquid) it depended only on Re. In gas flow, ($f^*\text{Re}$) was found to take values below the theoretical ones, which decreased with Re. This was attributed to rarefaction phenomena. Choi, et al (1991), using
laminar gas flow in very smooth circular tubes (diameter 3-81 μm) found that \( (f \cdot Re) \) was constant but below 64.

Apart from the friction factors, the Re where transition from laminar to turbulent flow occurs was also different in microchannels. Peng, et al (1994) reported that the transition Re decreased with decreasing channel hydraulic diameter because instabilities could spread faster in small channels than in large scale systems. Contrary to this, Stanley et al (1997) found that when the channel size was reduced, the transition from laminar to turbulent flow appeared at higher Re for gas flows while for water flows turbulence did not appear even for Re up to 10000. Wu and Little (1983) observed reduced transitional Re for the rougher glass channels they used, which decreased as the channel roughness increased.

Compressibility and rarefaction effects can appear during gas flow in small channels (Gravesen, et al 1993). Guo and Wu (1997) studied (theoretically) gas flow in circular channels and found that gas acceleration induced by compressibility changed both the magnitude and the shape of the velocity profile; as a result the \( (f \cdot Re) \) would increase along the tube length and would also depend on Re. Rarefied gas dynamics show that the continuum approach assumptions are invalid when the mean free path of gas molecules (ca. 60 nm at 1 atm) is of the order of the characteristic channel dimension. At continuum flow the velocity of the gas at the wall boundary will be zero. At the free molecular flow, which represents the other extreme, the gas moves along the wall boundary due to a net velocity in the flow direction. In between these two extremes, slip flow occurs with slight rarefaction effects (Bailey, et al, 1995).
Another phenomenon that can become significant in microchannel flow is the appearance of an electrical double layer (EDL) which is established between a liquid containing ions and a charged solid surface. When a polar liquid flows in a channel with charged walls, then due to the EDL a streaming potential and a flow opposite to the main flow direction is established (Adamson & Gast, 1997). In small channels, this results in higher apparent viscosity and friction factor (electroviscous effect). Even small amounts of ions can result in the formation of an EDL. In fact when the ionic concentration is low, EDL thickness becomes large (for pure water and oils it can be as large as several microns) and has a greater effect on the flow (Mala, et al, 1997). The presence of an EDL, however, would only justify the appearance of higher friction factors than those expected from traditional theory.

2.1.2.2 Two-phase Flow

The study of two-phase fluid flow in microchannels has concentrated on gas-liquid systems. Stanley, et al (1997) studied gas-liquid flows in rectangular channels with hydraulic diameters between 56 and 256 μm. Unlike their single-phase flow results, no turbulence suppression was observed; in the smallest channels they observed some influence of the surface tension. Triplett, et al (1999, 1999b) presented a comprehensive experimental study on the flow patterns, void fraction and pressure drop during air-water flow in circular and triangular tubes with hydraulic diameters 1.1 and 1.45 mm. In all tubes the same flow patterns appeared as in large scale flows (i.e. bubbly, slug, churn, annular) but the transitions from one pattern to the other happened at different flow conditions. Compared to large channels, the velocity slip between the phases was less. Bubble, slug (with bubbles 2-23 times larger than the channel width) and annular flow were observed in channels with hydraulic diameters
Xu, et al (1999) presented results in channels with depths as small as 0.3 mm, and found differences between the smallest channels and the ones with diameters above 0.6 mm: no bubble flow appeared in the smallest channels, while during slug flow isolated drops were seen to adhere to the tube wall surface.

Burns and Ramshaw (1999) presented flow patterns during the flow of two immiscible liquids in microchannels. They found that the two phases flow, in most cases, in separate layers but contrary to what would be expected, the lighter oil phase flowed beneath the denser aqueous phase, under the influence of surface tension forces. Using different distributors to mix the two liquids, they observed slug flow patterns with slug lengths depending on the geometry of the distributor (Burns and Ramshaw, 2000).

A particular case of slug flow, Taylor flow, has attracted interest since the well defined interface renders its experimental and theoretical study relatively easy in some cases. It is characterised by long bubbles (with lengths larger than the channel hydraulic diameter), separated by a liquid thin film from the wall, with a leading edge shaped like prolate spheroids and a trailing end that can take different shapes depending on the prevailing forces in the flow (Edvinsson and Irandoust, 1996). Taylor flow offers good mass transfer characteristics and is the preferred flow pattern for two-phase reactions in monolithic catalytic reactors. The recirculation within the liquid plugs and the film that surrounds the bubbles ensures fast mass transfer from gas to liquid and from liquid to wall (Irandoust and Andersson, 1989). Bi and Zhao (2001) observed that in non-circular geometries bubble rise velocity in stagnant liquid
decreased with channel hydraulic diameter but did not become zero at $1/E_o > 0.297$
(where $E_o$ is the Eötvös number) as was found for circular channels.

2.1.2.3 Fluid delivery

A major problem with the pumping of liquids is that the channel sizes tend to preclude the use of fouling, viscous and/or particulate fluids as they may cause blockages, operational difficulties and damage in microsystems with moving parts, such as pumps and valves. Liquid flow can be driven by conventional or micropumps. But, the former can be difficult to interface with microstructures while the latter have poor back-pressure and result in leakage (Freemantle, 1999). This has led to alternative methods, such as electro-osmotic flow (EOF). An electrical double layer is formed by ions in the fluid and surface charges immobilised on the channel walls. Applying an electric field causes the solution to move towards an electrode (Freemantle, 1999). This only works in small channels ($< 500 \mu m$), though studies have demonstrated that EOF can be used in larger channels filled with silica frits (Haswell, 1999, Christenson, 1999).

Fluids can also be moved on the submillimeter scale using surfactants with redox-active groups. Electrochemically switching them between surface active and surface-inactive states controls the concentration of the surface-active species in solution. The concentration gradient causes changes in surface tension, leading to controlled motion. Aqueous and organic liquids and solid microparticles can be made to flow. Low voltage ($< 1V$) is required as opposed to the kilovolts needed by typical electrokinetic methods (Gallardo, 1999, Freemantle, 1999).
A new wetting phenomenon was reported at the Max Planck Institute of Colloids and Interfaces. Stripes were patterned on hydrophobic substrates to form liquid channels. Channel volume increased with liquid volume until a critical volume where a single bulge formed. This channel remains stable as long as its volume is small. Bulges preferentially form at the corners and if formed close-by can merge into a bridge, which can be used to mix liquids or even to react compounds. A whole network of such channels could be formed. (Freemantle, 1999, Gau, 1999).

2.1.3 Thermal Characteristics

Microsystems have high heat fluxes (100 W/cm²) and convective heat transfer coefficients (up to 54000 W/m² °C in liquid-liquid systems, 350000 W/m² °C for boiling conditions and 1000 W/m² °C in gases) (Brandner, et al, 1999, Wegeng, et al, 1996, Chopey, et al, 1997).

A major industrial problem is thermal control since the size of reactors makes rapid heat removal difficult. As such, many exothermic processes operate adiabatically. In highly exothermic reactions, malfunctions in the control system can result in rapidly rising temperatures, leading to runaway reactions. In processes taking place in the region of an unstable steady state, good, steady heat removal is required. Finally, when multiple reactions take place, temperature control is important to reduce by-products. Endothermic processes tend to operate at high temperatures. As such, durable and expensive structural materials have to be used. The overheating of such structures, seen repeatedly in steam reforming, is disastrous and costly. Also, many heating designs are inefficient, which incurs huge additional operating costs.
Microreactors solve most of these problems. With their heat transfer characteristics, heat removal/input is quick, allowing exothermic reactions to be carried out without risk of thermal runaway and safer operation at high temperatures. Heat transfer in endothermic reactors becomes more efficient. Isothermal operation is also possible while temperature-sensitive reactions will benefit greatly. Previously unworkable reaction routes with very large heat generation and/or spontaneous ignition may also be exploited. This is due to rapid heat removal and/or the flame trap dimensions of the channels (Paratte, et al, 1997). Rapid heat removal also gives rise to rapid quench rates. Reactions can be halted very quickly at the end of the desired reaction period, which can improve selectivity, purity and production.

However, the increased surface area to volume ratio may also result in increased loss of heat to the surroundings. Also, at this size, the recovery of useful heat may prove inefficient. Also important are temperature gradients. While usually equalised very quickly in microstructures, they are very sensitive to them. Sudden or even prolonged heating at elevated temperatures may result in buckling (or crumpling) of structures (Srinivasan, et al, 1997).

2.1.4 Structural Characteristics

Microreactors are versatile in the sense that the channels can be as complicated or as simple as desired. A quick reaction not involving catalysts can take place in a parallel set of straight tubes while a catalytically enhanced reaction can be performed in a convoluted series of porous channels to give a larger surface area.
Microreactors have the potential to enhance catalytic reactions. With thinner boundary layers and therefore more effective molecular diffusion, mass transfer limited catalytic reactions should be enhanced. Porous silicon or aluminium structures can be made by anodisation in which pore size and depth are controlled by current density and time (Drott, et al, 1997, Laurell, 1997). This allows greater loading of catalyst, thus improving yields. Structures with micropores running throughout the entire structure, such as concrete and zeolites, can also be utilised as micro-component separation units. This is because the size of the pores can be controlled to a certain extent. As such, they can be used to separate molecules by size.

Many microsystems are made on thin substrates, allowing sheets containing different operations to be stacked into an integrated reaction system. The eventual aim would be to fabricate production units which could fit on a table, in a car, handheld dispenser or even into a biomedical system within the human body. This will allow distributed manufacturing and point-of-use production of harmful chemicals or chemicals required in small amounts. Also, by manufacturing self-contained stacks, the capacity of a plant can be increased by “plugging in” as many stacks as required. Failed stacks can also be replaced easily. This will bring economic and maintenance advantages.

However, this area remains largely unexplored and much more work is required in the packaging of microreactors, manifold design, interfacing with external equipment and the integration of control systems into reactor modules (a microreactor stack containing hundreds of modules could require thousands of electrical connections). It is very likely that the full range of structural possibilities opened up by the use of such
reactors has not been realised yet as they require a line of thought which may be
different from that of conventional macro-scale reactor design.

2.2 Fabrication Methods

The advent of microreaction technology was initially underpinned by silicon
microfabrication methods originally developed by the microelectronics industry.
However, as new or improved precision engineering methods and tools became
available, they were utilised as well. These are the enabling technologies that form
the cornerstones of microreaction technology. They allow the manufacture of micro-
engineered structures from metals, ceramics, silicon, glass and plastics.

2.2.1 Photolithography and Etching Techniques

The earliest forays into microfabrication typically involved photolithography and
etching (see Figure 2.1) as they were the most well-developed of all microfabrication
techniques. Photoresist is spun on to a masking layer on a substrate, typically silicon
oxide or nitride on a clean, polished silicon wafer (Madou, 1997). There are two types
of resists: positive and negative. In positive resists, UV radiation breaks up polymer
chains in exposed areas, making it more soluble in a developer. In negative resists,
the exposed parts become insoluble due to crosslinking (Morgan, 1991). A pattern is
formed by placing a chromium-patterned glass mask between a UV source and the
wafer. The resist is then developed to form a patterned protective layer. The
unprotected areas of the masking layer and the substrate are then etched, using either
wet or dry etching, to form the required structures.
There are 2 types of wet etchants for silicon: isotropic etchants (usually acidic) etch at equal rates in all directions, resulting in slightly rounded features (Vossen, and Kern, 1978). Etch rates are fast, but it is difficult to etch to high precision. Anisotropic etchants (usually alkaline) etch at different rates in different crystallographic planes (Madou, 1997). While precise etching is more easily obtained, etch rates are low and rough surfaces often result. Relatively high temperatures (85-100 °C) are usually required to improve etching rates. Anisotropic etching is made possible by silicon’s crystalline structure. See Table 2.1 for a comparison of anisotropic and isotropic etching. A large variety of metals and stainless steels can also be structured using wet etching, however etching is isotropic (Ehrfeld, 2000).
Isotropic Etchants

Advantages
- Fast
- Etch rate can be influenced by doping. Heavily doped Si is etched more quickly
- Additives can modify etch rate, surface finish or isotropy

Disadvantages
- Rounded features, difficult to etch to a high precision
- Etch rate sensitive to agitation - makes it even more difficult to control dimensions
- Temperature sensitive
- Diffusion limited - rates improved by stirring, which is difficult to reproduce

Anisotropic Etchants

Advantages
- Results in geometric shapes bounded by crystallographic planes
- Etch-stop techniques result in high accuracy
- Reaction rate limited - rates improved by higher temperatures, easier to control
- Not sensitive to agitation

Disadvantages
- Very slow (etch rates < 1 μm/min)
- Require high temperatures for such rates
- Can leave rough surfaces, requiring a quick isotropic etch for smoothing
- Precision alignment of mask required to produce desired vertical structures

Table 2.1: Comparison of isotropic and anisotropic etchants

Dry etching comprises of plasma- or discharged-based techniques. They carry out accurate etching at very small dimensions and have good vertical and lateral etching control irrespective of crystallographic orientation or substrate. This causes less undercutting and broadening of photoresist features. Pattern transfer is good and the resulting surfaces are cleaner. The various methods used are (Rangelow, et al, 1997, Jansen, et al, 1996):

i) chemical plasma etching - involves little ion bombardment and is mostly chemical etching. Most often used for resist stripping and where high selectivity is required.

ii) reactive ion etching - characterised by low plasma potentials (10-50 V) leading to small sputter contamination. However, there are difficulties in controlling the process (temperature, flux of species, etc.) giving rise to a lack in consistency.

iii) ion beam etching - plasma is sputtered on to the substrate surface at low pressure using a directed energy flux. The target areas are vaporised, forming structures. Because this process is very slow (1-30 nm/min), a reactive feed gas is sometimes added to increase rates.
Fluorine-based gases are usually used in isotropic etching while chlorine-based, bromine-based and mixed molecule gases are used for anisotropic etching. Oxygen-based plasmas are used for polymer etching (Jansen, 1996). Recently, a Deep Reactive Ion Etching (DRIE) process was developed which utilised a fluorine-based system in conjunction with passivation to achieve structures with large aspect ratios (Thornell and Johansson, 1998). These processes are all very sensitive to various parameters. For example, temperature has a very strong effect and is one of the major causes of inconsistency. Small amounts of contaminants can drastically affect the final product by reacting with the target or by changing the plasma chemistry. As such, while versatile and useful, some difficulties are involved.

Combinations of dry and wet etching techniques can allow fabrication of difficult-to-make structures, such as circular silicon nitride tubes buried in silicon (Gardeniers, et al, 1999).

2.2.2 Chemical Vapour Deposition (CVD)

In this family of techniques, gaseous species react on a solid surface to form a uniform film that conforms to the surface. They find application in making masks, membranes, cantilevers, catalyst layers or sacrificial layers (Stoffel, et al, 1996, Vossen and Kern, 1991). Commonly deposited films include silicon, polysilicon, silicon nitride, silicon dioxide, phosphosilicate glass (PSG), diamond and diamond-like films. There are many CVD processes, all able to deposit a variety of film structures including amorphous, polycrystalline, epitaxial and uniaxially oriented polycrystalline layers, though to varying degrees of quality. They include:
i) Atmospheric Pressure CVD (APCVD) - This process is most often used to produce epitaxial films. It is mass transfer controlled. The reactor walls have to be cooled to prevent impurity problems resulting from deposition on the walls.

ii) Low Pressure CVD (LPCVD) - The most important process, it allows large numbers of wafers to be coated simultaneously with uniform films. Due to the low pressures involved, growth rate is limited by the rate of surface reactions, which are temperature-sensitive. High temperatures necessitate frequent cleaning of the reactor walls to avoid contamination.

iii) Very Low Pressure CVD (VLPCVD) - These processes are used to produce epitaxial films at relatively low temperatures.

iv) Metallorganic CVD (MOCVD) - Hydrides or organo-metallics are used in these processes, which are the most important in the production of epitaxial layers. This is due to the fact that the thickness of the deposited film can be controlled to within one atomic layer.

v) Plasma-Enhanced CVD (PECVD) - Energy is transferred to reacting gases using a plasma, subjecting the substrate to lower temperatures than in APCVD and LPCVD. Dry etching equipment can be used for this process as well. The quality of deposited films is lower than that of the higher temperature LPCVD process, but as more variables are available for manipulation, the film properties desired for certain applications can be more readily made.

vi) Spray pyrolysis - Here, a reagent is dissolved in a carrier liquid is sprayed on to the hot surface where it either decomposes or reacts with oxygen to leave a solid residue. The resulting grain sizes are small (< 0.1 μm) but the process is difficult to control and relatively thick films are produced.
2.2.3 *LIGA*

*LIGA* is a German acronym for lithography, electrodeposition and moulding. In this method, X-rays are used to perform photolithography on thick resist. After development, the gaps between the remaining resist are filled by electroplating. The resist is then removed to leave a metal mould insert for injection or reaction moulding (Thornell and Johansson, 1998, Madou, 1997). The use of highly coherent X-rays results in submicron resolution and large aspect ratios (~1000).

The substrate has to be conductive or coated in a conducting layer for electroplating. It must also be sufficiently adhesive to the resist. Steel, titanium, nickel and copper have been used. Poly(methylmethacrylate) (PMMA) was the traditional resist of choice due to its excellent contrast and stability. However, due to its low sensitivity, a new negative resist based on a novolak resin was developed. A large range of metals, alloys and dispersion composites have been used for electroplating, such as nickel, gold, copper, nickel-cobalt, and nickel-diamond nanoparticles (Ehrfeld, et al, 1999c).

Either injection or reaction moulding can then be performed. Rubber-type polymers with small adhesive power can assume such structures easily but have low shape stability. On the other hand, shape-preserving polymers require a mould with extremely smooth inner surfaces to prevent form-locking. Usually, internal mould release agents are required. Suitable polymers include PMMA, polyoxymethylene (POM), polyvinylidene fluoride (PVDF), PEEK and PC. Other materials in use include cement, zirconium oxide and aluminium oxide. Due to the high aspect ratios involved, difficulties such as high packing density and reproduction fidelity during exposure and moulding have arisen.
While allowing the fabrication of high aspect ratio structures, the X-rays required are produced using prohibitively expensive synchrotrons. This inaccessibility has resulted in the development of LIGA-like processes using UV-photolithography and thick layers of resist (Thornell and Johansson, 1998). While the resolution and aspect ratios are reduced, these microstructures can be fabricated using standard equipment. The widely used SU-8 epoxy based resist can reach a thickness of 1200 μm (Lorenz, et al, 1997, Loechel, 2000).

2.2.4 Laser Machining

Laser machining can be used for both additive and subtractive machining. Used in short pulses, it vaporises the material. At longer pulses or continuous beam, it melts, melding discrete surfaces (Madou, 1997). Even hard materials such as diamond and tungsten can be cut (Bremus, et al, 1999). Aspect ratios (for holes) of up to 1:50 can be achieved and cutting can be performed even at difficult angles. Lasers are, in fact, the most cost-effective tool for drilling holes 0.01-1.5 mm in diameter.

Lasers can also be used to enhance other microfabrication methods such as wet and dry etching. Laser-assisted chemical vapour deposition (LCVD) is used to build 3D-structures layer by layer, scanning the surface with a laser beam in the presence of reactive gases. Surfaces can be built at various heights by changing the focal depth of the beam. Both single-element and compound material objects can be made. Even more importantly, selected materials can be added at specific sites. Typical materials used are silicon, nickel and tungsten. Laser-LIGA employs an excimer laser for the photoablation of polytriazine resists followed by injection moulding or hot embossing (Ehrfeld, et al, 1999c). Laser ablation can also be used to pattern thin metal films for

The most common lasers are carbon dioxide lasers and neodymium yttrium aluminium garnet lasers (Nd:YAG). CO\textsubscript{2} lasers produce beams in the infra-red region (10.6 μm) while Nd:YAG beams are in the near infra-red region (1.06 μm). The more powerful excimer lasers use rare gas halides and cover the ultraviolet range (157-353 nm). Nd:YAG and excimer lasers can be used to drill holes 30-50 μm in diameter. The smallest feature machinable by excimer lasers is about 0.8 μm in thin metal foils.

The main advantage of laser machining is flexibility. One machine cuts, welds, deposits and melds. It also allows site-specific operation, i.e. specific materials can be deposited at specific locations. Only the site targeted by the beam will heat up due to the short pulses. As such, the surrounding area will be unaffected, leading to little heat stress.

2.2.5 Ultraprecision Machining

Conventional machining is become more promising for producing microsystems. This is due to recent advances which have led to machined parts with great accuracy (0.01 μm) and resolution (Madou, 1997). Microgrooves with width 100 μm and depth 70 μm in 100 μm thick aluminium foil have been made (Schubert, et al, 2001). Milling has produced trenches more than 60 μm deep with wall thickness of 8 μm in
PMMA (Friedrich, et al, 1996). Even die forging can be done, though only when applied to superplastic materials (Thornell and Johansson, 1998).

2.2.6 Electrodischarge Machining (EDM)

This method uses a controlled electric discharge between an electrode and a conductive substrate to erode the substrate. The electrode and substrate are immersed in a dielectric medium, with a gap (~25 μm) between them. Upon applying a voltage (~80 V), intense sparking (up to 500,000 s⁻¹) occurs across the gap generating a localised temperature of 12,000 °C to vaporise the substrate (Madou, 1997; Richter, et al, 1997, Dario, et al, 1995). Metal removal rates range from 0.001 to 0.1 cm³/hr depending on conductivity and melting temperature. Increasing spark frequency reduces surface roughness and tolerances of up to 5 μm can be achieved. Shaped-electrodes fabricated using LIGA allow more complicated geometries to be produced (Ehrfeld, et al, 1999c). EDM has also been used in conjunction with photolithography to produce structures without the use of the conventional glass mask (Reynaerts, et al, 2000).

2.2.7 Soft Lithography

This range of techniques typically uses elastomeric masks, stamps or moulds. Because elastomers can be deformed, patterns can even be transferred onto non-planar surfaces. Liquid prepolymer is cast against the master (made through normal silicon fabrication) and cured. Copies can then be made from the mould by contact printing, replica moulding or embossing. The elastomer used must be capable of achieving conformal contact with the surface. It must have low interfacial free energy and be durable, chemically inert, homogeneous and isotropic. Much work has been done
with poly(dimethylsiloxane) (PDMS). Other elastomers which have been used include polyurethanes, polyimides and crosslinked Novolac resin (Xia and Whitesides 1998, Duffy et al, 1998, Jackman et al, 1998). Oxidising the surface of PDMS with plasma converts -OSi(CH₃)₂O- groups to OₙSi(OH)₄₋ₙ. Bringing together two such surfaces creates a covalent siloxane bond and results in irreversible bonding. Other surfaces which can be bonded in this way include glass, silicon, silicon oxide, silicon nitride, quartz, polyethylene, polystyrene and glassy carbon (Duffy et al, 1998). Alternatively, harder plastics such as polymethylmethacrylate (PMMA) have been used with imprinting methods. A piece of PMMA is clamped to the template (one example used a length of wire) and heated to its softening temperature. Upon cooling and separation, the desired pattern is left behind (Martynova, et al, 1997). Since developed SU-8 is an inert substance, it can be a suitable reactor material. Jackman, et al (2000) formed multi-layered structures with different patterns on each layer using multiple spin-coatings of SU-8 and exposures.

2.2.8 Glass Microfabrication

Glass is a material that is encountered in fine chemical and pharmaceutical industries and is attractive because of its inertneses. It can be etched using conventional photolithography and wet etching with dilute buffered hydrogen fluoride (BHF: HF/NH₄F) (Jacobson, 1994). Typically, a Cr/Au layer is deposited and then etched to form a mask for patterning the glass. However, Stjernström and Roeraade (1998) found that adding concentrated HCl to a buffered HF solution prolonged the integrity of photoresist long enough for it to be used as a mask to etch 70 μm deep structures. Glass is an isotropic material and so the etch rate is equal in all directions as defined by the mask, which leads to rounded channel structures (Thornell and Johansson,
Photoetchable glass, e.g. Foturan, is also available. The glass is exposed to UV-light through a mask, forming silver in exposed areas. Heat treatment (500-600 °C) results in crystallisation around the silver. Wet etching is then performed using a 10% HF solution. The crystalline regions etch 20 times faster than the unexposed regions. The smallest structure which can be made using Foturan is about 25 μm in size (Freitag, et al, 2000).

2.2.9 Microstereolithography

This is an additive method for manufacture of plastic components, based on solidification of a liquid under illumination. The basic principle involves the focusing of a beam of UV-light onto the surface of a light sensitive liquid, which polymerises upon exposure. A three-dimensional model of the object is first drawn and then sliced into horizontal two-dimensional pieces (Madou, 1997, Mougin, et al, 1998, Knitter, et al, 2000). These layers are then developed in the liquid using either the photomask method or the scanning method. The photomask method involves transferring each layer on to a mask and then exposing the liquid to each mask in sequence. The more commonly used scanning method uses a computer-controlled laser, which scans each layer according to a CAD programme. The size of the minimum solidification unit (voxel) is 5 x 5 x 3 μm (Thornell and Johansson, 1998; Dario, et al, 1995). The main advantage of this method is that it allows quick production of complex three-dimensional structures, and hence is deemed a rapid prototyping method.

2.2.10 Mass fabrication techniques

While many of the techniques mentioned previously can be used for mass fabrication, they can be relatively slow, especially when structures several hundred microns in
depth are required. However, the precision that is achievable with these methods make them suitable for making masters for use in more conventional mass-replication techniques. For example, as mentioned previously injection moulding can be used in the final stage of the LIGA process. Apart from LIGA, it can also employ masters made through ultraprecision machining, EDM and laser machining, amongst others (Ehrfeld, et al, 2000, Niggemann, et al, 1999, Hessel, et al, 1997). While most moulding is done using plastics, processes using ceramics have also been developed (Knitter, et al, 1999, 2000). Another method is embossing, which has been performed on ceramics, aluminium and stainless steel (Ehrfeld, et al, 2000, Knitter, et al, 1998, Hessel, et al, 1997). By keeping the embossing tool at high temperature, hot embossing of polymers can be realised (Becker, et al, 2000)

2.2.11 Bonding Techniques

Most of the fabrication methods can structure the material but cannot form sealed structures that are imperative if the chemicals are to be contained. Use of gaskets and a suitable housing which is kept tightly clamped is a common sealing method, offering the advantage of easy assembly and disassembly. However, there are also many techniques for irreversible bonding. The most popular one for silicon structures is anodic bonding. Two wafers, one of which must be at least semiconducting, are heated to 180-500 °C and a DC voltage 0.2-1 kV applied across them. At such high temperatures, the positive ions (e.g. sodium) in glass become mobile. These will then drift towards the cathode. The negative oxygen ions, however, will remain immobile and will form a negative layer adjacent to the metal substrate. This results in a strong electrostatic force bringing the two wafers very close together and allowing covalent bonds to form, thus making a permanent seal.
While the process is, it does have some shortcomings. Wafers have to be cleaned and polished before the procedure. And, most importantly, the temperatures used are quite high, making it unsuitable for many materials as mismatching thermal expansion coefficients will result in mechanical stress. The process is, therefore, restricted to certain combinations of materials. Silicon and Corning 7740 Pyrex glass are most frequently used (Madou, 1997, Schomburg, et al, 1995). Two silicon layers can be bonded by sputtering a layer of glass 3 μm thick between them. GaAs can also be bonded to Corning 0211 (Madou, 1997). However, poor bonding due to poorly adhering oxides necessitates pre-baking the glass first.

Alternatively, silicon fusion bonding allows the bonding of silicon wafers without using intermediate layers. Immersing the wafers in a hydrating solution, e.g. H₂O₂-H₂SO₄, forms hydrophilic layers. When the wafers are contacted and heated to 1000 °C, a strong bond (20 MPa) forms (bond strength can be increased by applying pressure during the bonding process). In comparison, typical values for anodic bonding are 5-10 MPa (Madou, 1997). This process can be used for any smooth and hydratable surface such as silicon, silicon oxide, silicon nitride, GaAs, glass and quartz. Options to reduce the temperature include activating the surface by oxygen plasma treatment or using an intermediate layer, e.g. sodium silicate (Puers and Cozma, 1997). Bonding large areas of glass can occasionally be difficult, especially thin pieces which are manufactured by a drawing process. In such cases, reduction of the surface area by introducing a matrix of posts has been shown to improve bonding (Stjernström, et al, 1998).
Recent attempts have also been made to bond silicon, glass and polymers using laser joining technology (Bremus, 1999). For metallic sheets, diffusion bonding is the most common method of sealing. Typically, several structured layers are stacked and then heated to 500-1000 °C under pressure to allow diffusion of material at the points of contact. Optimisation for each system is required to obtain good sealing without compromising structural stability (Schubert et al, 2001). For example, a stack of structured stainless steel shims were heated to 920 °C and clamped down with 4000 psi pressure for 4 h to obtain complete bonding (Matson, et al, 1999, Martin et al, 1999). This lamination method has also been extended to green ceramic tape (Martin, et al, 2000).

Adhesive bonding involves the use of epoxy resins. It works on a variety of materials: metals, glasses, plastics. Low temperatures (< 150 °C) are involved (Schomburg, et al, 1995, Madou, 1997). After curing the adhesive remains elastic, reducing mechanical strain caused by thermal effects. The properties of the adhesive (elasticity, thermal conductivity, electrical conductivity, transparency and chemical resistance) can be varied as well. Problems of adhesive bonding include layer non-uniformity, low operating temperature and incompatibility with solvents. Non-uniformity can be avoided in some cases by using sheet adhesives in place of epoxy resins. These adhesives can be machined using laser micromachining. By laminating the microstructure with adhesive layers, a sealed microfluidic system can be realised (Macounová, et al, 2000).
2.3 Catalyst Incorporation Techniques

While other aspects of microreactor design can be very different from conventional reactor design, some of the established methods of incorporating catalysts have proven useful. Fixed bed microreactors have been made by flowing particles into the reaction chamber (Schmidt, et al, 1997, Losey, et al, 1999). Reactants and catalyst particles can enter either through the same or different inlets, while pillars with spacing smaller than the diameter of the particles are required at the outlet of the reaction channel to act as a trap for the particles. Pressure drop can be an issue due to the small particle size. Another relatively easy, albeit expensive, catalyst incorporation method is to machine plates from the catalytic metal itself (Mayer, et al, 1999). The microstructured layers are then sealed by diffusion bonding.

When high catalytic surface area is required, various techniques can be employed to create porous surfaces. A method (for conducting materials) is anodisation, which is performed by immersing the substrate into a suitable acidic solution and passing an electric current through it. Varying the current density and time gives rise to a range of surface morphologies and porous layer thicknesses. Surface area increase factors of 100 are readily achievable. Normal impregnation or immobilisation methods can then be used for catalyst deposition (Wießmeier and Hönicke, 1996b, Drott, et al 1997, Fichtner, et al, 1999, Hönicke, 1999, Wunsch, et al, 2000). Kursawe, et al (2000) used sputtering after anodisation to deposit the catalyst. Sol-gels based on alumina, silica, titanium have been used to make porous catalyst supports as well. The use of stabilising chelating agents to improve adhesion has been recommended. Thermal annealing at different temperatures gives rise to different surface areas, with crack-free highly porous layers which are mechanically stable. Following that, the surface is
ready to be impregnated with the catalyst (Fichtner, et al, 1999, Kursawe, et al, 2000). Zeolites (silicalite, ZSM-5, TS-1) with controlled crystal orientation have been grown by hydrothermal synthesis on silicon and stainless steel microstructures producing uniform thickness layers (Wan, et al, 2001, Rebrov, et al 2001). By prior seeding of the microchannel area, selective zeolite growth can take place only within the confines of the microchannel.

Anodisation and surface coating methods mentioned above result in regular, porous catalyst layers with controlled thicknesses. Anodised structures are formed from the substrate itself, thus adhesion is usually not an issue, while sol-gel structures can have their adhesion modified by the addition of various additives. Porous silica can also be formed within the whole micro channel by passing potassium silicate solution mixed with formamide. The catalyst can then be immobilised by impregnation (Christensen, et al, 1998, Greenway and McCreedy, 1999).

Alternatively, aerosols of metal salt can be applied to the microreactor surface and evaporated at the point of contact to give rise to high surface area catalysts. This method was developed after it was determined that drying an aqueous or organic solution to deposit the catalyst precursor results in the catalyst coating the corners of the channel due to surface tension effects. Platinum, silver and rhodium were deposited in this manner (Franz, et al, 1999b). Preformed catalyst particles can be immobilised on the reactor walls by first dispersing them in suitable liquids. Pfeifer, et al (1999) applied nanoparticles of palladium or copper catalyst mixed with ZnO promoter dispersed into a polymer (hydroxyethylcellulose) to a microreactor. After drying, and sintering a BET surface area of up to 9.3 m²/g was achieved, with a
catalytic layer thickness of 20 μm. Alternatively, catalytic particles can also be incorporated on to a layer of PDMS coated microchannel and then baked to give an immobilised high surface area catalyst (Wilson and McCreedy, 2000).

Chemical vapour deposition (CVD) can also be used to deposit catalysts or carriers. Activated carbon catalyst has been deposited by polymer CVD followed by carbonisation, or using a sooting flame (Franz, et al, 1999b). Atmospheric pressure CVD was used to deposit a porous ceramic coating (alumina) with a surface enhancement factor of 100 and thickness of 100 μm (Fichtner, 1999).

If high catalytic surface area is not required, less conventional methods from the microfabrication avenue can be used, especially sputtering processes. Either the shadow mask or lift-off technique is used to define the target area. In the former, a sheet (usually metallic) containing the deposition pattern is placed against the substrate. In the latter, conventional photolithography is used to pattern a layer of photoresist on the substrate. Once the mask is in place, the catalyst material is sputtered on to the substrate. In the lift-off process, the photoresist is then removed, bringing with it the excess deposited catalyst (Srinivasan, et al, 1997, Madou, 1997). It should be noted that these thin films have been reported to degrade when subjected to high temperatures (Firebaugh, et al, 1998).

If the substrate is electrically conducting, electroplating can be used to deposit the catalyst from suitable catalyst precursor containing solutions (Franz, 1999b). Another method that has been used recently is micro-contact printing. A master is replicated using a PDMS stamp. The metallic catalyst is then deposited on to the stamp.
Meanwhile, the microreactor is covered with a suitable ligand using a self-assembly process to give rise to an ordered structure. The stamp is then contacted with the reactor and treated to transfer the catalyst. Submicron particles can also be deposited with a stamping process (Xia and Whitesides, 1998, Braun, et al, 1997).

2.4 Microdevices

2.4.1 Heat Transfer Devices

Microengineered reactors offer significant opportunities for high heat transfer rates when coupled with microengineered heat exchangers or heating elements. One of the first realisations of an enhanced microscale heat transfer system was an integrated microchannel combustor/evaporator which could be used as a portable or residential heating device as well as to provide heat for endothermic reactions (Drost, et al, 1997). It produced 30 W of thermal energy per square centimetre of external combustor area, with more than 70 % combustion efficiency operating on methane. The microchannels for the water and the combustion gases were 300 μm wide and 500 μm deep and resulted in heat transfer coefficients an order of magnitude larger for single phase flow and two orders of magnitude for two-phase flow than predicted for macroscale conditions. Using smaller microchannels (hydraulic diameters 70-160 μm) in a cross-flow arrangement, Schubert et al (2001) measured heat transfer coefficients for heat exchange between cold and hot water of up to 25 kW/m²K. Heat transfer coefficients were doubled by continuously splitting and recombining the fluid flow, through channel segmentation. The only drawback was the higher pressure drop. Similarly Hardt et al, (2000) using a checkerboard array of 100×100 μm microfins in a
500 μm deep channel, observed a theoretical overall heat transfer enhancement of more than an order of magnitude as compared to unstructured channels.

Another approach to provide heat in microengineered reactors is via electrical heating elements. Through a combination of microchannel structures and cartridge resistor heaters, Brandner, et al (1999) achieved heat transfer coefficients of 20 kW/m²K, while avoiding overheating. These devices were used to control processing temperatures up to several hundred degrees Kelvin. Srinivasan, et al (1997) deposited thin film Pt serpentine heaters on the external wall of microreactors.

Heat transfer efficiency in microchannels can be affected by the wall conductivity, due to the presence of axial conduction. Low wall heat conductivity can result in better efficiency as axial heat conduction along the walls of the microchannels decreases (Bier et al, 1993). However, as the heat conductivity of the wall material reduces, radial heat transfer is also hindered. As a result, an optimal value exists for maximum heat exchanger efficiency based on the heat conductivity of the wall material (Stief, et al, 2000).

2.4.2 Mixing Devices

Before reaction between two components can take place, the corresponding molecules must be brought into intimate contact by mixing. Because laminar flow is usually encountered within microdevices, mixing between fluids is accomplished mainly through diffusion and not through the much faster convective processes present in turbulent flow. The diffusive mixing efficiency is usually described by the Fourier number, Fo, defined as follows:
\[ Fo = \frac{Dt}{l^2} \]

where \( D \) = diffusion coefficient
\( t \) = contact time
\( l \) = characteristic length over which diffusion takes place

Good mixing occurs when \( Fo \) is between 0.1 and 1. From the above equation it is obvious that mixing time increases with the characteristic dimension. Fast mixing times can therefore be achieved by minimising the diffusion distance. Löwe, et al (2000) presented a comprehensive review on the different types of micromixers and identified various mixing approaches, which will be discussed as follows:

a) contacting of two substreams

Here, two streams merge and sufficient length is allowed afterwards for the mixing to be completed. Gobby, et al (2001) studied both T- and Y- geometries using CFD simulations and found that for gas-phase mixing, different Y-junction angles had negligible effect on the length required for complete mixing (mixing length) and the pressure drop. Mixing lengths less than 3 mm were obtained for fluid velocities 0.3 m/s in 500 \( \mu \)m wide channels.

b) decrease of the diffusion path perpendicular to flow direction

After two fluids are brought together, decreasing the thickness of the resulting stream decreases mixing time according to the Fourier number definition mentioned above. Veenstra, et al (1999) achieved this by combining two fluids in a 300 \( \mu \)m wide channel which was then reduced to 100 \( \mu \)m. Complete mixing was achieved in the outlet at total flowrate 10 \( \mu \)L/min while for flowrates above 50 \( \mu \)L/min there was no mixing. A similar idea was also investigated by Gobby, et al (2001) where a "throttle" mixer was found to reduce the length required for

c) injection of small substreams of one component in a main stream of another component

In this approach, a liquid stream is guided through the mixing chamber while a second liquid stream is split into many small jets and injected perpendicularly through small holes in the mixing chamber. Koch, et al (1998) achieved complete mixing within 1 s for flowrates of about 1 μL/min using 42 100x100 μm holes, while Elwenspoek, et al (1994) split the flow into a larger number of smaller holes (400 15x15 μm holes) to achieve similar mixing times for larger flowrates (240 μL/min).

d) injection of many substreams of the two components

This approach has widely been used in microsystems. In these mixers, the two streams are first split into substreams with reduced width and then brought into contact. In the mixer used by Bessoth, et al (1999) the combined substreams were brought sequentially into contact (from 16 to 8 to 4 to 2, and finally to 1, see Figure 2.2), until all partial flows were united in one broad outlet channel. The presence of walls and bends affected the velocity profile in each substream and thus the mixing time. In other multilamination-based micromixers all the combined substreams simply join in a large channel as shown in Figure 2.3 (Ehrfeld, et al, 1999, Zech, et al., 2000, Schubert, et al., 2001). Depending on
mixin configuration, flowrates and fluids mixed, mixing times and lengths of 30 μs and 150 μm, respectively, have been reported.

Figure 2.2 Example of a micromixer utilising the multilamination concept (Bessoth, et al, 1999)

Figure 2.3: Example of a interdigital micromixer utilising the multilamination concept (IMM, 1999)

e) manifold splitting and recombination of a stream consisting of two fluid lamellae

By careful splitting and recombining streams using a 3-dimensional flow pattern, the surface area available for mass transfer can be increased, while diffusion distances decrease. Ehrfeld, et al (1999b) developed a “caterpillar” mixer with a ramp-like channel architecture in which the fluid lamellae width is reduced to 2 μm after 6-8 passages. Other ways to accomplish splitting and recombination

36
include the use of fork-like elements (Schwesinger, et al, 1996) or separation plates (Branebjerg, et al, 1996).

In the above mixers, the flowrates of the phases to be combined affect mixing efficiency. In addition, producing thin fluid layers usually results in high pressure drops. Comparing the different types of mixers is not easy since different fluids, channel geometries and flowrates have been used. A number of techniques have been implemented for characterising mixing efficiency in micromixers such as colour changing reactions (Koch, et al, 1998, 1999), fluorescence quenching (Bessoth, et al 1999) and a system of fast and slow competing reactions (Erhfeld, et al 1999).

It is worth noting that it is possible to enhance diffusive mixing by various methods. Bökenkamp, et al (1998) obtained submillisecond mixing times in T-mixers by increasing flowrates so that turbulent flow was achieved. Woias, et al (1999) proposed an “active” micromixer, where the pulsation of a membrane enhances mass transfer. Compared to the static mixers, which use fluid multilamination, mixing time would not depend on the flowrates.

The multilamination approach has been used for mixing of two different phases (gas-liquid or liquid-liquid). Hessel, et al (1998) studied the bubble sizes formed in micromixers during gas-aqueous solution mixing (bubble coalescence was prevented by using a surfactant). The mixer produced mean bubble sizes in the range 120-800 μm. Size was affected by liquid flowrate, viscosity and mixing channel width. The same mixer was also used for the mixing of two immiscible liquids (Schiewe, et al, 2000). Compared to a standard laboratory shaker, the micromixer gave a smaller
average drop size (1 μm for an oil-in-water dispersion) and narrower size distribution.
It was also found that such a mixer required less energy compared to a stirred tank to
produce the same average drop size and distribution (Bayer, et al, 2000).

2.4.3 Chemical Analysis Devices
Analysis of product streams from microengineered reactors can be carried out by
conventional analytical equipment. However, integrating analysis with reaction can
provide advantages such as portability, continuous on-line measurement and faster
process control. It is worth noting that the first reported attempt at creating a
microfluidic system was a micro-GC (Terry et al, 1979). Recently, interest in
microreactors has re-kindled the desire to produce micro-GCs. Besides having a
shorter column length, the micro-GC developed at the Institut für Mikrotechnik Mainz
(IMM) features improved heating and cooling systems over conventional systems. A
planar module measuring 80 x 80 x 75 mm³ comprising a capillary column support
sandwiched between 4 resistive heaters (50 W each) and an axial-flow cooling fan
was constructed. The heating rate was 2 °C/s, while the cooling rate was 0.5 °C/s.
The total analysis time for ethylene oxidation products was 8 min, as compared to 25-
35 min in conventional analysis (Schiewe, et al, 1999). To increase cooling rate, a
cylindrical system was designed where the capillary column was coiled helically
around axial cooling microchannels and a heating cartridge. A heating rate of 4.7 °C/s
and a cooling rate of 5 °C/s (using air flowrate of 5.8 l/s) were obtained (Richter, et al,
2000). Another improvement to micro-GC technology was reported by Lehman, et al
(2000) who developed a new method for coating the analysis column with the
stationary phase. The column was etched into a silicon wafer (2 m length on a 20 x 25
mm wafer) and covered with a 500 nm thick silicon organic stationary phase
deposited using PECVD. The corresponding areas of a glass lid were also covered in this way before being bonded by anodic bonding. An injector and a miniaturised TCD detector were also incorporated. Heating was supplied by a Peltier element. Excellent separation of methane and ethane was achieved.

In-situ analysis can be often performed using IR-spectroscopy. Guber, et al (1999) cut a reaction channel straight through a metal substrate and covered it with IR-transparent discs (AgCl). The assemblage was then placed in the object carrier of an IR-microscope and coupled to an FTIR spectrometer. Micrometer-precise movement of the object carrier allowed nearly any number of measuring points. It is also possible to do away with transparent discs as silicon is IR transparent. Microreactors made entirely from different types of silicon were tested for IR-transmittance. Undoped silicon was found to be the best (48.4 %), followed by boron-doped wafers (41.7 %). Phosphorous doped samples had almost no transmittance. Use of anti-reflective coating was found to increase transmittance by 30 % (Floyd, et al, 2000).

An interesting development was the application of photoacoustic detection to a microreactor. When a gas is illuminated, if the optical wavelength couples to an energy transition in the gas, the light will be absorbed and the gas will exhibit periodic expansion. Firebaugh, et al (2000) placed an optical fibre beneath the reaction channel etched through silicon and capped by thin silicon nitride layers on the top and bottom. A displacement sensor was placed on top of the reactor to monitor movement of the membrane due to gas expansion. This microsensor produced a larger signal than a larger analogue.
2.5 Integration of Microdevices

In order for a microengineered reactor to operate effectively, it may have to be connected to other microengineered equipment. Architectures for integration of various units (e.g. mixers, separators, heat exchangers, valves, pumps, sensors and actuators) have to be considered in order to minimise dead volumes. Additionally, different units may require different operating temperatures. The end result of such integration schemes would be microchemical reaction units/modules or compact chemical plants.

2.5.1 Vertical integration

In vertical integration architecture, a microsystem may consist of several layers/sheets, each one performing one or more functions as demonstrated by Wegeng, et al (1998) for a fuel processor unit. Layers were stacked and bonded together to assemble a compact system. This integration architecture is compact but once layers are put together they cannot be altered.

2.5.2 Horizontal integration

Horizontal integration has been demonstrated by Elwenspoek, et al (1994) using a fluid injection analysis system, in which two micro dosing systems, a micro mixer/reactor and a detector were fabricated on one wafer. This horizontal integration is less flexible but since there is no need for assembly it might be a cheap method for large scale production of simple devices.

Another version of horizontal integration is based on a fluid distribution unit or circuit board, a concept borrowed from integrated circuit industry, on which various devices
such as pumps, mixers, reactors and separators can be mounted. The circuit board contains channels which bring fluid(s) from one device to the next without the need for conventional tubing connections. Schabmueller, et al (1999) reported the design and fabrication of a microfluidic circuitboard using a structured Pyrex wafer anodically bonded to a silicon wafer. Various microfluidic devices were then mounted on the circuit board via anodic bonding to form a microfluidic system. Two microfluidic analytical devices reported by Lin, et al (1999, 1999b) were based on polymer microfluidic motherboards which were fabricated using laser machining. The platforms allowed integration of all the components using plug-and-play modules. This takes more space but provides more flexibility since:

a) a different system can be realised by changing the mask layout for channels
b) components from different manufacturers can be incorporated into the system (provided they have compatible inlet and outlet designs)
c) part replacement and repair is easier

The above integration architectures relate mainly to complete microchemical plant designs. However, reactor level integration of components is sufficient in many cases. This includes integration of the reactor with heat exchangers, catalyst, mixers, sensors and separation units.

2.5.3 Integration of heating and catalytic reaction

Microstructured catalyst plates and heat exchanger plates can be assembled by stacking plates on top of each other with a 90° rotation between each plate, resulting in two sets of perpendicular channels. This was demonstrated by Wörz, et al (2001a) for the oxidation of alcohols to aldehydes using a 1 cm³ microreactor made of silver foils
with 200 microchannels for reactants and the same number for the coolant. The heat transfer coefficient was as high as 20 kW/m²K. A similar microreactor for the oxidation of hydrogen was assembled from stainless steel plates (Hagendorf et al, 1998). The reaction channels were coated with Al₂O₃ and impregnated with Pt catalyst. In a wafer-based microreactor for the synthesis of methyl isocyanate (Lerou, 1996), heat transfer was accomplished between adjacent wafers, one carrying the reactant.

Heating elements can also be combined with catalysts on a chip. Kusakabe, et al (2001) reported a microreactor made from a silicon wafer that was etched on both sides. A Pt heating wire was installed in the channel on the backside of the reactor. The channels were sealed with glass plates using anodic bonding. Similar integration was reported by Wilson and McCreedy (2000) with a heating wire immobilised in the top plate of a glass microreactor. Alépée, et al (2000) reported the design of a microreactor for the hydrogenation of gaseous methanol to formaldehyde that combined heating and cooling on a single chip. A thin film Pt heating element deposited on the silicon nitride layer that capped the microchannel was used to pre-heat reactants while the product gas was quenched using a plate heat exchanger.

2.5.4 Integration of mixing and catalytic reaction

This was demonstrated by a microreactor for the synthesis of ethylene oxide (Richter, et al, 1998). The microreactor was made by integrating two stacks of mixing and catalytic plates in a metal housing. Two reactants were introduced into alternating layers of the mixer unit from opposite sides, and met at a diffusion zone. The reaction unit, which was made up of catalyst plates with channels 500 μm wide and 50 μm
deep, was located immediately after the diffusion zone. Calculations showed that even without a heat exchanger, a hot spot of less than 1 K could be achieved.

2.5.5 Integration of mixing, heating, catalytic reaction and sensing

An example of this is a T-microreactor for the oxidation of ammonia (Srinivasan, et al, 1997). The T-shaped channel etched in a Si wafer was capped by a 1-μm-thick silicon nitride wall and sealed from the bottom with an aluminium plate having three holes for gas inlet and outlet. Heaters, flow sensors and temperature sensors were made by depositing Pt on the top face of silicon nitride. Pt catalyst was deposited inside the channel. This provided the microreactor with a hot zone that was localised in the reaction zone while the channel walls and the bulk of the chip were at room temperature. Heat transport properties were improved by replacing the silicon nitride supporting the catalyst with more thermally conductive silicon (Quiram, et al, 2000). The small thermal mass of the reactor walls led to very fast open-loop thermal response times (< 20 ms), allowing excellent feedback temperature control. These heaters could be used up to 700 °C, beyond which degradation was observed (Firebaugh, et al, 1998).

The integration of mixing, heat exchanger and temperature sensor was demonstrated by a liquid phase microreactor (Floyd, et al, 2000). The reactor was fabricated on a silicon wafer using standard photolithography techniques and DRIE. Channels for mixing, reacting and heat exchange were 50-400 μm wide and ~500 μm deep and capped with a Pyrex wafer using anodic bonding. Temperature sensors were fabricated on the thin silicon film on the backside of the silicon wafer and beneath the reaction channel. The mixing section consisted of two sets of inlets which distributed
fluids between five inlet ports per reactant. After lamination, the fluids were hydrodynamically focused to promote fast mixing. Hot or cold fluid flowing in channels next to the reaction channel were used to control the reaction temperature.

2.5.6 Integration of heating, sensing and separation

The integration of separation with chemical reaction using a permeable membrane allows a reaction to be carried out beyond equilibrium conversions as the products and reactants can be separated continuously. Compared with conventional scales, microstructured membrane reactors possess particular advantages because of their small size, fast thermal response times and high efficiency. A palladium membrane microreactor reported by Franz, et al (1999) consisted of two channels separated by a thin palladium membrane. The 0.2 μm thick membrane was supported by two perforated silicon oxide and silicon nitride layers and allowed hydrogen fluxes of the order of 600 sccm/m². Thin Pd films were deposited on the silicon nitride side to form integrated temperature sensing and heater elements.

A micromembrane reactor developed by Cui, et al (2000) for the catalytic dehydrogenation of cyclohexane to benzene also integrated separation and catalysis. The microreactor consisted of three parts: reaction chamber, separation membrane and reactor top. The silicon reaction chamber had 80 microchannels (50 μm wide, 400 μm deep and 8 mm long) with 20 nm Pt sputtered as catalyst. Another wafer was double-side etched and coated with Pd on the microchannel side to form an 80-fold rectangular corrugated Pd foil structure (4 μm thick). The folded microstructure enlarged the separation area, thereby improving separation efficiency.
2.6 Applications of Microengineered Reactors

2.6.1 Chemical Analysis

Miniaturisation of analytical systems can improve reliability, decrease analysis time, reduce sample size and reagent consumption (Leistiko and Jensen, 1998). The goal is to incorporate sample introduction, sample pre-treatment, mixing, chemical reactions, product separation, detection and product isolation into a complete micro total analysis system (μ-TAS). The pharmaceutical industry is the main driving force for developing this technology. This is because it will greatly improve and speed up high-throughput screening of combinatorial libraries, clinical diagnostics, DNA analysis and drug discovery (Freemantle, 1999). Affymetrix has developed a credit-card-sized chip which is capable of carrying out seven different processes needed to extract DNA from blood, amplify, prepare and dilute it before sending it to a DNA array. Fluids are moved around the chip with pressure-backed air bubbles, allowing accurate positioning of fluid slugs in different reaction chambers. At Orchid Biocomputer, work is being carried out to synthesise analogues of drug compounds in parallel. Electric fields and pressure are used to move reagents through channels, valves and into various reaction chambers. The chips measure 2.5 cm\(^2\) and contain 144 reactor systems to synthesise compounds simultaneously (Service, 1998).

DNA chip arrays are also being produced. In one method, a silicon surface was coated with linker molecules to provide binding points for the base molecules of DNA. The linkers are first capped by a light-sensitive compound, then the chip is exposed to light through a mask to ‘un-cap’ certain areas. One of the four bases is then bound and capped. The process is repeated to create longer combinations of oligonucleotides. These chips can then be exposed to fluorescence-tagged unknown
gene fragments. When such fragments bind themselves to their complementary fragments on the chip, their sequence can then be worked out. Another technique employs a controlled electric field to manoeuvre DNA fragments around the chip to speed up the process. Electrical signals instead of fluorescence can be used to detect bound pairs (Service, 1998b). Kopp, et al (1998) developed a glass microreactor for performing continuous flow polymerase chain reaction (PCR). It consists of a 2.2 m long channel which passes through 3 temperature zones (95 °C, 77 °C, 60 °C) for a total of 20 cycles, thus providing an amplification factor of $2^{20}$. Multiple plugs of samples can be run through the reactor simultaneously, increasing the throughput. This reactor can be used for online amplification and monitoring of a specific gene to determine the usefulness of a drug or antibiotic.

A popular alternative to conventional pumps is the use of electro-osmotic flow (EOF), which has no moving parts and can be used to drive liquids in non-metallic structures, typically glass or a polymer. This technique allows a high level of control and results in a flat velocity profile. Because different species move at different rates, capillary electrophoresis leads to efficient separation of compounds with little band broadening (Haswell, et al, 2001). Its application was demonstrated by the rapid separation of fluorescent dyes using channels etched in glass (Cowen, 1999).

Research has also been carried out on detection systems suitable for integrating on-chip. In the so-called T-sensor, the sample, a receptor solution and a reference solution are introduced into a common channel in parallel flow. As interdiffusion occurs, sample and reagents bind and react. The larger the particles, the longer they take to diffuse. Using a suitable detector, changes in the sample-indicator and
reference-indicator interaction zones, such as colour or fluorescence, can be tracked and used to determine the concentration of the analyte. This system has been applied to measure clinical assays such as blood pH and oxygen, electrolytes, proteins, enzymes and drugs. Monitoring signal intensities along the flow direction also gives kinetic data (Weigl and Yager, 1999).

In another system, an electrochemical cell consisting of an iridium working electrode, platinum auxiliary electrode and silver electrode was fabricated as one layer of a microreaction system. The sensor integrated three electrodes, based on either thin-layer or wall-jet designs. The advantage of the second system is that sensors more specifically geared towards detecting certain substances could be plugged in when desired. Cells with different working electrodes were fabricated, e.g. glassy carbon, iridium, platinum and gold. This system was used for detecting minute quantities of lead (1 ppb) in water (Lin, et al, 1999b). In a similar plug-in fashion, a 'clip-on' detector was designed to be used with a microcapillary chemical system. The microcapillary is inserted into a groove machined perpendicular to optical waveguides. Light from an optical fibre passes via a series of 5 waveguides, through the microcapillary, and to 25 photodiodes, which detect changes in light intensity. In this way, differential measurements can be made (Leistiko, et al, 1998). The above are only selected examples of the large area of μ-TAS, which is currently experiencing significant research activity. While much of the work has been done with the biochemical industry in mind, many of the ideas can be applied to chemical engineering as well.
2.6.2 High Throughput Screening and Experimentation

The advantages of μ-TAS can be utilised in combinatorial methodologies utilising high throughput screening and experimentation systems. In these applications efficient thermal control, short response times, defined flow characteristics, large surface areas, small volumes and small amount of samples required are advantages. Orschel, et al (1999) used a mass spectrometer and synthesis robot which moved a specially-designed capillary (for delivering reactants and guiding products to the analyser) over an open slate plate with 33 2 x 2 mm wells containing the catalysts and heated by electric heating plates. Selectivity of different components of catalyst libraries for selective oxidation of propene with air was studied.

Cong, et al (1998) used a similar approach where the products were “sniffed” from the reaction chamber and analysed by mass spectrometry to evaluate a 144-member library of Rh-Pd-Pt for CO oxidation. Localised heating was provided by a CO₂ laser. The catalyst precursor solutions were prepared by automatic liquid dispensing and the resulting solutions were dispensed onto a quartz plate containing 144 wells. Liu, et al (2000) similarly prepared a 144-member library of V-Al-Nb and Cr-Al-Nb for ethane dehydrogenation. Photothermal deflection spectroscopy was used simultaneously with mass spectroscopy for screening catalyst activity. Cong, et al (1999) prepared a thin-film library containing 120 ternary combinations of Rh/Pd/Pt using radio frequency (RF) sputtering through masks onto a 75 mm diameter quartz wafer. Each catalyst on the wafer had a diameter of 1.5 mm, thickness of 100 nm and weight 2-4 mg, and was used for oxidation of CO and reduction of NO. The total deposition time of such a library was only one hour. The same research group also designed a set-up which contained a large number of diffusion-mixed microreactors where
microfabricated gas manifolds were utilised for distribution and handling of the reactant and product streams from each reactor (Bergh and Guan, 2000).

Senkan, et al (1999) used on-line mass spectroscopy, but in conjunction with array microreactors which could employ small catalyst pellets. Each reactor array consisted of 20 rectangular channels, micromachined on a flat non-porous silica ceramic slab. The channel dimensions were 0.1 x 0.1 cm and 2 cm long, with a cylindrical well to hold catalyst pellets. By stacking four arrays in an aluminium heating block, it was possible to test up to 80 different catalysts in parallel. A Pt/Pd/In library with 66 combinations was prepared for the catalytic dehydrogenation of cyclohexane to benzene and due to the rapid analysis, time-on-stream performance of all catalysts could be monitored. In a modified system the analysis was carried out by resonance enhanced multiphoton ionisation (REMPI) spectroscopy which has the advantage of measuring the concentration from all reactors simultaneously, but only of the component that produces REMPI ions for the laser wavelength employed (Senkan, 1998, Senkan and Ozturk, 1999). Preparation and screening of the entire catalyst library took 2.5 days and included checks for reproducibility. Zech, et al (1999, 2000) reported a reactor module consisting of 35 stainless steel microstructures for screening catalysts for methane oxidation. Each of these microstructures was anodised and impregnated with solutions of Pt, Zr and V precursors. Products were analysed using mass spectrometer. The results showed good reproducibility and very low influence from adjacent catalysts.

For liquid phase systems, high throughput experiments based on dynamic sequential operations were performed by de Bellefon, et al (2000). Liquid/liquid isomerisation
and gas/liquid asymmetric hydrogenation were carried out using a static micromixer before entering into stainless steel capillary reactors. Reactants and/or organometallic catalysts were injected periodically in carrier liquid phases entering the micromixer. Total screening time for 18 tests of liquid/liquid isomerisation of alcohols (performed twice for reproducibility) was less than one hour. For gas/liquid asymmetric hydrogenation of acetamidocinamic methyl ester with Rh/diphos catalysts, only 3-5 min were required for each test. Greenway, et al (2000) constructed a flow injection microreactor for high throughput continuous flow organic synthesis. The synthesis of 4-cyanobiphenyl based on a modified Suzuki coupling was carried out in micro-channels 300 µm wide and 115 µm deep etched into borosilicate glass and sealed with a borosilicate top plate using a thermal bonding technique. The movement of fluids was achieved using electro-osmotic flow assisted by a microporous silica structure within the microreactor channel on which the catalyst (1.8 % Pd on silica) was immobilised. Higher yields of the product were obtained by a flow injection mode in the microreactor, as compared with a batch reactor. Similar types of reactors were also applied in Wittig chemistry (Skelton, et al, 2000, 2001), nitration of benzene (Doku, et al, 2001) and alcohol dehydration on sulphated zirconia (McCreedy and Wilson, 2001). These reactors coupled to autosamplers and in-situ detection offer the possibility of combinatorial organic synthesis.

2.6.3 Access to New Chemistry and Operating Conditions

The unique properties of microreactors, such as safe operation due to very small reactor volume, well-specified reaction conditions, low heating inertia allowing direct control of reaction temperature, efficient heat exchange due to large surface to volume ratio can be used to exploit new operation regimes and access new chemistry.
2.6.3.1 Systems with efficient heat exchange

Microreactors have been used for safely carrying out high temperature oxidation processes in the explosive regime. A microreactor with cross-flow heat exchange and Pt/Al₂O₃ catalyst used to perform catalytic oxidation of hydrogen is one such example (Hagendorf, et al, 1998, Janicke, et al, 2000). Explosive reaction mixtures with hydrogen and oxygen concentrations up to 50 % by volume were operated safely and complete conversion of hydrogen to water was obtained without explosion. This was attributed to the channels having a diameter below the quenching distance for hydrogen and efficient heat removal. The catalytic oxidation of hydrogen was also performed in a single-channel microreactor and a micro quartz glass reactor with inserted Pt-wires as catalyst (Veser, et al, 1999, Veser, 2001). Both were capable of operating over a wide range of feed and reaction conditions with effective suppression of homogeneous flames and explosions which was attributed to kinetic quenching of the radical chain mechanism.

The direct oxidation of ethylene to ethylene oxide was performed partially in the explosive regime in a microreactor developed at IMM (Richter, et al, 1998, Kestenbaum, et al, 1999). Ethylene oxidation is a series of reactions to produce either ethylene oxide or carbon dioxide and water via total oxidation of both ethylene and ethylene oxide. The total oxidations benefit from high temperature and contribute to temperature rise due to high exothermicity. Therefore, isothermal operation is crucial for the formation of ethylene oxide. The microreactor consisted of two stacks of mixing and catalytic plates. The design of the mixer allowed the reactant gases to reach a homogeneous mixture before entering the catalytic zone. The catalytic structure was fabricated from silver foil (which was the catalytic material) thus the
whole structure had uniform heat distribution and enabled isothermal operation. Conversions of ethylene increased only slightly with increasing oxygen concentration from 10 to 50 %, whereas selectivity increased by up to 50%. Although the selectivity was lower than the industrial benchmark, operation with reaction mixtures within the explosion limits demonstrated that the microreactor was able to function with minimal risks.

Thin-wall microreactors have been used successfully to carry out oxidation and partial oxidation reactions of hydrogen, ammonia and ethane in the flammable regime (Srinivasan, et al, 1997). Heat dissipation can be controlled by varying the thickness and the thermal conductivity of the top wall, enabling the microreactor to access a wider window of operation conditions and milder oxidation conditions than can be achieved in conventional systems. This was demonstrated by Franz, et al (1998, 1999b) using three thin-wall microreactors with different wall materials and thicknesses (SiNx, 1 μm, Si, 1.5 μm and 2.6 μm). Under identical conditions for ammonia oxidation, 1-μm-thick SiNx exhibited typical ignition/extinction behaviour. As the wall could not dissipate sufficient heat, the temperature increased rapidly to a new steady state, i.e. the catalyst operated in an autothermal mode. This operation mode was not ideal since the reactor could not be operated at intermediate temperatures between upper and lower steady states. However, with Si, which is more conductive than SiNx, the ability to remove heat was increased. The autothermal behaviour could be surmounted, and the distance between upper and lower steady states reduced as the thickness of the silicon wall increased. This allowed the microreactor to access intermediate temperature regimes. With effective control of the reaction temperature range, control of selectivity can be realised.
2.6.3.2 Systems with good residence time control

Wießmeier and Hönicke (1998) compared the hydrogenation of c,t,t-1,5,9-
cyclododecatriene (CDT) to CDE over various catalytic reactors. A microreactor was
realised using a stack of microstructured and activated Al foils. Irregular fixed beds
were made from pieces of activated Al wires and Al foils. All these catalysts had
regular pore systems produced through anodisation and the catalytically active
component was uniformly distributed on the pore walls. An irregular fixed bed (filled
with conventionally coated granule catalyst) gave yields of about 62 % at 80 %
conversion and 44 % at 98 % conversion. For the fixed bed with small pieces of Al
foil, a nearly constant yield of 73 % for conversions up to 90 % was observed. The
best results were obtained from the wire pieces and the microchannel reactor, both of
which showed high yields (86+ %) at up to 98 % conversion. The results show that
ordered packing, which reduces dead volumes within the reaction zone, and uniform
diffusional distance within the catalyst pores reduce further reaction of CDE thus
improving selectivity.

hydrocarbons like CDT, 1,5-cyclooctadiene (COD) and benzene to their
corresponding cyclic monoalkenes with microchannel reactors using Pd and Ru-Zn
catalysts. The microreactors consisted of 24 stacked, etched alumina wafers (8.5 mm
wide, 30 mm long and 0.3 mm thick) on which anodisation was performed to give an
18 μm thick porous alumina layer and 0.18 wt% Pd catalyst deposited via
impregnation with an organic solution of palladium (II) acetylacetonate. Each stack
was placed in a stainless-steel housing to give 672 200 × 200 μm microchannels. A
similar procedure was used for the fabrication of the Ru-Zn microchannel reactor with
0.2 wt% of each. Hydrogenation of CDT was carried out at 423 K and 110 kPa with CDT partial pressure of 0.11 kPa and a residence time of 87 ms. A high conversion of CDT (>99 %) with >80 % selectivity to cyclododecene was obtained. For the hydrogenation of COD, conversion increased from 75 % to 99.5 % as residence time increased from 35 to 115 ms, while selectivity to cyclooctene decreased slightly from 99.5 % to 98 %. With increasing COD partial pressure at a constant p_{Hz}/p_{COD} ratio of 2, cyclooctene production was increased 10-fold from 50 to 500 mg/h but the conversion to cyclooctene remained >80 %. The partial gas phase hydrogenation of benzene in the Ru-Zn-microreactor, however, led to the desired cyclohexene with low conversion of benzene.

Rouge, et al (2001) examined a microreactor for the catalytic dehydrogenation of isopropanol with periodic operation. Alternatively feeding two reactants can considerably increase selectivity for certain reactions. Reactor behaviour depends strongly on the amplitude and frequency of the imposed concentration changes. Due to the high inertia of conventional reactors, the range of operational frequency is in the order of $10^{-4}$ to $10^{2}$ Hz, while due to small dimensions of microchannels very narrow residence time distributions can be obtained which allow high frequencies for concentration cycling. The microreactor consisted of stacked stainless steel plates. Each plate contained 34 quadrangular channels of 300 μm width, 240 μm depth and 20 mm length and triangle-shaped entrance and exit areas with inlet and outlet on opposite sides of the channel array. Hydrodynamic experiments showed that plug flow was obtained and the residence time distribution showed a relatively small extent of dispersion. Frequencies of up to 1 Hz could be imposed for periodic operation.
2.6.3.3 Systems with efficient mass transfer and heat exchange

This was demonstrated by a microreactor designed for the catalytic partial oxidation of methane to syngas (Mayer, et al, 1999, Fichtner, et al, 2001). In conventional processes, due to low heat conductivity of ceramic-supported catalysts, high hot-spot temperatures can cause a fast degradation of the catalyst. The core part of the microreactor was a microstructured rhodium catalyst which was constructed by welding Rh foils, each having channels micromachined by EDM. The channel width and depth were smaller than 140 µm. The microreactor was examined at millisecond residence times, pressures up to 2 Mpa and catalyst temperature of 1000-1250 °C. This metallic microstructured catalyst promoted heat transfer in the direction of flow and would help to minimise hot-spot formation. This was due to the fact that total oxidation of methane took place at the reactor inlet area while further downstream endothermic reforming reactions consumed part of the energy released. The improved heat distribution and more efficient mass transfer due to small channel size resulted in significantly higher methane conversion and hydrogen selectivity as compared to those obtained using commercial Pt/Rh gauzes.

Richter, et al (1999) reported a microreactor for investigating the direct oxidation of propylene to propylene oxide, which has not been established as an industrial process so far. The reaction has a consecutive heterogeneous/homogeneous mechanism that required significant temperature changes along the reaction pathway. A microreactor was designed and fabricated with four modules to meet this requirement. The reactant gas stream (e.g. propylene diluted in nitrogen) is heated up to 500 °C in the inlet module to ensure equal temperature profiles along the flow axis. Flowing through the catalyst support module, heterogeneous catalytic hydrogen abstraction of propylene
produces allyl radicals. To prevent decomposition of these highly reactive radical species, the reaction gas is guided through an oxygen inlet module where fast mixing with oxygen and efficient cooling brings the stream temperature below 300°C. Homogenous reaction with oxygen is complete within ~2 ms to produce allylperoxy radicals. Epoxidization takes place by reacting allylperoxy radicals with excess propylene in the reaction module at elevated temperatures to yield propylene oxide. The work has shown the feasibility of combining short reactor lengths and steep temperature gradients to allow fast processing of unstable reaction intermediates.

Liquid-liquid nitrations in capillary reactors, where two liquid reactants form alternating slugs, were performed by Burns and Ramshaw (1999, 2000). The large surface area to volume ratio of the reactors allowed for efficient heat exchange. As nitrations are highly exothermic and sensitive to temperature, a large number of secondary, consecutive and decomposition reactions can result in low yield and purity. For benzene nitration, although reaction rates comparable to those of current processes could be achieved for certain conditions, high concentrations of by-product or low conversion were also observed. It was argued that shorter liquid slugs would improve reactant mixing and reactor performance. Since the slug length depended primarily on the channel inlet conditions, improved designs were required for the distribution of the two liquids. Antes et al (2000) used dissolved or gaseous dinitrogen pentoxide (N₂O₅) as a nitration agent for naphthalene using various types of micromixers in front of a capillary reactor as well as microreactors integrated with mixers and heat exchangers. Mononitro naphthalene was obtained with high selectivity. The researchers demonstrated that nitration processes, which are carried out at low temperature (-80°C to 0 °C) in conventional reactors can be performed in microreactors at ambient
conditions or even higher temperatures (up to 50 °C) and short residence times of 15-45 s with different product distributions.

2.6.4 Process Development

Microreactors have the ability to accommodate reaction regimes and conditions not accessible using conventional equipment, and this can be exploited in process development. Reactor performance can be tested quickly using microreactors. The processing conditions and characteristics can then be used to develop a conventional reactor and identify optimal conditions based on standardised components. This can all be accomplished by using a small amount of chemicals.

The attributes of microreactors that make them important tools in process development are good temperature and residence time control and fast mixing. BASF, in collaboration with IMM, developed a microreactor for the synthesis of vitamin precursors (Richter, et al, 1999b, Wörz, et al, 2001). The reaction is highly exothermic and the reactant, intermediate and product very quickly form a by-product. The reaction channels were 900 μm deep and 60 μm wide and surrounded by cooling channels. The reaction was carried out isothermally with rapid mixing and no hot spots were observed. The microreactor further allowed operation of consecutive reactions for immediate processing of unstable products with a second reaction step. The short residence time, isothermal operation and fast quenching achieved with the microreactor were not possible using existing laboratory equipment. Within a few weeks optimisation was carried out and a maximum yield of 95 % was obtained, resulting in reduction of by-product formation by half, as compared with the technical process (Wörz, et al, 2001). The same company studied the oxidative dehydrogenation
of alcohol to aldehyde, which is also highly exothermic. The microreactor developed by Forschungszentrum Karlsruhe was made of silver (the catalytically active material) and allowed very short residence times and good heat transfer. The rectangular channels had a cross-section of 320 μm x 400 μm. With this reactor, higher selectivities were obtained than in the technical reactor (96 % vs. 85 %), proving that the time that the reactants spend in the reaction zone and the reaction temperature were key issues.

For ketone reduction using Grignard reagent, a relatively long operating time was required for sufficient heat transfer due to the fact that the reaction is a fast exothermic process (Krummradt, et al, 1999). This liquid phase reaction was part of an existing Merck process yielding a fine chemical as final product. An array of ten mixing devices of IMM was employed, resulting in higher product yields (up to 95%) with increasing volumetric flow at high process temperature. The best result in a conventional 0.5 l semi-batch reactor was 88 % at the significantly lower temperature of -40 °C. In a 6000 l production reactor, the yield dropped to 72 % due to inefficient heat transfer which dictated a long residence time (5 h). Due to blockage of the microreactors by solid deposition, a ‘minireactor’ was developed which was still small enough to achieve the beneficial fast mixing and good heat transfer. A production unit was designed using five of these minireactors operating at much lower residence times than the previous production reactor and with improved yield. The batch organometallic reaction was transferred into a continuous process in only 18 months, and the process has run successfully since August 1998.
Axiva developed a process of continuous radical solution polymerization for acrylates (Bayer, et al, 1999). In order to provide sufficient mixing for the homogenization of monomer and initiator, a Sulzer static mixer was used at the reactor entrance. However this resulted in the fouling of the reactor because the mixing time of a few seconds was longer than the reaction time for the formation of polymer chains. The bad mixing conditions resulted also in the appearance of high molecular weight compounds. Fouling was tremendously reduced after the replacement of the Sulzer mixer with an IMM micromixer with 10 inter-digital mixing units. Furthermore, a more uniform molecular weight distribution was obtained.

2.6.5 Distributed and Mobile Processing

In distributed production, a large plant is substituted with distributed micro or intensified chemical plants that allow point of use production and adjustment of production capacity to varying needs. Although performance can be lower than that of a large scale plant, localised production can eliminate risks and costs concerning transport and storage. For example, natural gas coming out with crude oil in oil platforms is currently flared, because it is not economical to recover and transport it. On an oil platform, 5 kg of structural weight is needed to support 1 kg of equipment. If a microchemical plant which produces liquid hydrocarbons could be installed, then it would be economically possible to transfer this hydrocarbon to shore. The first proposal of distributed manufacturing with miniaturised plants was presented by Benson and Ponton (1993). With the rapid development of microreaction technologies, the potential application of distributed production in microreactors, at least for selected processes, is becoming possible (Rinard, 1998). Lohf, et al (2000) suggested unit operations based on standardised housings with hook-like connectors,
that could be assembled to provide modular systems. Advantages of such an approach include decrease in development time, reduced cost by mass production and flexibility.

It is worth noting that if all equipment associated with coping with failure were removed, the cost of most assets could be reduced by more than 50% (Benson, 1998). In addition, reduction of equipment size can result in further gains in safety since the quantities of hazardous materials that can be released in case of an accident and the potential energy contained in the equipment are reduced (Hendershot, 2000).

Research work has demonstrated the feasibility of safe operation of hazardous reactions in microreactors. For example, the synthesis of hydrogen cyanide from oxidative dehydrogenation of methane and ammonia (i.e. Andrussov process) at temperatures above 1000 °C has been tested in a microreactor, showing significant HCN formation (Hessel, et al, 1999b). The system consists of a stainless steel preheater/mixer, a Pt catalyst structure (incorporating an in-line temperature sensor) on a ceramic support, a stainless steel heat exchanger. The catalyst zone is structured with microchannels. These channels are heated by passing an electrical current through the thin walls between them. Uniform temperature profile at up to 1000°C was achieved by restricting the thickness of the channel walls to 40 μm. After exiting the reaction zone, the product gas is guided to four product channels of the micro heat exchanger, each product channel surrounded by two cooling channels operating in counter-flow mode. HCN yields of up to 31% were observed in this microreactor, nearly half the value of the industrial process.
Lerou, et al (1996) successfully conducted reactions to synthesise methyl isocyanate from methylformamide and oxygen at high temperature. This reaction is a high-temperature, hazardous catalytic reaction that requires intensive cooling. The microreactor consists of three etched silicon wafers carrying microstructured components and two capping wafers. Reactants were mixed and then heated by the product before entering the catalyst chamber filled with polycrystalline silver particles. Conversions up to 95 % for methylformamide were obtained at an operating temperature of 300 °C.

The fuel processor is another important application for on-site production of hydrogen for fuel cells. A micro-fuel processor is a small chemical plant consisting of multiple unit operations such as reactors, heat exchangers and separation units. Microreactors (integrated with heat exchangers) for producing syngas using methane, methanol and hydrocarbon as feedstock have been manufactured by PNNL (Tonkovich, et al, 1998, 1998b, 1999, Fitzgerald, et al, 2000) (see Figure 2.4). Heat was supplied for the endothermic reaction using combustion gas. This process can be intensified by using catalytic plate reactors which combine surface catalysed endothermic and exothermic reactions that take place on either side of a plate of a compact heat exchanger (Charlesworth, et al, 1995, Zanfiri and Gavrilidis, 2001). A conceptual design for a fuel cell-based man portable power system has been also proposed which consists of two units 21 cm long and 4 cm in diameter (Daymo, et al, 2000). Each unit is integrated with fuel storage, a fuel processor, a fuel cell and a lithium polymer battery for start and peak power. The size of the fuel processor is about 8-10 cm³ and includes a steam generator, heat exchanger, an integral steam reformer/combustor reactor and a water gas shift reactor. Microreactor-based fuel processors are of
particular interest for the automobile industry to realise the replacement of internal combustion engines by fuel cells. Efforts towards the development of miniaturised fuel cells for replacement of batteries in cellular phones and laptops are also underway (Mex and Müller, 1999, Mex, et al, 2000).

Other suggestions for distributing processing have also been made, which at this stage seem rather far from reality. These include desktop pharmacies, domestic recycling factories, mobile factories, domestic water treatment plants, cereal crop processing at the combine, purification of blood in the body, recycling of plastics in the collection vehicle, etc. (Kawahara, et al, 1997, Benson, 1998). For the mobile factory concept a microchemical plant would be so small that it would fit in the back of a truck. Once an order is placed the raw materials would be loaded on to the truck. Production would be carried out during transportation, so that the order would be ready when the vehicle reaches the customer.
2.6.6 Process Intensification

Micro-chemical systems can be considered as a limiting case of the Process Intensification (PI) approach to chemical plant design. In general, PI is defined as the development of novel apparatus and techniques that can bring dramatic improvements in manufacturing and processing, substantially decreasing equipment size, production/capacity ratio, energy consumption or waste production and ultimately resulting in cheaper, sustainable technologies (Stankiewicz and Moulijn, 2000). PI techniques would, therefore, include high pressure, temperature or concentration operations to improve mass transfer and reaction rates and utilisation of the fluid dynamic environment within reactors so that performance is dictated by intrinsic reaction kinetics and not by heat and mass transfer (Green, 1998, Green, et al, 1999). Process intensifying equipment includes microengineered reactors.

Gas-liquid catalytic reactions have been carried out in micro-packed beds of catalytic particles with size 50-75 μm (see Figure 2.5, Losey, et al, 1999, 2000). To improve gas-liquid contacting a multilamination mixer was used at the reaction channel inlet. Oxidation of benzaldehyde was safely operated at temperatures as high as 140 °C with pure oxygen and organic solvent due to the small reaction volume (4 μl).

Figure 2.5: Gas-liquid micro-packed bed with catalyst restrainer (Losey, et al, 2001)
Hydrogenation of cyclohexene was used to characterise the mass transfer coefficient. Values of the mass transfer coefficient \( (k_L a) \) were determined to be 5-15 s\(^{-1}\), which is two orders of magnitude larger than those reported for traditional multi-phase fixed bed reactors. The greatly improved mass transfer in the microreactor can be attributed to the large external particle surface area and the well-controlled distribution of gas and liquid over small catalyst particles, hence the high gas-liquid interfacial area generated by the microreactor.

Hessel, et al (1999) used direct contact of the gas and liquid phases, which were either introduced together in microchannels (microbubble columns) or were flowing in separate layers in falling film reactors. The falling film reactor consisted of two parts: a gas-liquid reaction chamber with a platelet comprising a large number of microchannels (100 x 300 μm cross-section) to generate a thin liquid film of several tens of microns thickness by means of gravity, and a heat exchanger located on the back of the platelet. The microbubble column consisted of a static mixer and a reaction channel array with heat exchangers. The flow pattern in channels was found to be Taylor or bubble train flow at low gas superficial velocities and annular flow at higher gas superficial velocities. Specific interfacial areas obtained were up to 15000 m\(^2/m^3\) and 27000 m\(^2/m^3\) for the microbubble column and the falling film reactor respectively. These represent a large increase compared to conventional bubble columns (50-600 m\(^2/m^3\)) or even impinging jets for intensive gas-liquid contacting (2700 m\(^2/m^3\)). The microbubble column gave much higher conversions (in some cases 100 %) in a model CO\(_2\) absorption reaction compared to other gas-liquid dispersing micromixers (for the same residence times). These reactors were also employed for the direct fluorination of toluene dissolved in acetonitrile or methanol.
Both reactors were able to operate at high hydrocarbon concentrations and high fluorine content in a nitrogen carrier (up to 50 vol% of fluorine) at a temperature of about -17 °C. Yields of up to 28% of monofluorinated ortho and para products for toluene conversions of 76% were obtained, which is comparable with the industrially applied Schiemann process. The space-time yield of the microreactors, based on the channel volume, was several orders of magnitude higher than those of a laboratory bubble column. Direct fluorination was also conducted in a microreactor developed by Chambers and Spink (1999). The microreactor was fabricated on a block of nickel (or copper) with a groove as reaction channel and channels beneath the groove as a heat exchanger. The gas-liquid mixing was carried out in the reaction channel through annular flow, offering the advantage of very large surface to volume ratio for the liquid phase. Various selective fluorinations were tested in this microreactor, e.g. sulfur pentafluoride derivatives were obtained from the direct fluorination of di(m-nitophenyl) disulphide with 44-75% yield.

Another approach for bringing two phases in contact was proposed by Robins, et al (1997). Open microchannels etched in silicon and glass wafers are brought together, so that slits with width as small as 5 μm are formed after careful alignment and bonding. When two different fluids (gas and liquid or organic and inorganic phases) flow in the two channels, an interface is formed at the slit which allows mass transfer from one channel to the other while keeping the two phases separated. Alternatively the interface can be pinned by using metal micromeshes or laser-machined polymer membranes to keep the phases separate (Turner, et al, 2000, Martin, et al, 1999). Fast mass transfer between phases can be achieved as demonstrated by acid neutralisation.
2.6.7 *Extraterrestrial Processing*

Utilisation of micro/nano-technologies in the space sector is very promising. Lightweight, compact chemical systems can be employed to reduce total resources required yet provide higher system performance per unit cost and mass. Research is being conducted at the Pacific Northwest National Laboratory (PNNL) for the NASA In-Situ Resource Utilization (ISRU) program planned for future missions to Mars. One aspect of this program is In-situ Propellant production (ISSP) and involves reacting carbon dioxide from the Martian environment with stored hydrogen from Earth to produce propellants and oxygen for the return trip so that the required launch mass from Earth is reduced. For this purpose a microchemical plant is being designed which includes the collection and pressurisation of atmospheric carbon dioxide, conversion reactors, chemical separators, heat exchangers and cryogenic storage (TeGrotenhuis, et al, 2000). Due to negligible convective heat transfer within the low-pressure environment of space, high energy efficiency is achieved through extensive recuperation and energy cascading from hot to cold unit operations to minimise thermal and electrical wastage. NASA plans to launch such microchemical plants to Mars in 2011, followed by human missions in 2013 (Wegeng and Drost, 1998). Other applications of microreactors in space include micro-fuel cells, compact clean-up units for waste treatment, portable heating and cooling systems. Mining and chemical processing of raw materials on the Moon, Mars, Mars’ moons, asteroids, etc. is also being considered.

However, there are significant challenges to extraterrestrial chemical processing plants. Energy management is one of the main concerns for space-based processes. The systems should be able to operate very efficiently and reliably for long periods of
time. Such developments require high cost for adaptation to space use due to the reduced gravity and pressure environment. These advancements though would result in a significant reduction in payloads and spacecraft size (de Aragón, 1998).

2.6.8 Scale-out

Repetition of basic units of microengineered reactors provides the ability to increase production throughput by scaling out (or numbering up) instead of scaling up (Lerou, et al, 1996). Hence, instead of following the usual laboratory-pilot plant-commercial scale reactor route, the microreactor architecture can first be optimised and then production increased by the use of a cascade of similar reactors. This approach guarantees that the critical features of the basic unit are kept constant thus minimising the risk of different performance at the large scale. The development time of a process from laboratory to production would also be reduced and phased increase in production can be achieved by progressively adding parallel reaction modules.

However, the concept of scale-out is not without its challenges. Microengineered reactors must achieve uniform flow distribution so that the flowrates in each unit are identical. This is accomplished in conventional catalytic multi-tubular reactors, but the different manufacturing methods and tolerances in microengineered reactors may require different approaches. Inlet regions in the reactors or their channel geometry must be designed to guarantee flow equipartition between channels (Ehrfeld, et al, 2000b, Commenge, et al, 2000). Where small channels and orifices are present, plugging by particulates can be a problem as this can cause flow maldistribution and eventually even reactor failure. Hence, filtration is required. Particles can also form
inside the reactors and in this case appropriate reactor design and surface engineering will be needed to avoid fouling.

For reliable operation of scaled-out systems, heat management systems need to achieve the same local thermal environment accomplish in each sub-unit. As such, the development of simple and robust reactor instrumentation and control is imperative. MIT and Dupont’s approach is to integrate feed gas valves, flowmeters, power supply and control circuitry (Quiram, et al, 2000b). These units along with electrical and fluidic interconnects will be packaged in a multiple microreactor test station for gas phase systems with a small footprint.

Despite the above problems, a few examples of the scale-out concept exist. Axiva followed this approach for an acrylate polymerisation system where a micromixer was demonstrated to aid in avoiding the production of high molecular weight compounds. On the laboratory scale, a throughput of 6.6 kg/h was achieved with one mixer array containing ten mixing units. For the industrial scale, 32 such micromixers can be combined in an assembly enabling an acrylate capacity of 2000 tons/year (Ehrfeld, et al, 2000). Merck used 5 minireactors for a ketone reduction production unit after successful trials of pilot-scale minireactors (as detailed in Section 2.6.4). This involved the automation of the entire process and the proper splitting of the feed streams to the individual minireactors (Krummradt, et al, 2000).

2.7 Modelling

In microreactors, laminar flow is usually encountered due to small length scales. Therefore, heat and mass transfer can be fully characterised, facilitating reliable
description of processes and improving the fidelity of the mathematical models. Modelling of microchemical systems can provide analysis of specific systems, assist in the design of new ones and evaluate potential performance advantages in relation to macroscale systems. However, the scale necessitates the modelling of heat transfer within the solid boundaries as well and can present problems of multiple length scales and complex geometries.

Wenka, et al (2000) modelled fluid flow and heat transfer in a cross flow microheat exchanger using 3-D numerical simulations. The effect of wall material conductivity on heat transfer efficiency was investigated and it was found that low conductivity materials such as glass and ceramics result in higher heat transfer efficiency because they reduce axial heat transfer (Stief, et al, 2000). Hardt, et al (2000) suggested three scenarios for improving heat exchanger performance, namely suppression of axial heat transfer by including low thermal conductivity structures in high conductivity walls, meandering flow channels which increase the heat transfer area, and mixing at the inlet with fins which result in vortices and higher heat transfer. CFD simulations showed the last design to be the most effective, while further simulations of combined reactors and heat exchangers proved the superior performance of these devices compared to conventional fixed bed technology. Luo, et al (1999) also found that introducing mixing within the flow channels can improve the performance of compact heat exchangers with channels in the mm range. Alépée, et al (1999), using Finite Element Modelling (FEM), found improved temperature uniformity in a double-side heated reaction channel for dehydrogenations compared to when only one reactor side was heated.
The velocity distribution from a single inlet to a number of parallel microchannels on a plate was modelled by Commenge, et al (2000), using a simplified system geometry and mass and pressure drop balances. This model allows optimisation of plate geometry so that equal velocities are obtained in each channel. The effect of channel dimensions and diffusion coefficients on axial diffusion and residence time distribution (RTD) was studied by Walter and Liauw (2000) using CFD, who commented that when many reactants are present, the optimum conditions for a narrow RTD for one reactant may be different from that of the others.

Bibby, et al (1998) used a finite volume CFD code to model the extraction between two immiscible liquids that flowed in separate channels and came in contact through a small slit. This configuration allows easy separation of the two phases at the end of the process. For the interface, mass transfer equilibrium partition coefficients were used, and the results of Fe\textsuperscript{III} fractional transfer compared well with experimental data (Shaw et al., 1998). Extraction between liquids separated by a perforated plate was modelled by TeGrotenhuis, et al (1998) by solving a convection-diffusion equation and using an equilibrium partition coefficient. For channel depths under 300 μm it was found that the resistance of the separating plate became significant. Rector and Palmer (1999), using the Lattice-Boltzmann method, modelled diffusion during co-current flow of two immiscible liquids in a microchannel; the liquids were either in direct contact or separated by a porous contactor plate. Mass transfer was found to be slower in the latter case due to decreased contact area between the two phases.

Angeli, et al (1999) studied gas-liquid hydrogenation reactions under isothermal conditions in a 2-D microchannel using CFD. Hydrogen was allowed to diffuse into
the liquid phase where the reaction took place, through an appropriate wall boundary condition. Štepánek and Marek (1999) used a systems approach to model a combined reactor-separator where an immobilised ion-exchange resin separated the product and increased yield. Biological reactions in microchannels have been simulated by CFD (Makhijani, et al, 1999), and by a diffusion-based mass transfer model (Dickey, et al, 2000).

Fedorov and Viskanta (1999) modelled wall adsorption during flow in 2-D parallel plates including both heat and mass transfer. For the wall they used both a no-slip and a slip boundary condition. The inclusion of slip reduced the rates of momentum and heat transfer between the gas and the wall; the former resulted in reduced pressure drop while the latter caused the gas temperature in the simulation to increase faster compared to no-slip flow. The inclusion of adsorption caused the velocity, temperature and adsorbed species concentration within the channel to oscillate, a behaviour not seen in large scale systems. The authors attributed this to the much smaller characteristic time scales for mass transport. A finite difference model that included material and energy balances was used for the study of dehydrogenation of cyclohexane to benzene in microreactors and demonstrated that Knudsen flow, which existed near the reaction channel exit, resulted in higher conversions than slip flow (Jones, et al, 2000).

Stief and Langer (2000) solved the balance equations in a non-homogeneous catalytic gas phase reactor for ethylene oxidation in order to investigate the effect of periodic reactant feed and heating on conversion and selectivity. Large amounts of wall material resulted in high thermal inertia and slower response to temperature changes
compared to concentration changes. For the combination of reaction and reactor used, periodic operation actually decreased conversion. Zheng, et al (2000) modelled a membrane reactor for cyclohexane dehydrogenation where a Pd membrane selectively removed H\textsubscript{2} from the product mixture, by dividing the reaction channels in slices and solving materials and energy balances. Hsing, et al (2000) used finite element simulations to model a T-reactor combined with heaters. As a model reaction they used Pt-catalysed ammonia oxidation. 3-D flow and heat transfer simulations were used to acquire effective heat transfer coefficients, which were then used in a reduced 2-D model that included reaction kinetics. The inclusion of the catalyst layer, the reactor wall and the heaters presented problems of large variations in characteristic lengths within the computational domain. To overcome this, the three different wall layers were reduced to one wall boundary condition, using Biot number analysis. For the particular reactor configuration modelled, it was found that the reaction was mass transfer limited, while ignition occurred downstream and the reaction front subsequently travelled upstream. Quiram, et al (2000) used the same model to design a micro-flow sensor based on hot-film anemometry. In order to account for heat transfer in the transverse direction, which is not modelled in the 2-D simulation, they added an extra heat loss term in the wall boundary condition. Snita, et al (1999) modelled electrophoretic separation and electroosmosis in microchannels by solving the momentum, heat, mass and electrical charge balances. They also studied the propagation of concentration profiles in channels under the influence of an electrical field.
2.8 Conclusion

A variety of unique advantages of microengineered reactors have been demonstrated by various researchers. These devices have the potential to alter the chemical engineering landscape by expanding the tools available to the reaction engineer, and by increasing the manufacturing speed of processes and the rate of information generation. Initially, only a few companies like Dupont, BASF and CRL promoted and actively investigated the use of microreaction technology. Currently many others, e.g. Axiva, Merck, Bayer and UOP, are becoming involved at various levels of commitment. Commercial interest is growing and this is also evidenced by increasing activity in the patent literature (Swift, et al, 1985, Breuer and Meyer, 1998, Drost, et al, 1997b, Wegeng, et al, 1997, Drost, et al, 1999, Ehrfeld, et al, 1999d, Ghosh, et al, 1999, 1999b, Friedrich, et al, 1999, Shaw, et al, 1999, Franz, et al, 2000, Oberbeck and Schwalbe, 2000). Microengineered reactors are moving steadily from research curiosities towards real applications. They are first expected to make an impact in niche areas where they will clearly demonstrate unique advantages over existing systems, for example where chemistry is strongly influenced by operation in the microscale or where equipment size is of paramount importance.

However, a variety of issues need to be resolved such as particulate management, fluid mechanics at the microscale and uniform heat and mass distribution. Catalytic components will have to firmly adhere on the support when they are present in the form of coatings. An additional obstacle is manufacturing cost. The ratio of construction material to reactor volume is high, and fabrication methods need to take that into account if the economies of mass production are to challenge the economies of scale. In that respect highly parallel manufacturing methods such as etching,
embossing and injection moulding may provide the required cost reduction. Performance reliability (e.g. corrosion) needs to be addressed. For all these reasons, wider application of microengineered reactors for chemical production is still debated. However, one of the applications with good prospects of realisation and commercial success is miniaturised chemical plants for hydrogen production from hydrocarbons to be used alongside fuel cells for power generation in automobiles and electronic devices.

The future of microreaction technology will further depend on the existence and the emergence of suitable market and societal forces. Some of these are already present: the need for sustainable development for sensible resource utilisation, environmental regulations which require minimisation of waste, the increasingly sophisticated customer base which demands improved products and services and the requirement for agile manufacturing due to rapid business conditions changes. These and other driving forces that currently may not even exist will influence the market penetration of microreaction technology.
3. T-Microreactor

With no previous experience in dealing with microreactors or microfabrication, it was decided that the first part of this project should be kept as straightforward as possible to work out the basic design methodology. As such, the first reactor was kept simple and intended for single phase reactions. A catalytic T-microreactor was designed for this purpose. This chapter focuses mainly on the work done to gain experience in microfabrication, microreactor design and interface design.

3.1 Design Basis and Rationale

Due to its apparent simplicity, a T-microreactor design was thought to be a good demonstration of the methodology and thought required to fabricate a microreactor. As shown in the figure below, the reactants enter at the ends of the horizontal channel, mix, react, and the product leaves at the end of the perpendicular channel.

As it turned out, this was a good choice as the T-microreactor ended up involving quite a few processes generally used in microfabrication, including chemical vapour deposition (CVD), photolithography, wet and dry etching, sputtering, electrodeposition and anodic bonding. However, to begin with, some preliminary studies had to be carried out before designing and fabricating the reactor.
3.1.1 Reaction

The gas phase partial oxidation of methanol to formaldehyde was chosen as the test reaction. It involves the following reactions (Ertl, et al, 1997, Satterfield, 1991):

\[ \text{CH}_3\text{OH} + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \quad -159 \text{ kJ/mol} \quad (1) \]
\[ \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2 \quad +84 \text{ kJ/mol} \quad (2) \]
\[ \text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

There are two industrial processes, based on different catalysts. The process based on silver catalyst involves both reactions (1) and (2). It is carried out at atmospheric pressure at 500-600 °C with a 50:50 methanol:air mixture with a residence time of about 10 ms. Methanol conversions range from 30-80 % with selectivities of 80-95%. Reactions (1) and (2) are thought to progress at similar rates, resulting in a highly exothermic reaction that needs quenching in the exit stream to minimise further decomposition of formaldehyde to carbon monoxide and hydrogen. Small amounts of formic acid and methylal are also formed. Due to the high water content and because water prevents polymerisation of formaldehyde, the product of this reaction is sold as formalin solution (McKetta, 1985, Robb, et al, 1974).

The other process, which uses a mixed catalyst (18-19 wt% Fe\textsubscript{2}O\textsubscript{3}, 81-82 wt% MoO\textsubscript{3} and chromium and cobalt oxide promoters), involves only reaction (1). The formalin product has a concentration of 37-50 wt% formaldehyde. Side products are carbon dioxide, carbon monoxide and formic acid. Methanol conversion and selectivity range from 95-99 % and 91-94 %, respectively (Weissemel and Arpe, 1993).

This reaction was thought to be suitable for testing a microreactor as it involved
several key terms often associated with microreactors:

1) highly exothermic: such reactions are difficult to control industrially due to the difficulty in keeping large volumes isothermal. In microreactors, the volumes involved are very small and therefore heat transfer is very rapid leading to isothermal operation.

2) rapid quenching: because of the rapid heat transfer, the product stream is easily quenched, thus greatly reducing product decomposition or further reaction, leading to better selectivity.

3) safety: a methanol:air mixture is potentially explosive. However, due to the flame trap dimensions of microreactors, an explosion cannot propagate, leading to a safer system. Also, because of the smaller volumes involved, leaks would not be as dangerous.

4) short residence time: a residence time in the order of milliseconds made this reaction inherently suitable for use in microreactors.

The first process was chosen because the catalyst had only one component: elemental silver. It had been realised at this stage that it would be difficult to insert catalyst pellets into the reactor. It would be less complicated to use microfabrication techniques to deposit a layer of silver at the bottom of the reaction channel. The catalyst required for the second process was deemed too complex to deposit at such an early stage in learning about microfabrication.

3.1.2 Materials

Next, a decision had to be made as to what material would be used. Given the facilities and literature available, silicon was determined as the material of choice.
The process would operate at well below the melting point of silicon. Silicon also conducts heat fairly well (thermal conductivity = 80 W/m K). From Yao, et al, (2000) silicon dioxide can catalyse methanol oxidation, but the conversion is very low at about 400 °C (~5 %) but increases to about 60 % at 500 °C (blank runs which were eventually made, however, showed negligible conversion even at 500 °C). To make the reaction channel visible during the course of the reaction, it was decided to use glass as a cover plate.

3.2 Design Considerations

The main consideration here was how long the reaction channel had to be. In microreactors, the length of the reaction channel can be tailor-made to give the required residence time. Published kinetic data was used to approximate the reaction rate in the microreactor and used to determine the appropriate length.

Also, because methanol exists as a liquid at room temperature, it would be necessary to vaporise it and then to bring it to reaction temperature before it reached the reaction section. As such, a pre-heating section was incorporated.

3.2.1 Flowrate Calculations

Calculations based on the reaction kinetics published by Robb et al (1974) were made. A vertically-averaged formulation model for flow in a parallel plate geometry involving a first order reaction developed by Gobby (2001) was used for this purpose, a brief description of which follows. Note that the kinetics for methanol oxidation are not in fact first order with respect to methanol concentration. An approximation to first order kinetics was made as the aim of this exercise was to obtain estimates only.
The model describes laminar incompressible microscale flow between two parallel plates with a heterogeneous catalytic reaction occurring only on the bottom plate. It assumes constant fluid properties, isothermal behaviour, no volume change and dilute reactants. The vertically averaged reactant concentration, $\bar{\theta}_a(\zeta)$, is given by

$$\bar{\theta}_a(\zeta) = \int_0^\eta \theta_a(\eta, \zeta) d\eta$$

When $Pe/R < 1$, this equation can be integrated to give

$$\bar{\theta}_a = \exp(-\lambda_a \zeta)$$

where

- $\theta = \frac{c_a}{c_a(0)}$
- $c_a$ = concentration of reactant a
- $c_a(0)$ = initial concentration of reactant a
- $\eta = \frac{x}{h}$
- $x$ = distance from the lower wall
- $h$ = distance between plates
- $\zeta = \frac{z}{L}$
- $z$ = distance from the inlet
- $L$ = length of channel
- $\lambda_a$ = concentration decay constant and can be determined from

$$\lambda_a Pe \frac{R}{Da} = \begin{cases} 3 \left( \frac{Da}{2} + 1 \right) & , Da < 2.0 \\ \sqrt{\frac{9Da^2}{4} + 3Da + 9} \left( \frac{\pi Da}{2(Da + 1)} \right)^2 & , Da > 2.0 \end{cases}$$

- $Da$ = Damkohler number = $\frac{kh}{D}$
- $k$ = first order reaction rate constant
- $D$ = molecular diffusivity
- $Pe$ = Peclet number = $\frac{Uh}{D}$
- $U$ = average velocity between plates
- $R = \frac{L}{h}$

By definition, the conversion, $X_a$, is given by

$$X_a = 1 - \bar{\theta}_a$$
The dimensions of the reaction channel used for these calculations are shown below.

For the estimation of the reaction kinetics, refer to Appendix 3-1.

<table>
<thead>
<tr>
<th>Catalyst/channel length</th>
<th>15 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel width</td>
<td>600 µm</td>
</tr>
<tr>
<td>Channel height</td>
<td>300 µm</td>
</tr>
<tr>
<td>Channel volume</td>
<td>$2.7 \times 10^{-9}$ m$^3$</td>
</tr>
<tr>
<td>Flow cross-sectional area</td>
<td>$1.8 \times 10^{-7}$ m$^2$</td>
</tr>
<tr>
<td>Rate constant (at 420 °C)</td>
<td>0.081 s$^{-1}$</td>
</tr>
<tr>
<td>Diffusivity of methanol in oxygen</td>
<td>$9 \times 10^{-5}$ m$^3$/s</td>
</tr>
<tr>
<td>Da</td>
<td>0.06</td>
</tr>
<tr>
<td>Pe</td>
<td>13.2</td>
</tr>
<tr>
<td>R</td>
<td>50</td>
</tr>
<tr>
<td>$\lambda_a$</td>
<td>0.22</td>
</tr>
<tr>
<td>Methanol:oxygen concentation</td>
<td>1:1</td>
</tr>
</tbody>
</table>

Table 3.1: Calculation data for the estimation of reaction kinetics for methanol oxidation

The results, calculated at $T = 420 °$ are:

<table>
<thead>
<tr>
<th>Methanol Conversion</th>
<th>Residence time, $\tau$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>27</td>
</tr>
<tr>
<td>0.5</td>
<td>12</td>
</tr>
<tr>
<td>0.2</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3.2: Residence times to achieve a range conversions for methanol oxidation

From these results, a reaction channel length of 15 mm seems to be adequate. However, in order to introduce flexibility (mainly to allow the use of larger flowrates), two reactors with longer channels (104 and 207 mm) were designed as well.

3.2.2 Pre-heat Channels

An estimate of the pre-heater length was required. To simplify calculations, several assumptions were used:

1) no heat losses to the surroundings
2) heat would only enter the channel from the bottom surface
3) macroscopic correlations would be applicable to this system
4) the properties of the fluids (within a certain phase) could be approximated by the values at the average temperature of that range

5) heating would be provided by a fluid that flowed through a channel that was on the back side of the wafer

6) both channels were straight

The reaction takes place in the gaseous phase at 450 °C. However, methanol is a liquid at room temperature. Therefore, three heating regimes had to be taken into account: liquid heating, boiling and vapour heating. The methods used for these calculations can be found in Appendix 3-2. The variables were channel height and width, and reactant flowrate. The variables on the heating side were kept constant, such as operating pressure (1 bar), heating fluid (steam), heating fluid flowrate (0.5 mg/s), heating fluid temperature (460 °C) and the cross-sectional area of the heating side (1 x 1 mm). Pressure drop in the liquid and vapour sections were calculated using friction factors while in the boiling section it was calculated using the method given by Mills (1999) (see Appendix 3-2 for the equations).

The results shown in Figures 3.2 and 3.3 were based on a 1:1 methanol:oxygen mixture with a methanol flowrate of 24.4 mg/min, which corresponded to a reaction residence time of 4 ms and methanol conversion of 0.2 as calculated in the previous section. This case was examined in particular as it was the upper bound of the range of flowrates that would be used and would therefore require the greatest channel length. The channel length required to heat the oxygen stream to the reaction temperature was not considered as it would always be shorter than the length required by the methanol stream (it had been decided that the length of both pre-heat channels
would be the same so as to allow either channel to be used for either reactant).

![Figure 3.2: Relationship between channel length, width and height (methanol flowrate 24.4 mg/min)](image)

Figure 3.2 shows that the pre-heat channel length required is almost independent of the channel height. Increasing the channel width past 600 μm resulted in very little decrease in the length required. Figure 3.3 shows that the channel height can have a strong effect on the pressure drop. However, there was very little change in the
pressure drop when increasing from 300 µm to 500 µm deep. There was also very little pressure drop in channels wider than 350 µm. Combining these results, a channel with height 300 µm and width 600 µm would be suitable, and would require a 6.49 cm long pre-heat section. In the final design, this length was increased to 10 cm to allow for some flexibility in the range of flowrates and reaction temperatures.

3.2.3 Reactor Configuration

From the calculations in the last two sections, modifications were made to the basic microreactor design. The entry arms were extended to incorporate the pre-heat section. Both pre-heat and extended reactions channels took on a serpentine configuration to minimise space. In addition, chambers were also etched around the reactor to minimise solid material through which heat can be conducted to reduce the amount of energy required to heat the reactor. The modified schematic for the reactor is shown below.

![Figure 3.4: Schematic of the reactor](image)

3.3 Reactor Fabrication

By selecting silicon as the substrate, the processing route was also locked in. Silicon microfabrication generally involves the use of a mask to transfer the desired pattern on
to a silicon wafer using the process known as photolithography. This pattern is then etched into the wafer. Following catalyst deposition, the silicon structure is bonded to another wafer to form a sealed reactor. This section details only the processes leading up to and including the etching of the wafer. Two masks were made. The first was a test mask which was used to explore the basics of microfabrication, the latter was the mask used for fabricating the actual reactors.

3.3.1 Mask

For the photolithography step, masks had to be made. Refer to Appendix 3-3 for the design of the first mask and Appendix 3-4 for the second. The masks were made of glass with a chromium layer sputtered on. Because they would be used with a positive photoresist, the regions to be etched were made transparent (the chromium was etched by electron beam machining). Several other features were included as well, such as test structures and alignment marks. Both masks were made at the Central Microstructure Facility (CMF), Rutherford Appleton Laboratories.

3.3.2 Choice of Etching Route

Decisions had to be made on the type of etching to be used at various parts of the process. Two etch steps were required: the first to etch the pattern defined by photolithography into the masking layer (which is either silicon oxide or silicon nitride), and the second to etch the pattern defined in the previous step into the silicon wafer itself. Wet etching is relatively fast, while dry etching is slow. This is balanced by the fact that dry etching is more controlled and etches practically vertically into the substrate. Wet etching is either isotropic or dependant on crystallographic planes and
is less easy to control precisely without using more advanced and complicated techniques.

In order to reproduce the mask pattern as closely as possible, dry etching was chosen to etch the pattern into the masking layer. Because the masking layer was less than 1 \( \mu \text{m} \) thick, even the slow reactive ion etching processes used would be quick. However, it was decided to perform the first experiment using wet etching for all the etching steps to simplify the initial learning curve.

Wet etching was chosen for the second etch step. This was mainly because this step involved etching to depths of 200-300 \( \mu \text{m} \). It would take upwards of 4 h to reach such depths using dry etching. The next decision was to choose between isotropic and anisotropic etching. Of the two, isotropic etching is much faster. Isotropic etchants produce rounded channels which are slightly larger than the mask pattern, whereas anisotropic etchants produce trapezoidal channels (when using standard silicon wafers with a <100> orientation) within the masked area. The latter was chosen as it would result in channels that matched the mask dimension more closely. Also, because the etch rate is slower, there would be less variation in depth resulting from small discrepancies in etching time. KOH was used as it was a well-documented etchant.

Later on in the experiments, a new technique known as Deep Reactive Ion Etching (DRIE) became available. This is a modified RIE process which allow much larger aspect ratios to be obtained. The final reactors in this series of experiments were produced using either KOH etching or DRIE.
3.3.3 Wet Etching (Small Depths)

As there was no previous experience with silicon microfabrication, a series of exploratory experiments had to be conducted to discover the peculiarities of the methods. This culminated in a set of optimisation experiments to determine the optimum parameters for etching the desired structures using wet etching. DRIE technique optimisation was performed by a different researcher at the CMF.

3.3.3.1 First Attempt

Microfabrication was performed at the CMF. The test mask was used for this purpose. The features of this mask were large (channels 1 mm wide) and the intended depth was 50 µm. Various test structures were included as well. The most important of these were reactors which had baffles (0.1 x 1 mm) in the arms and one reactor with a 60° angle between the inlet arms.

![Figure 3.5: Channel dimensions of the basic test reactor](image-url)
As mentioned previously, all the etching in this experiment was performed using wet etching. A dilute hydrofluoric acid solution was used to etch the masking layer, which was a pre-deposited 500 nm layer of SiO₂. The following procedure was used (refer to Figure 3.7 for an illustrated summary of the procedure):

i) The wafer and mask were cleaned by immersing in acetone for 5 min and then in acetone vapour for a 5 min. This was done in an ultrasonic chamber.

ii) The wafer was then baked in an oven at 150 °C for 20 min.

iii) A layer of positive photoresist (AZ5214E) was spun on at 4000 rpm for 40 s using a resist spinner to give a 1.15 μm thick layer. This was followed by soft baking, where the wafer was placed on a hotplate at 90 °C for 2 min.

iv) A mask aligner was then used to place the mask just in contact with the photoresist layer. The wafer was then exposed to UV-light for 2 s.

v) The photoresist was then immersed in its developer, AZ326MIF for 45 s.

vi) Using a diamond scriber, the wafer was broken up into 6 pieces, each with a complete pattern of a microreactor.

vii) The SiO₂ layer was then etched using a HF solution (20 %). As the immersion time required was not known, each piece was dipped into the solution for a different duration before being washed and examined under the microscope.
viii) From an etch rate chart (refer to Appendix 3.5), a 20 wt% KOH solution at 80 °C would take 42 min to etch to a depth of 50 μm. It would also strip the remaining photoresist and etch slowly into the SiO₂ layer (~ 28 Å/min) (Madou, 1997).

ix) The remaining SiO₂ layer would then be stripped using a buffered HF (5:1) solution for 110 s. Si is also etched by this solution (0.23-0.45 Å/min) and this will smoothen the rough channel surfaces left by KOH etching (Madou, 1997).

This experiment was not successful in fabricating useful structures. Patterning of the SiO₂ layer using HF resulted in distortion. It was found that it had attacked the oxide located beneath the protective photoresist, even after immersion for only 5 s. Also, KOH etching, which was supposed to take 42 min to etch 50 μm, was retarded such that only 2 μm had been etched after 30 min. The factors which seemed likely to account for this are:

i) The wafers were completely covered by bubbles formed during the etching procedure. It is likely that this prevented fresh KOH from reaching the silicon surface, preventing etching. From this, it was learnt that some form of agitation was necessary for wet etching deep structures.
ii) The etch rate was similar to that of boron-doped silicon. It is known that boron (in excess of $5 \times 10^{19}$ cm$^{-3}$ solid solubility limit) reduces etch rates by about 20 times (Madou, 1997). It is possible that the wafer used for this experiment might have been previously doped with boron.

iii) There was some residue photoresist after the HF etch. As the resist is soluble in KOH, it may have retarded the etch rate.

3.3.3.2 Second Attempt

The procedure was changed to use dry etching (RIE) to etch the masking layer. The changes are described below, with an illustrated summary shown in Figure 3.8:

i) The wafer was pre-coated with silicon nitride on both sides using plasma enhanced chemical vapour deposition (PECVD). The operating temperature was 350 °C and the process took 80 min.

ii) After developing the photoresist, the nitride layer was etched using RIE. O$_2$ (at 4 sccm) and CHF$_3$ (at 70 sccm) were used. The power was set to 150 W while the pressure was kept at 100 mT. The process took 6 min.

iii) This was then followed by resist stripping using O$_2$ at 35 sccm and a pressure of 200 mT. The power level was at 100 W and the process took 8 min.

![Figure 3.8: Summary of the fabrication procedure using dry etching](image-url)
The results of this experiment and relevant comments are tabled below. Depths were measured using a profilometer, which uses an electrical probe to measure topography.

<table>
<thead>
<tr>
<th>Reactor Description</th>
<th>Etch depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) T, standard, no baffles</td>
<td>97.7</td>
</tr>
<tr>
<td>2) T, 2 equally-spaced baffles</td>
<td>94.9 - 100</td>
</tr>
<tr>
<td>3) T, 2 closely-spaced baffles</td>
<td>160.7 (~ 100 between baffles)</td>
</tr>
<tr>
<td>4) Y</td>
<td>160.9</td>
</tr>
</tbody>
</table>

Table 3.3: Results of the second attempt at microfabrication

There is a large variation in the results. This was due to the experimental conditions. For samples 1 and 2, etching was divided into 3 parts: initial etching at the CMF followed by inspection in the profilometer to determine etch rate. A second etch was then carried out. Then, a third etching was done at UCL. Samples 3 and 4 were etched entirely at UCL. The total etch time required to obtain a channel depth of 50 µm was based on that determined at the CMF, at what was thought to be 80 °C. It was later discovered that the experiments conducted at the CMF were at about 60 °C. As such, upon performing the experiment at 80 °C at UCL the etch rate became much greater resulting in the channels being much deeper than desired.

However, this was not a loss as the deeper etch resulted in other effects. The depth between the two closely-spaced baffles of Case 3 was less than that of the rest of the reactor. This was due to the slow-etching <111> planes. As they were sloped at 54.74° to the horizontal, etching stopped completely as soon as both slopes met, forming a channel of triangular cross-section (Madou, 1997).

It was also evident that the baffles had shortened. In Case 2, the length of the baffles were reduced by 20% from 1 mm to 813 µm. All convex corners had also been “blunted”. These effects were due to the etching of the <411> planes (Madou, 1997).
This undercutting is a function of etch depth and is less noticeable at smaller depths. These factors combined in case 3 to produce diamond-shaped baffles (see Figure 3.9). Undercutting also affected the Y-reactor, causing a widening of the arms. From this, it was learnt that deeper channels would have to take into account the effects of undercutting. In the case of greatly increased depth, corner compensation designs could be required. Alternatively, dry etching could be used.

![Figure 3.9: Sketch of the resulting baffles in Case 3 (not to scale)](image)

3.3.3.3 Third Attempt

A similar process was used as before, except for the following changes:

i) Silicon nitride was deposited using a DP800 PECVD machine. NH₃ and SiH₄ flowrates were 120 sccm and 19 sccm, respectively. Pressure was 320 mT and power input was 13 W, for a deposition rate of 67 Å/min. A 30 min process gave a 2010 Å thick layer. The process was repeated on the backside of the wafer.

ii) Silicon nitride removal was performed using a RIE 80 reactive ion etcher. CHF₃ and O₂ flowrates were 30 sccm and 5 sccm respectively. Chamber pressure was 100 mT and 250 W power was supplied. Process time was 8 min.
iii) The temperature of the etching solution, 20 wt % KOH, was 74 °C.

The aim for this experiment was to check the etch rate. As such, the wafer was removed from the etching solution at 20, 30, 40 and 45 min to check the etch depth. From the figure below, the etch rate was 1.26 μm/min. This was comparable to that found from empirically calculated etch rates (1 μm/min) (Appendix 3-5).

![Graph showing etch depth vs time](image)

Figure 3.10: Estimation of the etch rate of 20 wt % KOH at 74 °C

However, another unforeseen problem became evident: the bottom of the channel had rough patches, which were found only towards one side of the reactor. A likely explanation was that bubbles formed during etching were getting caught on the edge of one side of the reactor instead of being removed by the stirring. As such, fresh KOH solution was not as readily available to those regions, resulting in a less uniform rate. The rougher patches had dimples measuring less than 1 μm in depth.

It should be noted that anisotropic etching can result in notching and rough surfaces. Notching is described as a phenomenon in which the centre area of an exposed surface etches at a lower rate than the sides of those areas. However, while the notching effect was evident, neither it nor the predicted surface roughness came close to the
results. The expected surface roughness was less than 200 nm (Madou, 1997), whereas it was 5-10 μm in this experiment.

3.3.3.4 Optimisation of Etching Parameters

Due to unacceptable surface quality, four sets of experiments were conducted to optimise the etching parameters. Surface quality was examined using a profilometer.

i) Etch duration: 20 wt% KOH solution at 74 °C was used for etching. A magnetic stirrer was used (150 rpm). Wafers were examined after 20, 30, 40 and 45 min.

ii) Etchant concentration: Etching was done in 4M, 6M and 8M KOH solutions for 45 min each at 75 °C. A mechanical glass stirrer was used (~250 rpm).

iii) Temperature: Etching was carried out in 20 wt% KOH solution with agitation provided by a mechanical glass stirrer (~250 rpm). 5 experiments were carried out in the temperature range 60-90 °C.

iv) Agitation: Etching was carried out at 74 °C in a 20 wt% KOH solution. Stirring rates ranged from 248-760 rpm using a mechanical glass stirrer.

a) Etch duration

The results in Figure 3.10 above show a linear increase in depth with time. The final rate was higher as water had evaporated, thus increasing the concentration. To keep the concentration constant, a condenser would have to be attached to the etching rig.

b) Etchant concentration

The resulting surfaces were all smooth, with that performed in 8M KOH solution being the best. This is in accordance with results from other sources (Madou, 1997).
<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of KOH (wt%)</th>
<th>Agitation speed (rpm)</th>
<th>Average depth (µm)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, 4 baffles</td>
<td>20 (4M)</td>
<td>248</td>
<td>51</td>
<td>Smooth surface, except between baffles</td>
</tr>
<tr>
<td>Y</td>
<td>25.1 (6M)</td>
<td>244</td>
<td>48.8</td>
<td>Smooth, except at end of one arm</td>
</tr>
<tr>
<td>T, 4 baffles</td>
<td>30.9 (8M)</td>
<td>250</td>
<td>82.5</td>
<td>Smooth</td>
</tr>
</tbody>
</table>

Table 3.4: Effect of KOH concentration on etching

However, published data (Madou, 1997) has shown that the maximum etch rate for the <100> plane in silicon occurs at a KOH concentration of 4M (1.2 µm/min at 80 °C) and then decreases to 1 µm/min at 8M concentration. This contradicts the above results, in which the etch rate increased to 1.8 µm/min in an 8M solution KOH.

c) Temperature

The etch rate increases with temperature, as does surface smoothness.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Agitation speed (rpm)</th>
<th>Duration (min)</th>
<th>Average depth (µm)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, 4 baffles</td>
<td>40</td>
<td>749</td>
<td>60</td>
<td>2.7</td>
<td>Rough surface</td>
</tr>
<tr>
<td>T</td>
<td>60</td>
<td>250</td>
<td>45</td>
<td>22.4</td>
<td>One arm unetched</td>
</tr>
<tr>
<td>T, 2 equally spaced baffles</td>
<td>72</td>
<td>248</td>
<td>45</td>
<td>42.3</td>
<td>Smooth, except at baffles</td>
</tr>
<tr>
<td>T, 4 baffles</td>
<td>74</td>
<td>248</td>
<td>45</td>
<td>51</td>
<td>Smooth, except at baffles</td>
</tr>
<tr>
<td>Y</td>
<td>80</td>
<td>250</td>
<td>82</td>
<td>161</td>
<td>Smooth surface</td>
</tr>
<tr>
<td>T</td>
<td>90</td>
<td>250</td>
<td>45</td>
<td>111</td>
<td>Smooth, except at ends</td>
</tr>
</tbody>
</table>

Table 3.5: Effect of temperature on etching

Assuming a linear dependence of depth on duration, the above data would give the etch depths shown in the figure below after a period of 45 min. These were compared to literature values from another source (Rai-Choudhury, 1997). The difference between the experimental results and those reported by other sources is most likely due to differing methods of agitation. The best result was produced at 80 °C. The smoothest surface was obtained and the etch rate was high.
d) Agitation

The smoothness of the channel surfaces rose with agitation speed to a maximum and then decreased. The optimum was found to be 500 rpm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Agitation speed (rpm)</th>
<th>Average depth (μm)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, 4 baffles</td>
<td>248</td>
<td>51</td>
<td>Smooth surface, except between baffles</td>
</tr>
<tr>
<td>T</td>
<td>500</td>
<td>44.3</td>
<td>Very smooth surface</td>
</tr>
<tr>
<td>T, 2 widely spaced baffles</td>
<td>760</td>
<td>6.3</td>
<td>Very irregular</td>
</tr>
</tbody>
</table>

Table 3.6: Effects of agitation speed on etching

e) Effect of etch depth on etching

From the results obtained, another parameter which affected the smoothness of the channel was etch depth. It was found that as depth increased, so did the smoothness. These results are summarised in Table 3.7.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of KOH (wt%)</th>
<th>Temperature (°C)</th>
<th>Agitation (rpm)</th>
<th>Duration (min)</th>
<th>Average depth (mm)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, 4 baffles</td>
<td>20</td>
<td>40</td>
<td>749</td>
<td>60</td>
<td>2.7</td>
<td>Rough</td>
</tr>
<tr>
<td>T, 2 widely spaced baffles</td>
<td>20</td>
<td>74</td>
<td>760</td>
<td>45</td>
<td>6.3</td>
<td>Very irregular</td>
</tr>
<tr>
<td>T</td>
<td>20</td>
<td>60</td>
<td>250</td>
<td>45</td>
<td>22.4</td>
<td>One arm was almost unetched</td>
</tr>
<tr>
<td>T</td>
<td>20</td>
<td>74</td>
<td>500</td>
<td>45</td>
<td>44.3</td>
<td>Very smooth</td>
</tr>
<tr>
<td>T, 4 baffles</td>
<td>30.9</td>
<td>74</td>
<td>250</td>
<td>45</td>
<td>82.5</td>
<td>Smooth surface</td>
</tr>
<tr>
<td>T, 2 closely spaced baffles</td>
<td>20</td>
<td>80</td>
<td>250</td>
<td>82</td>
<td>161</td>
<td>Smooth surface</td>
</tr>
</tbody>
</table>

Table 3.7: Effect of etch depth on smoothness of channel surface
f) Optimised parameters

From the results, the optimum conditions for the fabrication of the T-microreactor are:

a) KOH concentration of 8 M (30.9 wt%)

b) KOH temperature of 80 °C

c) Agitation speed of 500 rpm

The duration will depend on the etch depth required. From section (e), an etch depth of 44.4 μm or more would result in a smooth channel surface.

3.3.4 Wet Etching (Large Depths)

With the optimisation of parameters and reasonable expertise gained, experiments were conducted to etch deeper to 300 μm. Using the optimised parameters, 257 min would be required for the etching (refer to Appendix 3-5 for the etch rate chart).

Agitation was provided by either an ultrasonic bath or a mechanical glass stirrer.

The use of the ultrasonic bath proved to be unsatisfactory due to several reasons:

i) While ultrasonics were on, the temperature of the KOH solution increased. The rate of increase varied with bath volume, ranging from 5-10 °C over 50 min. These changes in temperature resulted in changes in etch rate, which would affect the reproducibility.

ii) 'Pinpricks' developed on the surface of the nitride layer. These grew larger and deeper as etching progressed. By the end of the experiments, the wafers resembled sponges, as some portions of the wafers had been etched through completely. Also, the distinctive coloration of the nitride had disappeared completely from both sides of the wafer, indicating that it had been etched away.
The use of mechanical stirring also resulted in complete removal of the silicon nitride layer from both sides of the wafer. The channel areas of the wafer were completely etched through. Some 'pinpricks' were noticeable but the final wafer appearance was much smoother than that resulting from the ultrasonic bath experiment.

Since both methods of agitation resulted in removal of the nitride layers leading to etching through the wafer, the fault had to lie in the nitride layers. It was discovered that the process used for nitride deposition resulted in a low density layer (Madou, 1997), which was not suitable for deep etching (however, it was sufficiently resistant to KOH attack in the experiments where the etch depth was 50-150 μm). Therefore, subsequent wafers were coated with low pressure chemical vapour deposited (LPCVD) silicon nitride. This process results in a high density silicon nitride layer, which has an etch rate of less than 0.1 nm/min in KOH (Madou, 1997).

As for the difference in surface quality resulting from the two different agitation methods, it is believed that ultrasonic agitation may have caused increased stress throughout the nitride layer thus affecting the structural integrity which could have led to the higher density of 'pinpricks'. This, together with the difficulty in maintaining a uniform temperature, precluded the use of the ultrasonic bath in the future.

3.3.5 Finalised Etching Procedure

Based on the optimisation performed previously, the finalised procedure using KOH etching is summarised below. Also included is the dry etching process using Deep Reactive Ion Etching (DRIE).
3.3.5.1 Wet Etching using KOH

- Wafers: Single-side polished
  
  Diameter: 100 mm
  
  Orientation: <100>
  
  Thickness: 525 μm
  
  type/dopant: n-type/phosphorous
  
  100 nm LPCVD silicon nitride on both sides

- Photoresist AZ5214E: spun at 3000 rpm (60 s)
  
  baked at 90°C (60 s)
  
  exposed (2 s)
  
  developed in 4:1 AZ400 water/developer (60 s)
  
  hard baked at 120 °C (30 min)

- Nitride etch: 70 sccm CHF₃
  
  5 sccm O₂
  
  100 mT
  
  150 W
  
  duration: 8 min

- KOH etch: 30.9 wt% solution
  
  80 °C
  
  etch rate 70 μm/h
  
  duration: 2 h 51 min

Two different set-ups were used for KOH etching, one at the CMF and one at UCL. In the CMF set-up, the silicon wafer was suspended vertically in KOH solution, with agitation provided by nitrogen bubbling. However, in the initial configuration, the
bubbling occurred only near the surface of the solution and very close to the wafer. This resulted in very rough surfaces near where the bubbling occurred, and etching gradients (deepest just after the heavily agitated region and shallowest at the bottom end of the wafer). The bubbling was adjusted, and good results were obtained.

At UCL, the etching vessel was designed to allow a 4” Si wafer to be placed flat on the bottom of the etching vessel. Agitation was provided by mechanical stirring. The glass stirrer was offset to one side because in former experiments where the stirrer was placed in the centre of the vessel, there was a tendency for the wafer to be sucked up by the resulting vortex to smash against the stirrer. A condenser was incorporated to help maintain the concentration of the etching solution, and therefore the etching rate. The etched microreactor can be seen in Figure 3.13.

Figure 3.12: Etching vessel used at UCL
3.3.5.2 Dry Etching using DRIE

DRIE is essentially the same process as RIE, except that higher aspect ratios can be achieved. First, silicon oxide is deposited on the wafer and patterned (it plays the same role as silicon nitride in wet etching). Then, a passivating layer is deposited on top of that to allow the RIE process to etch deeper without compromising the “verticalness” of the sidewalls. Process optimisation and fabrication were performed by a researcher at the CMF, as the process required specialised equipment.

- Wafers: same as those used in wet etching but without the nitride layer. The polished side was coated with a 100 nm silicon oxide layer
- Photoresist: Etch depth < 200 μm: same conditions as for wet etching
  
  Etch depth > 200 μm: thick resist AZ4562 used
  
  spun at 4000 rpm
  
  film thickness 5.6 μm
  
  developed in 4:1 AZ400 water/developer (90 s)
  
  hard baked at 120 °C (30 min)

  Thick resist required because of poor selectivity (1:1) during the oxide etch
- Oxide etch: 20 sccm C₂F₆

  2.5 sccm CHF₃
50 mT
400 W

etch rate = 0.016 μm/min

- Deep etching using STS (Multiplex ICP): 130 sccm SF₆ (etch gas)
  5 sccm C₄F₈ (passivation gas)
  APC: 30 mT (etch)
  5 mT (passivation)
  coil power: 600 W
  platen power: 2 W
  etch rate: 2 μm/min

The results of the DRIE fabrication process are as follows:

- Si:SiO₂ selectivity 100:1
- Si:photoresist selectivity 50:1
- Sidewall angle 91°
- Roughness 200 nm (peak to peak)
- Initial mask undercut 0.5 mm/edge
- Uniformity of depth (across wafer) 7 %
- Uniformity of depth (wafer to wafer) 5 %

These results were within acceptable limits. The sidewalls of the etched channels were more vertical compared to those obtained through KOH etching, which was desirable. Furthermore, corners were not etched away, resulting in sharp, square corners. Some residue was left around the edges of most of the wafers, rendering the affected structures unusable. However, this method of fabrication is still definitely
preferable to KOH etching. But, it is slower and can only be performed at the CMF and there is a long waiting list to use the machine. As such, reactors were fabricated using both techniques.

Figure 3.14: Close-up view of DRIE reactor, note the sharper edges compared to wet etching

3.4 Anodic Bonding

To complete the reactor, the channels had to be covered. It had been decided to use glass plates as channel caps to allow observation of any changes to the reactor during and/or after reaction. The temperatures which would be used limited the choice of bonding techniques to anodic bonding and fusion bonding. Of the two, fusion bonding requires smoother surfaces for successful bonding and higher temperature. As such, anodic bonding was chosen, with fusion bonding as a possible alternative.

Pyrex 7740 glass was used as it has a similar thermal expansion coefficient with silicon. This is important to reduce the stress in the structure during and after the bonding. Because silicon is rather brittle, the glass wafer was made fairly thick (3 mm) to make the structure stronger. The added thickness would also make the reactor easier to handle and be connected to inlet and outlet tubing. However, there was the possibility that the thickness of the glass would cause difficulties in bonding.
Therefore, as with etching, exploratory work had to be performed. The commercial anodic bonders used comprised essentially of two metal plates located within a pressure chamber. The items to be bonded would be placed between the plates and heated, while the chamber was depressurised. Once the desired temperature was reached, a high voltage would be applied across the plates to cause bonding to occur. During this investigation, changes of equipment occurred, resulting in interruption of work. In the end, a simple system was built at UCL to perform this function.

In each of the following cases, the etched silicon wafer was cut up into its component reactors. The Pyrex wafers obtained were slightly larger than each reactor to provide protection against chipping the sides of the silicon. Each Pyrex wafer had 3 holes pre-drilled, corresponding to the location of the inlets and outlet of the reactor.

It must be noted that because the reactor is catalytic, a catalyst had to be deposited. Several techniques were attempted, both before and after bonding. To reduce repetition, all references to catalyst deposition in this section will be brief, with more details given in Section 3.5.

3.4.1 Initial Attempt

This was done at the CMF using an AML Anodic Bonder. The procedure used was:

i) Silicon nitride was first stripped using the RIE 80. CHF$_3$ and O$_2$ flowrates were 70 sccm and 4 sccm respectively. Chamber pressure was 100 mT and 150 W power was supplied. Process time was 8 minutes.

ii) Silicon and glass wafers were then cleaned in acetone using an ultrasonic bath.
iii) The anodic bonder was designed such that the silicon wafer would be loaded on a bottom plate that was vertically mobile, while the glass wafer would be loaded on to the bottom of a fixed top plate which was part of the cover for the pressure chamber. Alignment would then be performed visually using a microscope by looking through a glass window. Unfortunately, as the glass wafers used in electronics are much thinner than those used in this project (3 mm), the glass wafer could not be clipped to the top plate. As such, it had to be placed resting on top of the silicon wafer and properly aligned before sealing the chamber.

iv) The pressure chamber was then brought to a vacuum. This is not necessary for making a microreactor, but was part of the procedure for using the machine, which is used to package electronic components.

v) The temperature of both plates was then ramped up gradually to 365 °C. Heating was provided by 8 heat lamps placed around each plate to provide even heating.

vi) A voltage of 1.5 kV was then applied across the plates for bonding.

vii) After 90 min, the power was switched off and the chamber pumped to atmospheric pressure. Following this was a lengthy wait for the chamber to cool down before the completed reactor could be removed.

When the voltage was first applied, a large current was detected. As the bonding proceeded, the current decreased until it reached zero (with corresponding increase of voltage to 1.5 kV). Interference fringes which had formed at the surface of the silicon and glass interface upon clamping slowly disappeared throughout the process, to be replaced by a darker grey “wetted” colour. The initial results were promising. Bonding was achieved over most of the reactor, with only small isolated unbonded patches towards the edges.
3.4.2 Further Exploratory Work

Two further attempts were made at anodic bonding, the first with the machine used previously, and the second using a new AML anodic bonder. For the older machine, the procedure used was as before. The sample was KOH-etched, and had silver deposited in the reaction channel through evaporation (refer to Section 3.5). However, during the process of preparing the sample for silver deposition, the bonding surface was dirtied. A cleaning attempt was made by immersing the sample in acetone in an ultrasonic bath for 5 min. Some marks were still noticeable, but it was decided to carry on with the experiment.

After the process time elapsed, the sample was cooled using the recommended cooling procedure. At first, the sample seemed to be completely bonded. However, upon cooling, the structure rapidly de-bonded at various spots. When tested, the glass and silicon wafers were relatively easy to pull apart. The poor bonding in this experiment may have been due to the following reasons:

a) dirty surface: grease or other contaminants such as silver may have been present on the silicon wafer’s bonding surface. This would have interfered with bonding
b) rapid cooling: the unbonding was noticed to speed up whenever the cooling rate was increased. This may be due to stress within the silicon and glass wafers.
   There is also the possibility that either wafer had been warped during processing.
c) contaminants: a greasy smell emanated from the bonding chamber after the experiment. It is possible that some oil from the diffusion pump had leaked into the chamber during the process, thus contaminating the bonding surfaces.
The next attempt was performed using a new machine. This machine was an improvement over the last one, as it used a turbo pump instead of diffusion and backing pumps. As such, the pump down cycle was rapid. The heating arrangement was similar, as gradual heating was required to reduce stress in the wafers.

Because acetone did not seem to remove all traces of organic material, a new cleaning procedure involving a conventional plasma de-scum process using the RIE 80 was introduced. The process is the same as that used for photoresist removal, and would, in theory, remove all traces of organic compounds. The anodic bonding conditions were the same as before, except that a longer bonding time of 1.5 h was used.

A new development occurred during the bonding cycle: a crackling sound was heard when the voltage was applied. Also, the current dropped from 10 mA to virtually zero in 5 s. None of the interference fringes usually seen at the initial stages of bonding were evident. Instead, the entire interface had taken on the 'wetted' appearance seen upon complete bonding. As this had taken only a fraction of the prescribed time, it was decided to leave the sample in the chamber for the original period of time.

More care was taken with the cooling process this time. Unfortunately, the pieces still de-bonded as cooling proceeded. Again, it was observed that each time a quicker cooling phase was entered, more unbonding took place.

3.4.3 Development Work

Because of the samples were still de-bonding, it seemed likely that the surfaces were still not sufficiently clean. Therefore, instead of using an oxygen plasma for cleansing purposes, a commercial organic cleaner, EKC 265, was used. The solution was first
warmed to 70 °C before the reactor was immersed in it for 30 min. Distilled water was then used to rinse the reactor. Nitrogen was first used to dry the sample, followed by baking at 100 °C for 15 min.

The following procedure was used for the bonding process:

- chamber at vacuum
- platen temperature: 385 °C
- voltage: 1.0 kV
- current limit: 1.4 mA
- duration: 10 min

Additionally, stainless steel washers were placed on top of the inlet/outlet holes on the glass. It was thought that this would help focus the electric field and therefore improve bonding as, previously, the areas most susceptible to unbonding were around the inlets/outlet. Bonding is believed to have taken place after 2-3 min, as the current was seen to drop to about zero by then. However, the experiment was left running for the full 10 min. Bonding was successful, with no noticeable large unbonded areas.

Anodic bonding was also performed at the Central Research Laboratories (CRL) following the above procedure, but instead using a piranha solution (1:1 H₂SO₄/H₂O₂ mixture) for cleaning and without the use of the stainless steel washers. Bonding was also successful, suggesting that the washers were not required to aid the process. It was also decided to use the piranha solution for all future bonding experiments as well, as it removes inorganic substances as well. Another reason was that the organic solvent proved incompatible with the deposition of silver through evaporation, as detailed in section 3.6.1.
3.4.4 Simple Anodic Bonder

In an attempt to perform as much of the fabrication at UCL as possible, a simplified version of the anodic bonder was set-up. Because the reactor did not need to be vacuum sealed, a pressure chamber and vacuum pumps were unnecessary. A hot plate was used as the heat source. A flat stainless steel plate was placed on top of the hot plate as the cathode. The silicon wafer was placed on top of the cathode, with the glass resting on top of it. A screw, which was mounted on a clamp, would press on to the top of the glass wafer to provide clamping pressure and serve as the anode. The main concern was that the temperature of the glass would be far removed from that of the silicon wafer, thus causing a lot of stress after the bonded reactor cooled.

Both silicon and glass wafers were first cleaned in piranha solution before bonding. The bonding behaviour differed from that outlined above. As the voltage increased, the current would increase slowly as well. However, past 1 kV, the current would start fluctuating wildly and sparks would start appearing. Therefore, in this set-up, the voltage was manually increased from 500 V to 1.5 kV. The process took about 2 h. The longer period was due to the fact that bonding was not complete over the entire
wafer. Once the anode contact point was to be moved to the unbonded sections, bonding occurred as before. This difference in behaviour may be due to the use of a point as the anode as opposed to a plate. While complete bonding takes a lot longer with this set-up, it does allow the process to be carried out in-house at UCL.

3.5 Silicon Fusion Bonding

As a back-up alternative to anodic bonding, a brief investigation into using silicon fusion bonding was carried out. Normally, fusion bonding takes place at 1000 °C. However, by applying a thin layer of sodium silicate solution between the bonding surfaces, bonding can occur at as low as 150 °C.

When a silica surface is contacted with water, it reacts to form silanol groups (SiOH). The addition of sodium silicate makes the surface more hydrophilic and planarises the roughness of the wafer. When two such wafers are contacted, they are pulled close together by the attraction between the hydroxyl groups and water molecules. As the samples are heated to 150 °C, the adsorbed water vaporises, leaving hydroxyl groups which form Si-OH-OH-Si bonds between the wafers. Dehydroxylation then occurs, in which siloxane (Si-O-Si) bonds are formed. The presence of the alkali ions from the sodium silicate solution lowers the temperature of the dehydroxylation by 100-200 °C. The process works better at 150 °C than at higher temperatures because water from the dehydroxylation process needs to diffuse away. At higher temperatures, water is produced too quickly and is unable to diffuse out of the sample, which results in bubbles. These bubbles prevent bonding from occurring (Puers, et al, 1997).
A semi-bonded sample from a previous anodic bonding exercise was used to test the applicability of this method. The sample was first boiled in nitric acid (1M) for 10 min to increase surface hydrophilicity. Next, the entire sample was dipped into a 2% sodium silicate solution. It was left until all unbonded regions had been filled with sodium silicate solution through capillary forces. Then, the sample was placed on a hotplate at 150 °C. Unfortunately, the wafer unbonded further around the already unbonded regions. It is believed that this occurred because the heating was too rapid. In addition to this, the water in the solution most likely vaporised too quickly, resulting in a sudden expansion of vapour in the unbonded regions. These two effects caused even more stress to the unbonded areas, thus causing further unbonding.

Fresh pieces of silicon and glass were then used in a subsequent experiment. The conditions were as before, with the difference that the temperature was slowly brought up to 150 °C. The result was a bonded sample. However, trapped bubbles could be seen, suggesting that an even slower temperature ramp might be preferable. The seal, though, was fairly strong and it took a fair amount of effort to prise the wafers apart.

It was later determined that a concentrated nitric acid solution should have been used instead to make the surfaces hydrophilic. This main drawback to this method is the application of the sodium silicate solution, which is difficult to keep out of the channels. Anodic bonding was clearly the better method for fabricating the reactor.

3.6 Catalyst Deposition

Catalyst deposition proved to be a major hurdle, as conventional impregnation methods were not applicable without complicating the device further. The methods
had to be compatible with microfabrication methods as well, especially those that were performed before anodic bonding. All the deposited material took the form of thin films. As such, they all had to be tested for adhesion as degradation of thin films has been reported (Firebaugh et al, 1998, Sharma et al, 1979).

3.6.1 Evaporation

In this method, the entire reactor, with the exception of the reaction channel, was covered. This was done using either a shadow mask or the lift-off method. In the case of the shadow mask, a solid mask (made either from silicon or cut-out foil) was placed in contact with the reactor such that only the reaction section was exposed. The evaporated silver would therefore only go in the channel. This was vital as the presence of silver on the top surface of the wafer would prevent anodic bonding.

For the lift-off method, photoresist was painted on to the wafer by hand. Conventionally the resist is patterned by photolithography, but the features in this case were large enough to be marked out by hand. Again, only the reaction channel was left uncovered. Exposure to silver vapour resulted in coverage of the entire wafer. The wafer was then immersed in acetone to remove the photoresist, and therefore, the silver that was deposited on the photoresist, leaving behind silver in the reaction channel only. This lift-off process took longer than that shadow mask process.

An Edwards Evaporator (E306A) was used. This machine utilised resistive heating to vaporise the coating metal. Some silver wire (Goodfellow, 99.99% Ag, 0.8 mm diameter) was coiled up, and placed on to a molybdenum boat, which was then connected to electrical contacts. The sample was placed directly above the boat, with
the reactor side facing down towards the boat. The chamber was then sealed and pumped down to vacuum. The current was gradually increased until the silver wire melted. Some of it was allowed to evaporate off to get rid of any surface impurities before a sensor detecting deposition rate was switched on.

The sensor comprised of an oscillating crystal. The frequency of oscillation depended on the weight of the crystal. Therefore, deposited material would change the frequency and this could be used to determine the deposition rate. Since the evaporated material spread uniformly in a hemispherical fashion and the sensor was located at the same distance from the boat as the target, this would give the rate at which the evaporated material was deposited on the target and allow the thickness of the deposited material to be determined. The deposition rate was kept in the 4.8-5.8 Å/s range. A 0.1 μm thick layer was deposited.

Unfortunately, adhesion proved to be poor, as some of it got blown off at a later time using blasts of air. The same occurred to samples that were washed using the EKC 265 organic cleaner prior to anodic bonding. This suggested that the bonding surface of the reactors had to be cleaned prior to silver deposition. This would certainly prove to be a problem with the lift-off process as it involved the deposition of an organic layer. As such, the lift-off process was deemed unsuitable. At the same time, it was concluded that the evaporation method was not the best way to do this due to the relatively low degree of adhesion.

3.6.2 Manual Placement

Silver foil (Goodfellow, 99.95+, 25 μm thick) and wire (Goodfellow, 99.99%,
annealed, 125 µm diameter) were used for this investigation. They were cut so that they could be physically placed into the reaction channel prior to bonding.

An attempt was first made to melt the silver wire in order to increase the surface area available for reaction. This was done by placing the wire on a piece of silicon in a furnace at 970 °C (the melting point of silver is 961.9 °C). Unfortunately, this led to the melting of the wire followed by agglomerisation into two droplets. Molten silver clearly did not wet silicon, and this method would not be applicable. Therefore, catalyst surface area would have to be increased by placing multiple wires in parallel. In theory, four pieces of wire would fit side-by-side.

The process of fitting the wires or foil into the channel was not simple. The wire came coiled and had to be straightened. This proved to be difficult to do in practice. Initially, it was attempted to place a single long piece of wire in the long serpentine reaction channels. This turned out to be exceedingly difficult due to the fragile nature of the wire. To solve this problem, lengths of wire were cut to fit into the long sections of the serpentine channels, leaving the shorter adjoining sections empty. Yet another problem showed up in the attempt to place four pieces of wire into each channel. Because it was almost impossible to straighten the wire completely, only three pieces could be placed into each channel. And additional difficulty was that the slightest disturbance to the reactor would spill the wires out of the channels.

As for the foil, it had to be cut into strips 600 µm wide. Each strip was then pressed into the channel. The problem lay in the cutting process, where the stress would curl the strip. Each strip had to be straightened, and a technique had to be developed to
place them flat in the channels. Comparing the two methods, the foil was preferable as the strips were easier to place, and, more importantly, filled up the entire width of the channel. Another advantage was that the foil was firmly pressed and fixed into the channel, while the wires were placed with no anchoring. While this was not likely to have any impact on the serpentine reactors, the wire method would not be as useful in the straight configuration, as they could move into the mixing or quenching sections.

The main test was whether either method would affect anodic bonding. For this investigation, the reactors were cleaned in the organic cleaner before the catalyst was placed inside. The silver wire had an obvious effect on the bonding, as the current did not drop down to 0 mA as quickly as previously observed. In fact, it took about 8 min for it to do so. Upon removing from the bonder, it was found that bonding was very bad, with lots of little bubbles.

For the silver foil, the current took 9 min to drop to 0.1 mA and did not reduce any further. However, the reactor turned out to be perfectly bonded which led to the conclusion that the sample with the silver wire had its bonding surface contaminated while the wire was being placed within the reaction channel. This was very likely as that process took much longer to accomplish.

It is believed that the silver may act as a conduit for transferring charges. This would explain the presence of a small electric current even at the end of the bonding period. However, based on the successful bonding of the sample with the foil, this phenomenon does not seem detrimental to the bonding.
The placement of the silver foil was less tedious than the silver wire. Both these methods seem implementable, however, less tedious methods would be preferable.

3.6.3 Electrodeposition

As silicon is a semiconductor, it would be possible to deposit silver on it using electrodeposition. A rudimentary rig involving a power supply, a plating solution and electrodes was made up to investigate this possibility. A 0.2 M solution of silver nitrate was used for this purpose. A piece of silver wire (0.8 mm diameter, 99.99%) was used as the anode, and various pieces of silicon were used as the cathode. The following experiments were performed:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Current (A)</th>
<th>Voltage (V)</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>1</td>
<td>33</td>
<td>Very quick deposition. Deposit not washed off by water but could be wiped off. Annealing at 400 °C seemed to improve adhesion</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.02</td>
<td>2</td>
<td>Slow deposition. Deposit not washed off by water but could be wiped off. Annealing at 400 °C seems to improve adhesion</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.02</td>
<td>3</td>
<td>Sparse yellow strings formed initially, but they changed to silver strings after a while. Annealing at 400 °C left an uneven surface</td>
</tr>
<tr>
<td>Partially coated by silicon nitride</td>
<td>0.02</td>
<td>30</td>
<td>White deposit formed. No changes even after prolonged period (1 h). Washing left the layer, but it came loose upon light brushing.</td>
</tr>
</tbody>
</table>

Table 3.8: Electroplating experiments

The first two results were very non-uniform. This may have been due to the solution being dirty from the initial set-up tests. The solution was cleaned before the third experiment, and filtered before the fourth.

The last experiment was different in two ways. First, the substrate was partially coated with silicon nitride to determine whether silicon nitride would prevent
deposition of silver. Being an insulator, it could be assumed that this would be true.

However, it was decided to test whether exposure to an electric current would affect the nitride layer. The result was that the deposit only formed in the areas where silicon was exposed, and there were no noticeable changes to the nitride layer.

The second difference was that the deposit had a sandwich structure. After removal from the silicon wafer, one side of the white deposit was scratched off to reveal a thin silver foil underneath it, i.e. the deposit took the form of a silver foil sandwiched between two white layers. The outer white layers were not well adhered to the silver foil. It is possible that the bottom-most white layer formed due to a dirty silicon surface, and the third layer formed due to oxidation of silver upon deposition. It is known that the solution and electrodes have to be very clean for electroplating. The silver electrode had been oxidised during the set-up experiments and this may be the cause of the oxidation. Industrial silver plating is performed with other additives, which serve to prevent such oxidation (Paunovic, et al, 1998, Canning, 1978).

Following these exploratory experiments, electrodeposition was attempted on actual reactors. To ensure that silver was only deposited in the reaction channel, silicon nitride-coated wafers were used. Therefore, the wafers were KOH-etched. Following etching, the silicon nitride on the backside of the wafer was removed to provide an area for attaching an electrical contact to the wafer. Photoresist was then painted over the non-reaction sections of the exposed channels to restrict deposition of silver to the reaction channel only. Photoresist was left overnight to dry in each case.
In the first attempt, the reactor was dipped into a 0.1 M solution of silver nitrate. A current of 0.02 A was used. Unfortunately, after 100 min, no appreciable deposition could be seen on the reaction channel. However, a layer of silver could clearly be seen on the back side of the wafer where the nitride layer had been stripped off completely. It was thought that because the backside provided much less resistance due to the much larger surface area, the silver preferentially deposited there.

Therefore, the backside of the second sample was painted with photoresist as well (apart from an area for electrical contact). This time, silver could be seen in the channels after 2 h. The sample was subjected to further electroplating for another 2 h 40 min to obtain a thicker deposit. However, deposition was uneven. It was observed that the silver had preferentially deposited on the sloping side walls, with little on the bottom of the channel. In comparison, a previous test done on a DRIE sample, which had vertical side walls, had resulted in deposition on all surfaces. This led to the conclusion that the $<111>$ crystalline plane of the sloping sidewalls may have an effect on deposition. The photoresist was then stripped using acetone and the sample calcined in a furnace at 400 °C for 30 min before nitride stripping and bonding.

3.6.4 Silver Deposition using an In-situ Chemical Reaction

This method was different in that it would allow silver deposition to be performed after bonding. This would be definitely advantageous as the main worry with anodic bonding was the contamination of the bonding surfaces immediately prior to bonding, which would result in unsatisfactory bonding. This method would also open up the possibility of stripping deactivated catalyst, and then re-depositing fresh catalyst.
A silver mirroring solution was chosen for this reaction, similar to that used for making home-made mirrors (http://www.gaynor.co.uk/reports/secrets/sec14.html). It is similar to Tolren’s reaction, a test solution for aldehydes in which silver is deposited on a glass surface when Tolren’s reagent is mixed with a sample containing an aldehyde. The reaction requires the mixing of two solutions, the preparation of which are detailed below:

Solution 1

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver nitrate (A)</td>
<td>0.648 g</td>
</tr>
<tr>
<td>Silver nitrate (B)</td>
<td>0.518 g</td>
</tr>
<tr>
<td>Distilled water</td>
<td>142 ml</td>
</tr>
<tr>
<td>Ammonia solution (35 %)</td>
<td>amount used as detailed below</td>
</tr>
</tbody>
</table>

1) Silver nitrate (A) was added to 56.8 ml of distilled water in a glass beaker. The solution was stirred using a glass strip.

2) Using a dropper, ammonia solution was added one drop at a time. Initially, the solution became a murky grey, but upon addition of further droplets became clearer. Ammonia was added until the solution was clear.

3) Silver nitrate (B) was then added, stirring with a glass strip. A precipitate formed.

4) The solution was then added to the remaining distilled water, and was left aside for 1 h to allow sedimentation. The mixture was then filtered to obtain a clear colourless solution, and stored in a bottle in a cool dark cabinet.

Solution 2

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium potassium tartrate</td>
<td>0.389 g</td>
</tr>
<tr>
<td>Silver nitrate</td>
<td>0.405 g</td>
</tr>
<tr>
<td>Distilled water</td>
<td>342 ml</td>
</tr>
</tbody>
</table>

1) The distilled water was boiled, and then sodium potassium tartrate was added to it. The solution was boiled for 1 min.
2) Silver nitrate was then added, and the resulting mixture boiled for 5 min.

3) The mixture was left to cool, after which it was poured into another beaker as the original beaker was covered with precipitate. The mixture was then left to settle for 1 h and then filtered to obtain a clear colourless solution which was bottled and stored in a cool dark cabinet.

The procedure for precipitating silver on silicon is as follows:

1) A test piece of unpolished silicon was placed on a hot plate and warmed to 40 °C. The piece of silicon was cleaned before the experiment commenced.

2) Equal volumes of Solution 1 and Solution 2 were mixed quickly in a glass beaker. Using a dropper, 4 droplets of the mixture were placed on the silicon to form a small pool. The pools were left on the silicon for 10, 15, 20, 25 and 30 min respectively, before being rinsed off with distilled water and left to dry.

3) The main concern at this point was adhesion. As such, each of the precipitates was lightly wiped to test for adhesion.

4) The experiment was repeated at 50 °C with pools left on the silicon for 30, 40, 50 and 60 min respectively. A fresh mixture of solutions 1 and 2 was used.

5) A final experiment was performed using a piece of polished silicon at 50 °C, with the mixture being left for 70 min. A fresh mixture of solutions 1 and 2 was used.

The results of the experiments are shown in Table 3.9. In all of the experiments beside experiments 3-5, precipitation occurred almost immediately upon placing the mixture on to the warmed silicon wafer. In Exp 3 and 4, deposition was retarded, but did eventually occur. In Exp 5, however, no precipitation was noticeable. It is evident from this that the mixture of solutions 1 and 2 had to prepared immediately prior to
use, as a mere delay of 6 min resulted in significantly less precipitation, with no reaction whatsoever after 11 min. Before this experiment had been conducted, it had been thought that the reaction was heat activated. Examination of the beaker in which the solutions were mixed showed a silver layer had been deposited at room temperature. This is most likely why no precipitation occurred in Exp 5. As such, for the later sets of experiments, the solutions were mixed immediately before each application.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>30</td>
<td>Appreciable deposition, but can be wiped off</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>25</td>
<td>Appreciable deposition, but can be wiped off</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>20</td>
<td>Less deposition, but easily wiped off</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>15</td>
<td>Less deposition, but easily wiped off</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>10</td>
<td>No deposition</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>30</td>
<td>Appreciable deposition, better adhesion than tests 1-5</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>40</td>
<td>Appreciable deposition, better adhesion than tests 1-5</td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td>50</td>
<td>Appreciable deposition, better adhesion than tests 1-5</td>
</tr>
<tr>
<td>9</td>
<td>50</td>
<td>60</td>
<td>Appreciable deposition, best adhesion</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>70</td>
<td>Appreciable deposition, no adhesion</td>
</tr>
</tbody>
</table>

Table 3.9: Results of silver mirror experiment

While the source of the silvering solution suggested a duration of 30 min for precipitation, the experiment lasting 60 min had the best results. This may be due to a difference in application, i.e. when intended for mirrors, a layer of backing paint was applied, followed by affixing a backing board.

The final experiment resulted in appreciable deposition, but no adhesion whatsoever when the precipitate was wiped off. No effort was required to completely remove the precipitate. This was almost certainly due to the highly-polished silicon surface. The other experiments were performed using silicon surfaces which had been wet-etched in KOH solution. This would be advantageous if this method was applied before
anodic bonding as any deposition resulting from spillover of solution out of the reaction channel could be rectified simply by wiping it off.

Another observation was that the precipitate was not shiny. Examination of the precipitate that forms on the glass beaker in which the solutions are mixed showed that there were two layers: a shiny silver surface seen from the outside of the beaker, and a dull, brownish matt surface like the one on the silicon was noticeable on the inside of the beaker. As such, it is believed that a layer of silver does form under the matt surface seen on the silicon wafers. The matt surface is likely to be silver oxide.

The next stage was to test the compatibility of the method with anodic bonding. Fresh solutions were made, and silver was deposited on two samples. Excess silver deposited on the outside of the channels was wiped off. One sample was subjected to anodic bonding without further cleaning, as it had previously been cleaned in the organic cleaner. Bonding failed to take place around the reaction channel, where excess silver deposit had precipitated. While the area had been visually observed to be clean, it appeared that even traces of contaminants could disrupt the bonding process. The second sample was placed in the organic cleaner. Unfortunately, almost all of the silver deposit was removed. Therefore, this method was not easily compatible with anodic bonding.

Deposition was then attempted in a bonded reactor. Syringe pumps were used to pass the solutions continuously through the reactor, which would mix in the reaction channel forming a deposit. The continuous flow would bring in fresh reactants which would result in a thicker layer. A low flowrate was used to allow a chance for
deposition to occur. After almost no deposition occurred, the flow was stopped, and the reactor left on the hot plate at 50 °C. Some deposit formed, and as soon as no further change appeared to take place, the reactor was flushed, and then dried by heating to 150 °C. In an attempt to improve the adhesion of the catalyst, the reactor was placed in a furnace at 400 °C for 30 min. An earlier test conducted by placing a beaker coated with the deposit into a furnace at those conditions resulted in the transformation of shiny silver layer backed by a matt layer to a light yellow residue. The same thing happened to the deposit in the reactor, though the deposit was of a darker colour. Of note is that no deposit had formed on the glass surface, suggesting that the reaction may either require a slightly rougher surface or that the precipitate actually forms in the solution before sinking to the bottom.

Upon closer examination of the sample, it could be seen that the deposit was uneven. One side of the reaction channel had more catalyst. In fact, some diffusion had occurred after the flow had been stopped and there was a small amount of deposit noticeable in the pre-heater on the same side of the reactor. It seems as if most of the reaction occurs in the solution which does not contain the tartrate salt.

A different approach was attempted next. A small amount of both reactants was mixed in a beaker and then taken up in a syringe. The mixture was dripped into the outlet of the reactor, drop by drop. Capillary forces sucked in the mixture. Whenever the movement of the liquid front stopped another drop was added to drive it further into the reactor, until it reached the beginning of the reaction zone. After allowing 30 min for the precipitate to settle, the reactor was heated to 150 °C to dry off the remaining fluid. It was then placed in the furnace at 400 °C for 30 min to anneal the
deposit. The volume of the deposit visibly decreased after annealing. This process was performed 3 times before the channels appeared to be in danger of blockage. This method was clearly applicable, with only the activity of the catalyst to be determined.

The yellowish coloration of the deposit threw some doubt on the activity of the catalyst as it was not clear whether it was a simply a silver oxide layer or whether there was some organic contaminant present as well due to the tartrate solution used. Therefore, a different reaction was tested as well. First, an ammoniacal silver nitrate solution was prepared. Dilute ammonia solution was added dropwise to 10 ml of a 0.1 M silver nitrate solution until a precipitate formed. More was added until the precipitate dissolved again. 1 ml of formalin solution was added to 3 ml of the ammoniacal solution and the mixture was agitated. Droplets were placed on to 2 small pieces of polished silicon, and some was injected into a microreactor. Silver should precipitate according to the following reaction:

\[
\text{HCHO} + 2[\text{Ag(NH}_3\text{)}_2]\text{OH} \rightarrow \text{HCOOHN}_4 + 2\text{Ag} + 3\text{NH}_3 + \text{H}_2\text{O}
\]

All the samples were then heated at 50 °C for 1 h. They were then washed in hot distilled water (70 °C) and dried at 110 °C. One of the silicon samples was calcined in an oven at 550 °C for 4 h, while the other sample was calcined at 800 °C for 4 h. The sample in the microreactor was calcined in the reactor set-up. A white layer was seen on all of the samples. It was thought that this reaction, although involving formalin, used organic compounds which could be easily decomposed to give pure silver catalyst.
This catalyst was also tested in a laboratory fixed bed reactor by another researcher. A piece of silicon was ground into small particles. The above ammoniacal solution was prepared and the silicon particles were mixed in before the formalin solution was added. The entire mixture was then stirred for 30 min at 50 °C and then left to stand for 1 h at 60 °C. The particles were then filtered out of the solution and washed 5 times in distilled water. Again, the particles were dried at 110 °C and then calcined at 800 °C for 4 h. 0.03 g of the particles were then placed in a tube reactor for testing. The catalyst proved to have high activity, thus giving more confidence to the catalyst in the microreactor.

3.7 Experimental Set-up

In the original set-up, liquid methanol feed was pumped into the reactor using a syringe pump (Razel A-99). Pure oxygen was fed using a mass flow controller (Brooks 5850 TR, 0-20 ml/min O₂). The product stream led directly to a GC (Trace GC, CE Instruments) for online detection of products. Piping was 1/8” stainless steel tubing except for the tubing connections to the inlet/outlet clamps, which were 1/16”.

![Figure 3.16: Schematic of the experimental set-up](image-url)
The tubing between the outlet of the reactor and the GC was covered with heating tape to ensure that the products remained in a gaseous state upon entering the GC. It was vital that the temperature of the product stream never dropped below 80 °C between the outlet of the reactor and the GC as formaldehyde would polymerise. This section and the reactor was covered in lagging as well. Pressure drop in the reactor was monitored using a manometer and the temperature using thermocouples (K-type).

The heating of the reactor was a major concern, as was interfacing the reactor with the feed and product streams. These are discussed below.

3.7.1 Method of Heating

The heating stage went through several designs. In all designs, heating was provided by cartridge heaters (Watlow) which were inserted into a stainless steel base on which the reactor rested. A slot, corresponding to the quench section of the reactor, was cut through the platform to prevent direct heating of the reactor at that section.

The temperature profile in the initial design of the heating block was checked to determine the uniformity of heating. Four cartridge heaters were connected to a variable voltage transformer and placed into the block. A high temperature thermocouple (industrial mineral insulated probe, type K) was used to measure the temperature at 5 mm intervals along the centre of the block, starting from the edge of the quenching section closest to the heaters (shown in diagram below). One series of measurements was taken at each voltage setting, for a set of 6 results (10, 20, 40, 50, 70, 80 % of full scale). The set-up was lagged using insulating fibre, and was allowed up to several hours for the temperature to equilibrate at each setting.
The block was 0.6 cm thick. As can be seen in the diagram above, there were 5 cavities for cartridge heaters. Only the 4 closest to the quenching area were used as these covered the entire reaction zone and most of the pre-heat section. The temperature profile is shown below.

Figure 3.17: Heating block

Figure 3.18: Temperature profile of heating block
The profiles above show a relatively rapid drop-off in temperature just after the 25 mm mark at the higher temperatures. However, more importantly, the region around the reaction section (0-15 mm) had a fairly even temperature profile. And, there was only a slight drop in temperature in the region between 15-25 mm, which covered the pre-heat section which did not require temperatures as high as the reaction section. Therefore, the system appeared to be adequate for running experiments. To further improve temperature uniformity, the reactor was placed in a ceramic housing.

3.7.2 Input/output Interface

A clamping mechanism was used to connect the reactor to the inlet and outlet streams. Both interfaces screwed on to the heating block. As with the heating block, the interface went through several configurations. In the initial design, the position of the inlet interface was mobile while the position of the outlet was fixed. This was done to accommodate the possibility of having different reactor lengths eventually. The clamps were made of stainless steel. 1/16" stainless steel connectors (IMM) were used to connect to the feed or outlet systems (refer to Appendix 3-6 for a more detailed diagram of the assembly).
Teflon sheets were originally chosen for gaskets. They also acted as a compression layer to reduce the stress placed on the reactor by the clamp. While the operating temperature would be well above the maximum allowable temperature of Teflon, the gaskets would only come into contact with the top of the glass wafer which would be cooler. Therefore, an investigation was carried out to determine the temperature of the glass surface when the platform was heated to 450 °C. An anodically bonded reactor was used for this purpose. With the surface open to the atmosphere, the temperature on the top surface was found to be 320 °C. Unfortunately, this was above the operating temperature of Teflon. This necessitated a change in gasket material.

There was some difficulty in obtaining alternative gasket materials as the gaskets had to be both compressible to prevent damaging the reactors upon clamping and be able to operate beyond 320 °C. Finally, two materials were found: SGE Auto Sep T septa and Supergraf plain jointing flat compressible graphite sheets. The septa comprised of a Teflon sleeve containing silicone, but had an upper temperature limit of 350 °C. The graphite sheets were made of 98 % pure exfoliated graphite and had a maximum operating temperature of 500 °C in oxidising media.

3.7.3 Testing of the Set-up

The sealed reactors were connected to syringe pumps via the interface and water was pumped through to check for leakage. The clamping mechanism proved to be satisfactory. Next, the reactor was tested at the boiling point of water. Again, no leaks were detected (a mirror was placed near possible leak points to check for condensation). Because of this, it was decided to raise the temperature closer to 128...
reaction conditions to investigate the performance of the clamps, and also to observe the boiling behaviour within the channels.

As the temperature of the stainless steel bottom block was raised to 438 °C (70 % of full scale voltage), the evaporation front moved closer to the inlets. However, it should be noted that the front was not stable. A sort of pulsing ranging through the entire length of the pre-heat section could be visibly observed. As the temperature increased, the extreme end of the pulse came closer to the inlets.

It is believed that this phenomenon occurs in the following steps: first, liquid fills the channels. Then, as heat is transferred to the liquid, it evaporates. Since the reaction section of the reactor is hotter, the sections of liquid closest to it would evaporate first. The evaporation front then moves towards the inlets. At the same time, the evaporated liquid expanded in all directions. Some of the vapour moved forward through the reaction section and left the reactor, while some of it pushed liquid backwards. As the evaporation front moved backwards, a point would be reached where there would not be enough heat to evaporate the liquid, and the front would stop. Without additional vapour forming, an equilibrium will be reached between the vapour and the liquid. However, since the liquid was still being pushed forward by pumps, there would be a driving force behind the liquid, while there was none behind the vapour. And so, the liquid would enter the channels again, and the cycle repeated.

At a bottom block temperature of 438 °C, no leaks were detected. However, all boiling was found to occur as soon as or even before the water entered the pre-heat section. The inlet tubes were found to be very hot, above the boiling point of water.
As the boiling point of methanol is much lower, it seemed that the pre-heaters had been over-designed. The two heating cartridges closest to the pre-heat section were removed, and heating was still adequate.

It was previously known that there was a slight but acceptable temperature variation along the length of the heating block, due to the heaters being placed at one end of the block. It was found from this experiment that there was a significant temperature variation across the width of the block as well. The end which was further from the insertion point of the cartridge heaters was found to be cooler. This was deduced from the fact that water could be seen to penetrate further in that side of the pre-heater before being evaporated. A new heating block was made to correct this.

The new interface/heating block consisted of two parts, a top block containing the inlet/outlet interface and a bottom block containing the heating and thermocouples. The bottom block was flat, with 4 large holes on one side to accommodate heating elements and a series of small vertical holes in the middle for thermocouple placement. It has the same length as the reactor to minimise heating requirements and retained the air gap directly beneath the quenching segment of the reactor. The four corners extended outward (perpendicular to the length) to provide an area for screwing down the top plate. Refer to Appendix 3-7 for a diagram.

The inlet and outlet consisted of one plate instead of two separate pieces. It was decided to standardise the length of the reactor, thereby making two separate pieces unnecessary. A depression with the same width as the reactor passed across the entire length of the undersection of the plate to ease reactor alignment. A cavity was cut into
the centre of the plate to expose the reactor, so that any changes to the catalyst or reactor could be observed without taking apart the assemblage.

The completed structure was then placed in a ceramic fibre block to prevent heat losses. The block was wrapped in foil to avoid particulate contamination. The heating of the block was tested first. Again, this was done using just two heating cartridges. It was found that heating was slower than before, even though the amount of metal in the bottom block had decreased. This led to the conclusion that the top block acted as a heat sink as well, as it was much bulkier than its previous incarnation. However, the new interface was much easier to use and align.

The septa mentioned previously were tested first. Holes measuring about 2 mm in diameter were drilled through them using a hand drill. Alignment with the inlet and outlet holes was relatively simple to accomplish. When the bottom block was heated to reaction temperature, no leaks were detected and the septa did not appear to lose coherence. The assembly was heated and cooled for several days running before it was taken apart. Unfortunately, the Teflon coating had become harder and somewhat brittle over the course of the heat treatment. This presented problems when attempts were made to re-use them, as close contact between septa and glass surface could not be achieved after hardening, which led to leaks. The through-holes also appeared to have narrowed in some cases. Therefore, the septa could not be re-used. Eventually, experimentation involving reactants (as detailed in the next section) also led to the conclusion that some volatile material from the septa could have caused deactivation of the silver catalyst. Therefore, it was decided not to use the septa further.
This left the graphite sheets. The sheets obtained were 1 mm thick. Holes 4 mm in diameter were made through them, aligned with the inlets and outlet in the top block. No leaks were initially detected when the reactor was brought to reaction temperature. However, it was soon observed that oxygen was coming out through the outlet even when there was nothing flowing through the reactor besides helium. After much investigation, it was finally determined that the culprit was the graphite gaskets. When septa were re-substituted as gasket material, the rogue oxygen presence vanished. It is now thought that the graphite was either slightly porous or required more compression than was possible (due to the brittle nature of the glass and silicon substrates) to seal properly. In addition, as with the septa, it was eventually discovered that the graphite gaskets resulted in catalyst deactivation.

Therefore, yet another interface was designed (see Figure 3.20) using graphite ferrules which would not come into contact with the feed or product streams. However, this work was undertaken by another researcher and will not be detailed here.
3.8 Reaction Experiments

This section is split up based on the various catalysts used, and arranged in chronological order as the experimental set-up evolved gradually during this investigation. It should be noted that this project was a collaboration with another researcher who, at this point, became the more active party in the project. As such, this section will be less detailed than the previous sections to respect and preserve his intellectual right to his work.

3.8.1 Silver Foil and Wire Reactor

After successful leak testing, the reactors were deemed suitable for carrying out reactions. The initial interface design was used for this experiment. The reactor containing the silver foil was tested first. A preliminary experiment was run to gauge the activity of the catalyst. The ratio of methanol:oxygen used was 2 (oxygen was diluted with helium) and a reaction temperature of 360 °C was used. The experiment was then repeated at 380 °C. The results showed little or no formaldehyde formation, but significant carbon dioxide and water production, indicating that decomposition/combustion of methanol had taken place.

An attempt at activating the catalyst by oxidising it was made. A mixture containing 7.2 % oxygen (balance helium) was passed through the reactor at 380 °C for 1 h. Methanol was then passed through the system again at the same ratio as above. A significant amount of formaldehyde was formed, with little by-products. Yet almost no methanol was detected. It was then found that reducing the concentration of methanol resulted in an increase in formaldehyde formation.
However, a complication presented itself when the methanol flowrate was reduced: the pressure within the system prevented methanol from entering into the system. In fact, the methanol was pushed out of the inlet altogether. From this, it was deduced that the flowrates of both methanol and oxygen/helium had to be balanced. Because of this, some experiments were then conducted without the presence of helium, in order to reduce the flowrate on the gaseous side.

In a series of experiments, it was seen that formaldehyde production steadily declined, while carbon dioxide production increased. This suggested that the catalyst retained its activity for only a short period. The experiments using a silver wire had the same results. It is likely that both the foil and wire had similar surface characteristics, and could not remain active. Therefore, it appeared that neither catalyst was suitable.

In retrospect, it is a possibility that both the wire and foil had been poisoned by the septa that were used as gaskets at this point. In any case, the tediousness of placing either catalyst in the reactor would have precluded further use.

3.8.2 Silver Mirror Reactor(I)
Catalyst deposition in this reactor had been performed using the method involving sodium potassium tartrate. Because this reactor had already been heated in a furnace at 400 °C for over 30 min to anneal the silver deposit, it was thought that pre-treatment would not be necessary. The reaction was carried out at 380 °C, with a methanol: oxygen ratio of 2. There was insignificant production of formaldehyde. However, there was also very little methanol coming out of the system.
Upon closer inspection, it was observed that bubbles had formed in the methanol feed at the transition between PTFE tubing and stainless steel tubing, and had blocked the flow (in small channels, bubbles require a larger pressure drop to force them through a constriction, as mentioned in Chapter 2). This vaporisation occurred because the methanol flowrate was lower than in the previous experiments and it had vaporised completely within the stainless steel tubing. As such, there wasn’t enough pressure to continuously push methanol through to the reaction channel. At this point, the two cartridge heaters closest to the inlet were removed so as to reduce the temperature there. After this, blockage due to bubble formation did not occur again.

An attempt was then made to activate the catalyst by treating it with oxygen at 400 °C. Following this, experiment was conducted at reduced methanol:oxygen ratio. As with the previous catalysts, activity was shortlived. At this point, suspicion grew that the septa gaskets could be releasing some volatile component(s) and poisoning the catalyst as prolonged use had caused the silicone centre to melt and flow.

From these two sets of experiments, it was clear that a methanol-rich environment was detrimental to the reaction. More carbon dioxide was formed, while formaldehyde formation was insignificant. When the methanol:oxygen ratio was reduced to about 0.75, formaldehyde was produced in noticeable amounts.

3.8.3 Silver Mirror Reactor(II)

Here, catalyst deposition involved the second method detailed in the previous section. The catalyst was known to be active as the particulate version mentioned previously had been tested in a tube reactor and had proved to be fairly active. The second
interface design was ready at this point and was used, together with the graphite sheet gaskets. A new HPLC pump, Jasco PU-1580, was also tested. It was hoped that this pump would prevent or reduce the pulsation that was observed in previous experiments. Also, before, liquid methanol had shown some difficulty in entering the inlet tubing due to pressure resistances. This pump had a larger pumping pressure. The reaction was carried out at 450 °C, with a composition of 5.4 % methanol, 1.5 % oxygen and balance helium. This is a higher methanol:oxygen ratio than previously used, however, it had been the conditions used in the tube reactor. Unfortunately, conversion was very low.

It was now clear that there was something wrong with the system and not the catalyst deposition method, as this catalyst had been shown to be active outside of the reactor. There were several possibilities for the low conversion:

a) insufficient catalyst surface area: The catalyst was only on the surface of the reactor. As such, the surface area was relatively low.

b) different form of catalyst: The catalyst in the reactor was whitish in colour whereas the catalyst on the particles looked more silvery. It was possible that the silver deposited on the reactor had a different crystal structure and was less catalytically active or required a different pre-treatment procedure.

c) catalyst deactivation: the pump was not very effective, as methanol was still had difficulty reaching the reactor occasionally. It has been seen previously in the tube reactor that loss of methanol supply, even temporarily, could result in permanent loss of catalytic activity. This may have happened to the catalyst within the reactor too, as activity slowly died down.
d) catalyst poisoning: it was found that the graphite gaskets were not pure graphite but in fact comprised of a layer of metal sandwiched between 2 thinner graphite layers. As it was unknown what the metallic layer consisted of, it was possible that some poisoning had occurred.

At this point the graphite sheets were found to be too porous, thus leading to air being drawn in from the surroundings. This, together with the suspicion that they were responsible for catalyst poisoning led to the construction of another interface where the gasket material did not come into direct contact with the inlet gas flow.

3.8.4 Summary of Further Experimental Work Carried Out

Because the mechanism of feeding methanol to the reactor was not working as intended, major alterations were made. The methanol pumping system was replaced by an evaporation system. In this set-up, an oxygen/helium mixture was bubbled through methanol. This gas stream would then carry methanol vapour with it into the reactor, which would solve all the problems with irreproducible methanol boiling in the inlet/pre-heat section. The concentration of methanol in the gaseous stream was dependant on the temperature of the liquid methanol, which was kept constant in a water/ice bath.

When the new interface using graphite ferrules was put into use, rapid catalyst deactivation stopped being a problem. The method of catalyst deposition was changed yet again as well, this time to sputtering. High conversion was achieved using a mixture of 8.0 - 8.6 % methanol and balance oxygen, without any helium to quench the reaction. Please refer to Cao, et al (2002) for more detailed results.
3.9 Conclusion

The principles and method of fabricating a microreactor from scratch were demonstrated. While a lot of literature was available regarding microfabrication, the actual work of fabrication was not straightforward and experience had to be gained. Much time was also spent researching the relatively unconventional catalyst deposition methods which would be compatible with microfabrication, and even then there was always the uncertainty about the behaviour of the catalysts prior to testing.

As mentioned in the previous chapter, one of the major problems facing the commercialisation of microreactors was the difficulty in building an adequate interface. This proved to be a major problem in this case as well, as demonstrated by the difficulty in vaporising methanol in-situ and the susceptibility of the catalyst to poisoning. The major cause of this difficulty was the high temperatures required for the reaction. This was compounded by the brittle nature of the silicon and glass. Together, this resulted in a very limited selection of sealing methods and materials.

However, working microreactors were eventually fabricated thus completing the main goal of this exercise. The side goal of performing most of the fabrication in-house had also been achieved by the end of the project. A good foundation of the concepts involved in microfabrication, particularly silicon microfabrication, was built thus easing future work in this area. Also, with the identification of the difficult areas, i.e. sealing, catalyst deposition and interfacing, further work in this field will be more streamlined and it will be easier to focus attention on these points. A working knowledge of the timescale involved in producing a microreactor was also obtained.
All the experience gained from this exercise forms the basis for producing an algorithm for designing and testing microreactors, which is presented in Chapter 8.

The next generation of reactors has already been fabricated. The aim of these new reactors is to increase throughput either by enlarging the reaction channel or by having many channels in parallel. The reactors were also specifically designed to allow the use of impregnated catalyst particles.
4. Falling Film Reactor: Nitrobenzene Hydrogenation

With design methodology explored in the previous chapter, the project moved on to the next stage: application. The reactor studied in this chapter is a microstructured falling film reactor developed by the Institut für Microtechnik Mainz (IMM). The goal was to demonstrate that this microreactor could be used to perform a reaction that was carried out on an industrial scale.

4.1 Reactor Configuration

First, the reactor will be described. This section includes background information, geometry and basic operation details.

4.1.1 FallingFilm Systems

Falling film systems are named as such because they employ thin liquid films that are created by a liquid feed falling under gravitational pull, like a waterfall. Usually, the liquid film is in contact with a solid support, which is frequently either a thin wall or vertical stack of pipes. Due to the presence of thin films, heat and mass transfer is rapid. Therefore, falling film systems are used for extraction, evaporation and highly exothermic processes. Examples include air dehumidification (Rahmah, et al, 2000), absorption chillers (Kulankara and Herold, 2000), carbon dioxide absorption (Yih and Kuo, 1988), sulfur dioxide adsorption (Van Dam, et al, 1999), ammonia absorption (Chen and Christensen, 2000), sulfonation reactions (Knaggs, 1992, Walas, 1997) and evaporation (Bessenet, et al, 2000).
Conventional falling film systems generate films with thickness of the order of 0.5-3 mm (Dabir, et al, 1996, Karimi and Kawaji, 1998). A microstructured falling film reactor (μ-FFR) would allow the use of smaller volumes, thus reducing the risk of having large volume flows of hazardous materials. The application of a μ-FFR has already been demonstrated (Hessel, et al, 1999, Jähnisch, et al, 2000) for the direct fluorination of aromatics which is a highly exothermic and dangerous reaction. This reactor can generate films less than 100 μm thick and offers excellent heat removal capabilities. The aim of the work presented in this chapter is to demonstrate the applicability of the same reactor to a solid catalysed gas-liquid reaction, specifically a hydrogenation reaction. For this purpose, a suitable catalyst incorporation method had to be developed that provided a stable catalyst for continuous operation.

4.1.2 Description of the Reactor

Figure 4.1 shows the most crucial part of the reactor: the stainless steel plate where the falling film is generated. 64 straight, parallel channels (300 μm wide, 100 μm deep, 78 mm long separated by 100 μm wide walls) were fabricated using electrodischarge machining or wet chemical etching. At both ends on the channels, a slot was cut through the plate to form the inlet and exit ports. The entire plate measured 89 x 46 mm (see Figure 1).

Figure 4.1: Falling film plate
The plate was housed in a stainless steel enclosure shown in Figure 4.2. Liquid was fed to and removed from the back of the plate through slots machined in the bottom half of the housing which matched the position of the slots in the plate. Under the FFR plate, a smaller area was cut out of the stainless steel holder. A copper plate structured with larger channels was inserted into this cavity such that the FFR plate rested flat on top of it. This plate was used to pass the heat transfer fluid, which was circulated via two slots cut into the stainless steel housing. A Viton O-ring was used to prevent leakage of the heat transfer fluid. Teflon and stainless steel gaskets were placed on top of the plate. Their geometry was such that the channels were exposed with the exception of the first and last 5 mm and they helped to distribute the liquid across the channels.

![Figure 4.2: Components and schematic of the microstructured falling film reactor](image)

The top half of the housing held the gas inlet and outlet. It also had a view port (covered by a thick piece of glass) that showed the entire channel section of the \( \mu \)-FFR plate. When both top and bottom parts of the housing were placed together, a small cavity would be created above the falling film plate through which the gas would flow. The top and bottom housing were held together by a ring of screws.
placed around the edge of the reactor. A Viton O-ring was used to ensure that there would be no leakage. The reactor was designed to take up to 20 bar pressure and could operate in co- or counter-current flow. Figure 4.3 shows the complete microreactor.

![Assembled falling film reactor](image)

**Figure 4.3: Assembled falling film reactor**

### 4.1.3 Liquid Film Thickness

The main feature of the reactor is the generation of thin liquid films. The thickness of the film is controlled by the liquid flowrate and can be calculated using a modified Nusselt equation as shown below (Hessel, et al, 1999):

\[
\delta = \frac{3V\mu}{\rho b n g}
\]

where
- \( V \) = volumetric flowrate
- \( \mu \) = liquid viscosity
- \( \rho \) = liquid density
- \( b \) = channel width
- \( n \) = number of channels
- \( g \) = gravitational acceleration
Figure 4.4 shows the liquid film thickness and residence time as a function of the flowrate, assuming the liquid has a viscosity similar to that of ethanol. Since flooding of the channels is detrimental to the operation of the reactor, a maximum flowrate of 3 ml/min is imposed as the film thickness becomes equal to the channel depth at this flowrate. At the same time, the liquid film could not be allowed to become too thin as this could lead to film dry-out. Therefore, it was decided that the reactor would be operated at a minimum liquid film thickness of 44 μm which corresponds to a minimum flowrate of 0.3 ml/min. The above considerations limit the residence time in the range of 2.8-13 s.

4.2 Suitability of Hydrogenations for the μ-FFR

A huge variety of products ranging from polymeric precursors to pharmaceuticals to food products are made through hydrogenation. Hence the suitability of hydrogenation reactions as model reactions is examined next. This class of reactions tends to be limited by heat transfer in industry as they can be very exothermic. And
when not heat transfer limited, they tend to be mass transfer limited. The main advantages of microreactors, which are improved heat and mass transfer, make them seem particularly suited to performing hydrogenations. However, there is one particular limitation of the μ-FFR: it is suited for reactions which require short residence times (i.e. fast reactions). Hydrogenation reactions have a large range of reaction rates, and many are still performed industrially in batch reactors. Therefore, it was necessary to select a reaction which would have a reasonable conversion within a residence time of 2.8-13 s. The following are some important factors that need to be taken into account when considering hydrogenations (note: only liquid phase hydrogenations were considered).

4.2.1 Catalysts

Hydrogenation reactions are always performed in the presence of catalysts. Both heterogeneous and homogeneous catalysts can be used. Heterogeneous catalysts are more commonly used as they are relatively simpler to separate. However, homogeneous catalysts are gaining popularity as some have been shown to give rise to remarkable selectivity in the production of orientation-specific compounds. This section will focus on heterogeneous catalysts.

The catalysts used are, in general, either precious metals such as palladium, platinum, rhodium and ruthenium or Group VII transition base metals such as nickel, copper, chromium and cobalt. The choice of catalyst is dependent on the type of compound to be reduced. Also, process economics tend to play a large role since the transition metals, while cheaper, tend to require more extreme process conditions than the precious metals. However, in certain cases, the selectivity of the base metals cannot
be matched by that of the precious metals. Presented below is a table listing some of
the major types of hydrogenations and the most commonly used catalysts.

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkenes</strong></td>
<td></td>
</tr>
<tr>
<td>mono-alkenes and dienes</td>
<td>Pd, Ni</td>
</tr>
<tr>
<td>cyclohexenes</td>
<td>Pd</td>
</tr>
<tr>
<td>vinyl compounds</td>
<td>Ru, Rh</td>
</tr>
<tr>
<td><strong>Alkynes</strong></td>
<td></td>
</tr>
<tr>
<td>alkynes and alkynic carbinols</td>
<td>Ru, Rh</td>
</tr>
<tr>
<td>allylics compounds</td>
<td></td>
</tr>
<tr>
<td><strong>Aromatics</strong></td>
<td></td>
</tr>
<tr>
<td>to aromatic hydrocarbons</td>
<td>Rh, Pt, Ru, Pd, Ni, Cu</td>
</tr>
<tr>
<td>to cyclohexyl derivatives</td>
<td></td>
</tr>
<tr>
<td><strong>Aldehydes</strong></td>
<td></td>
</tr>
<tr>
<td>aliphatics</td>
<td>Ni, Co, Cu-Cr, Cu</td>
</tr>
<tr>
<td>aromatics</td>
<td>Ru</td>
</tr>
<tr>
<td>unsaturated</td>
<td>Os, Re, Pt</td>
</tr>
<tr>
<td><strong>Ketones</strong></td>
<td></td>
</tr>
<tr>
<td>aliphatics</td>
<td>Ni, Co, Cu-Cr, Cu</td>
</tr>
<tr>
<td>aromatics to aromatic</td>
<td>Ru</td>
</tr>
<tr>
<td>alcohols/hydrocarbons</td>
<td>Pd</td>
</tr>
<tr>
<td>aromatics to alicyclic alcohols</td>
<td>Rh, Ru</td>
</tr>
<tr>
<td><strong>Nitriles</strong></td>
<td></td>
</tr>
<tr>
<td>aliphatics to primary amines</td>
<td>Pd, Pt, Rh</td>
</tr>
<tr>
<td>aliphatics to secondary amines</td>
<td>Rh</td>
</tr>
<tr>
<td>aliphatics to tertiary amines</td>
<td>Pd, Pt</td>
</tr>
<tr>
<td>aromatics to benzyamines/ aldehydes</td>
<td>Pd</td>
</tr>
<tr>
<td><strong>Nitro compounds</strong></td>
<td></td>
</tr>
<tr>
<td>nitroaromatics to anilines/ hydrazobenzenes</td>
<td>Pd, Ni, Cu-Cr, Cu</td>
</tr>
<tr>
<td>nitroaromatics to aminophenols/aromatic hydroxylamines</td>
<td>Pd</td>
</tr>
<tr>
<td>halonitroaromatics to haloanilines</td>
<td>Pt, Rh</td>
</tr>
<tr>
<td>nitrocyclohexanes to cyclohexanone oximes</td>
<td>Pd</td>
</tr>
<tr>
<td>nitroalkenes to saturated amines</td>
<td>Pd</td>
</tr>
<tr>
<td><strong>Acids to alcohols</strong></td>
<td>Re, Ru</td>
</tr>
<tr>
<td><strong>Pinene</strong></td>
<td>Ni</td>
</tr>
</tbody>
</table>

Table 4.1: Selected types of hydrogenation reactions and the preferred catalysts (Farrauto, 1997)

As can be seen, specific reactions function best with different catalysts. The simplest way to select a catalyst is to use a catalyst which has been proven to be selective and active in the past for that particular type of reaction. Occasionally, two catalysts are used together to further improve rates and selectivity. The reasons for the improved performance could be due to:
1) the existence of several reaction steps for which neither catalyst is very effective
2) one of the catalysts actually removes or inhibits the formation of inhibitors

For bi- or multi-functional compounds, selection of a suitable catalyst is based on finding a catalyst which is effective for what is required and avoiding those which are also effective for reducing the other functional groups (Rylander, 1985).

The catalysts are generally used with supports, the most common being carbon (for the precious metals) and alumina (both nickel and the precious metals). The choice of catalyst support is very important as it can influence the selectivity and activity of the catalyst. In fact, carbon supports have been known to take part in catalytic reactions (Farrauto, 1997). Catalyst loading for precious metals generally are in the range of 3-5 wt%, while base metals generally have higher loadings (up to 100%) (Rylander, 1985).

It has also been reported that deactivating a proportion of the catalyst sites by the addition of surface modifiers has the effect of improving selectivity. This has been shown in the hydrogenation of α-pinene. The addition of surface modifiers to the nickel catalyst was claimed to increase stereoselectivity in favour of cis-pinane from a cis:trans ratio of 95:5 to 98:2. Suitable modifiers included organic halo-compounds, elemental halogens and inorganic metal salts from Groups 4 to 7 (Canova, 1977).

Typical catalyst poisons include sulphur, halogen, phosphorus and nitrogen compounds. Coking has also been known to block surface pores in the catalyst support. And, as with all use of heterogenous catalysts, the support and catalyst can be lost through mechanical wear.
4.2.2 Solvent

The use of a solvent is a major consideration. At the very least, the choice of solvent will affect the solubility of hydrogen, thus affecting the rate of reaction. They can also affect the diffusion characteristics of both reactants, thereby controlling reactant concentrations at the catalyst surface. Another effect they can have on the reaction rate is by adsorbing competitively on to catalytic sites (Rylander, 1985).

Many hydrogenation reactions are highly exothermic. The use of a solvent helps control the generation of heat. Many commercial reactors are constrained not by mass transfer or kinetic limitations, but by limitations of the cooling system (Concordia, 1990). For example, in the hydrogenation of m-dinitrobenzene (DNB), about 1.2 MJ of heat per kg of DNB charged needs to be removed to maintain isothermal operation. Typical reactor heat and mass transfer characteristics and sizes are shown in Table 4.2 (the minimum reactor sizes based on heat transfer were inclusive of cooling requirements).

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Heat transfer capability (J/l h)</th>
<th>Minimum reactor size based on heat transfer (l)</th>
<th>Typical bubble diameter (mm)</th>
<th>Ratio of interfacial surface area to volume (m²/m³)</th>
<th>Hydrogen transfer rate (kg/h)</th>
<th>Minimum reactor size based on mass transfer (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stirred tank</td>
<td>550-830</td>
<td>3030</td>
<td>3-6</td>
<td>1000-1500</td>
<td>0.6</td>
<td>680</td>
</tr>
<tr>
<td>Bubble column</td>
<td>300-470</td>
<td>5300</td>
<td>4-8</td>
<td>600-1000</td>
<td>0.3</td>
<td>1360</td>
</tr>
<tr>
<td>Bus loop</td>
<td>830-2200</td>
<td>1140</td>
<td>1-2</td>
<td>2000-3000</td>
<td>2.0</td>
<td>190</td>
</tr>
</tbody>
</table>

Table 4.2: Comparison of reactor sizes for processing 11360 l/day of DNB (Concordia, 1990)

It can be seen that the minimum reactor sizes based on mass transfer requirements are much less than those calculated based on heat transfer limitations. As such, the reactor sizing is controlled by heat transfer limitations. The use of a solvent decreases the heat duty for a reactor, thus reducing the minimum required size.
Some solvents also have an effect on selectivity. In general, the extremes of selectivity correspond to the extremes of the dielectric constants of the solvents, except when considering alcohols or reactants in which a change in the charge occurs. Also, in reactions where there is competition between hydrogenation and hydrogenolysis, hydrogenation is favoured by less polar solvents. Hydrogenolysis is favoured by acidic solvents (Rylander, 1985).

Sometimes, the solvent actually takes part in the reaction. They can take part transiently or permanently. An example of transient participation is in the use of ammonia in the hydrogenation of nitriles, oximes and anilines to prevent the formation of secondary and tertiary amines. Reductive alkylation of aldehydes and ketones is performed with ammonia (Rylander, 1985).

4.2.3 Operating Conditions

While the rate of reaction increases with temperature, several factors have to be considered before setting the operating temperature:

1) As mentioned earlier, hydrogenation reactions can be very exothermic (see Table 4.3). As such, with increasing temperature and reaction rate, heat generation also increases. If the cooling system is unable to cope, this could lead to a runaway reaction. Therefore, the operating temperature has to be determined by the heat-removal capacity of the cooling system.

2) Both the reactant and solvent are usually organic liquids which decompose at relatively low temperatures. This poses a limit to the highest usable temperature. In general, process temperatures range from room temperature to 150 °C.
<table>
<thead>
<tr>
<th>Reactions</th>
<th>$\Delta H_r$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C to C-C</td>
<td>125</td>
</tr>
<tr>
<td>C=C to C-C</td>
<td>300</td>
</tr>
<tr>
<td>Aromatic ring saturation</td>
<td>210</td>
</tr>
<tr>
<td>Carbonyl group to alcohol</td>
<td>65</td>
</tr>
<tr>
<td>Nitro group to amine</td>
<td>550</td>
</tr>
<tr>
<td>Dehalogenation</td>
<td>65</td>
</tr>
</tbody>
</table>

Table 4.3: Enthalpies of hydrogenation for selected organic functional group (Farrauto, 1997)

In contrast, operating pressures are usually high. This is mainly due to the fact that hydrogen is sparingly soluble in most liquids. By increasing the pressure, the concentration of hydrogen in the liquid can be increased, according to Henry’s Law:

$$C_{H_2} = H' P_{H_2}$$

where $C$ = concentration of hydrogen in the liquid

$H'$ = Henry’s Law constant

$P_{H_2}$ = hydrogen partial pressure

This will of course lead to an increase in the rate of reaction (many hydrogenation reactions can be approximated by first order reactions with respect to hydrogen concentration). Operating pressures can be in the range of $1 - 40$ atm.

4.2.4 Safety

Hydrogenation reactions can involve rather dangerous elements. Fortunately, most of them can be controlled relatively well. The first concern is hydrogen itself. An air-hydrogen mixture is dangerously explosive. As such, the reaction system is typically flushed with either nitrogen or argon before the reaction takes place.

The organic reactant and solvent are also sources of danger as they are potentially combustible and/or toxic. Such dangers, though, can be avoided with prudent
precautions. As an added measure, build-up of static electricity should be avoided as a rogue spark could cause an explosion.

Certain catalysts also present danger, most notably Raney-Ni catalysts. These are pyrophoric (i.e. can ignite in air) and are stored wet. Very active catalysts may also ignite flammable solvents and reactants if the reaction rate is too high. Such catalysts need to be used in small quantities. For example, Raney-Ni should only be used in concentration of less than 5% at temperatures above 100 °C (Rylander, 1985).

Care should also be taken if carbon or any finely divided supports are used to prevent the possibility of dust explosions. Other possible problems which could occur include overpressuring the reactor (which could be caused by runaway reactions) and the failure of cooling systems.

4.2.5 Reaction Selection Criteria

The following requirements were imposed in order to select suitable reactions for the µ-FFR:

a) Relatively fast reactions, with reasonable conversion within residence time of 15 s

b) Liquid phase reactions

c) Reactions for which kinetic and mass transfer data had been published

d) Reactions which had been used before as model reactions in other studies

e) Reactions which were generally carried out in the temperature range of 20-80 °C and at atmospheric pressure

f) Reactions for which the suggested catalyst was palladium, as these catalysts were already in use within the research group
g) Reactions involving relatively safe reactants, solvents and products

4.2.6 Hydrogenation of Nitrobenzene

The hydrogenation of nitrobenzene was chosen as a test reaction. It demonstrates clearly the importance of the process conditions on the final product. The catalyst, solvent and operation conditions all influence the product. Some of these effects can be seen in the Table 4.4.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>alcohol</td>
<td>50</td>
<td>aniline\textsuperscript{a,b,c}</td>
</tr>
<tr>
<td>Pd</td>
<td>basic</td>
<td>50</td>
<td>hydrazobenzene\textsuperscript{a,d}</td>
</tr>
<tr>
<td>Pt</td>
<td>alcohol</td>
<td>50</td>
<td>aniline\textsuperscript{b}</td>
</tr>
<tr>
<td>Pt</td>
<td>methanol + DMSO</td>
<td>25</td>
<td>phenylhydroxylamine\textsuperscript{b,e}</td>
</tr>
<tr>
<td>Pt</td>
<td>H\textsubscript{2}SO\textsubscript{4}</td>
<td>25</td>
<td>p-aminophenol\textsuperscript{b,f}</td>
</tr>
<tr>
<td>Ni</td>
<td>alcohol</td>
<td>70</td>
<td>aniline\textsuperscript{b,k,j}</td>
</tr>
<tr>
<td>Cu</td>
<td>vapour phase</td>
<td>210</td>
<td>aniline\textsuperscript{b,l}</td>
</tr>
<tr>
<td>MnO</td>
<td>vapour phase</td>
<td>300</td>
<td>nitrosobenzene\textsuperscript{m}</td>
</tr>
</tbody>
</table>


The variety of products is due to the fact that nitrobenzene hydrogenation progresses through 3 steps before aniline is produced. However, the intermediates, nitrosobenzene and phenylhydroxylamine, can also react with each other to produce aniline through another route, as shown in Figure 5 (Höller, et al, 2000). The hydrogenation of nitrobenzene is a highly exothermic reaction (545 kJ/mol). Good temperature control is essential to avoid violent decomposition of nitrobenzene or partially hydrogenated intermediates, particularly phenylhydroxylamine (Blaser, et al, 2001).

Most of the laboratory results in the literature show almost total conversion to aniline when a palladium catalyst was used (Höller, et al, 2000, Karwa, et al, 1988, 1987). However, these experiments were performed in batch reactors over many hours. Examining the reported results, it could be seen that the intermediate compounds were in fact produced during the course of the batch reactions but were eventually converted to aniline. It was suspected that due to the short residence time in the falling film reactor, some of the intermediate compounds would be present in the product stream. In addition, aniline can also further react to produce several side

Figure 4.5: Reaction scheme for nitrobenzene hydrogenation to aniline times (Höller, et al, 2000)
products such as cyclohexanol, N-ethyl aniline, toluidine, cyclohexyl amine and diaminobenzene (Turek, et al, 1986). But, due to the short residence time, these compounds were less likely to be formed.

Industrially, aniline is produced mainly through the hydrogenation of nitrobenzene (both gas and liquid phase), although the ammonolysis of phenol is also economically viable. For liquid phase route, supported palladium, platinum, nickel, copper or cobalt are typically used as catalysts. The processes generally operate at 80-250 °C at pressures 20 bar or greater. Du Pont employs a continuous plug flow process with a palladium-platinum on carbon catalyst, which attains conversions of 98-99% (Amini, et al, 1991). The vapour phase routes are usually performed in fluidised or fixed bed reactors at 150-300 °C and 5-15 bar. Copper is the most commonly used catalyst and conversions of 99% are obtained.

4.3 Catalyst Preparation

Most examples of microreactor technology typically involve the use of unsupported metallic catalysts deposited through sputtering (Srinivasan, et al, 1997). Where greater catalytic surface area is required for further process intensification, anodisation of metals (typically aluminium) can be utilised as a variety of surface morphologies and porous layer thicknesses can be made in a controlled fashion (Wießmeier and Hönicke, 1996). Since then, supports have also been prepared using sol-gel techniques (Cominos, et al, 2002, Kursawe, et al, 2000, Fichtner, et al, 1999) and by growing zeolites (Wan, et al, 2001, Rebrov, et al 2001). Finally, fixed bed microreactors have also been produced (Losey, et al, 1999). More examples of catalyst incorporation in microreactors can be found in Chapter 2.
Four different methods of preparing the catalyst for nitrobenzene hydrogenation were employed: sputtering, UV-decomposition of palladium acetate, wet impregnation and incipient wetness. The sputtering and UV-decomposition methods did not require modification of the surface of the stainless steel reactor plate, while the other two methods involved the prior deposition of a $\gamma$-alumina layer. The various methods are described below.

4.3.1 Sputtering of Palladium (SP)

The entire reaction side of the plate was coated with a 100 nm thick layer of palladium using the sputtering process, a conventional thin film technology. In this process, which is performed under vacuum conditions, the substrate (reactor plate) is operated as the anode whereas the coating material (palladium) is operated as the cathode which emits atoms to the substrate.

4.3.2 UV-decomposition of Palladium Acetate (UV)

The reaction channels were covered with a solution of palladium acetate which was then irradiated using a UV lamp for 30 min. This served to decompose the organic part of the palladium acetate molecule, leaving behind elemental palladium on the surface of the channels.

4.3.3 Wet Impregnation (IP)

The $\gamma$-alumina layer was deposited using the slurry/washcoating process at IMM. First, the area surrounding the channels was covered with tape. The channels were subsequently covered with an aqueous suspension of $\gamma$-alumina powder (20% solids
content, average particle size 3 μm), binder (PVA) and acid (acetic acid or nitric acid). Excess suspension was wiped off and the plate was then calcined at 700 °C for 2 hours. This resulted in a 10 μm thick film, with pore size of about 20 nm and surface area of 58 m²/g (Cominos, et al, 2002). A solution of palladium (II) nitrate (Aldrich, Pd 12-16% w/w) with ca 1.3 wt% palladium was prepared. The channel area was covered in 10 ml of this solution for 2 h, after which the remaining solution was removed and the plate left to dry in air for 2 h. The plate was then heated at 120 °C for 30 min to drive off all moisture before being calcined in air at 400 °C for 3 hours. It was then rinsed with distilled water and ethanol.

4.3.4 Incipient Wetness (IW)

The γ-alumina layer was prepared as above. The same palladium (II) nitrate solution (10 ml) was used to cover the channels and left to dry in a fume cabinet. The plate was then calcined in air at 400 °C for 3 h and subsequently rinsed with distilled water and ethanol.

4.4 Experimental Apparatus and Procedure

A schematic of the experimental set-up is shown in Figure 4.6. A HPLC pump (Knauer K-120, 50 ml pump head) was used to feed the reaction mixture into the reactor. Prior to entering the reactor, the feed mixture was passed through a water bath (Grant W14) to bring it closer to the reaction temperature. A syringe pump (Razel A-99) was connected to the other end of the 3-way valve. It was used to clean the system with ethanol before shutdown. The HPLC pump was not used for cleaning purposes as there would be a volume of ethanol left inside it, which would need to be
The hydrogen flowrate through the system was controlled using a rotameter (Cole Palmer). The gas line was connected to the top gas port of the reactor. The bottom gas port was blocked off. This was done to maintain pressure in the reactor, and to use the gas pressure within the reactor to push out the product fluid from the reactor. A nitrogen line was also connected later on for use as purge gas. A needle valve was used to control the outlet flowrate. This was necessary to maintain pressure within the reactor as well as to prevent flooding. Product was collected in a sample bottle for analysis using a gas chromatograph (Agilent 6890).

Stainless steel tubing was used throughout the system, except for the HPLC pump inlet (PTFE tubing), the product outlet (glass), the gas lines (copper) and the water bath inlet and outlet (silicone).
4.4.1 Heating

Because temperatures no greater than 80 °C would be used, water was used as the heating fluid. First it had to be determined whether the temperature of the water bath would match the temperature of the reactor. This was done by inserting a themocouple (industrial mineral insulated probe, type K) into the reactor from the product outlet. It was found that there was a discrepancy 3-6 °C over a temperature range of 50-70 °C. Therefore, the water bath temperature was kept higher to maintain the reactor at the desired temperature. Distilled water was used to avoid scale build-up, both in the water bath and in the heating channels of the reactor.

4.4.2 Liquid Flow Testing

Tests were run using both water and ethanol. Liquid flowing down the channels could be clearly seen in both cases. It was observed that the side channels would be wetted before the middle channels, but the flow would quickly become evenly distributed. As predicted by the film thickness calculations presented earlier, a flowrate of 3 ml/min resulted in flooding of the channels. Note however that the flooding occurred only in the middle channels.

Further testing was done using ethanol, as that was the solvent to be used in the reaction. Tests were made with hot water passing through the system (50-80 °C) and a system pressure of 4 bar. While ethanol has a boiling point of 78.4 °C at atmospheric pressure, there was a high chance that it would evaporate at temperatures lower than that due to the thin films involved even though the pressure was higher than atmospheric. This was indeed found to be true as shown in the Table 4.5.
An unforeseen phenomenon also occurred: at higher flowrates (above 2 ml/min), the liquid flow was not smooth, i.e. liquid would periodically spurt out from the entrance of the falling film section thus resulting in a thicker liquid film in the centre of the reactor. This spurting was caused by the fact that both gas and liquid phases shared the same outlet, and that the gas was used to push the liquid out of the reactor. If the outlet valve was not opened wide enough, liquid would build up faster than the gas would be able to push it out, leading to flooding. However, if the valve was opened too wide, the gas would flow too rapidly through the reactor and cause problems for liquid delivery. Therefore, it was necessary to balance the opening of the outlet valve. But, this was more difficult at higher pressures. The spurting essentially resulted from the following series of events:

a) liquid would build up at the outlet and trap the gas in the reactor, thus building up pressure
b) when pressure build-up exceeded the head of liquid trapped at the outlet, the gas would push the liquid out
c) the sudden drop in pressure would cause the liquid feed to spurt into the reactor, and restart the cycle

This occurrence was likely to cause some experimental error, especially at higher flowrates and pressures.
4.4.3 Estimation of Reactant Concentration

A simple model was used to estimate the nitrobenzene concentration that would be suitable for this system, based on kinetic and experimental parameters found in Bartholomew, et al (1997). Each channel of the falling film reactor can be described essentially as a plate reactor. Therefore, the falling film reactor can be assumed to be made up of several plate reactors operating in parallel. The liquid reactant flows in one direction. At the same time, the hydrogen pressure is kept constant. As dissolved hydrogen reacts with the liquid reactant on the catalyst, more hydrogen dissolves thereby maintaining the equilibrium concentration of hydrogen at the liquid surface. As such, there is constant renewal of the hydrogen supply at the gas-liquid interface. Assuming the reaction is first order with respect to hydrogen, a model which satisfies this condition was proposed by Gobby, et al (2001) (see Appendix 4-1 for the method used). The parameters used for the calculation are shown in Table 4.6.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel width (m)</td>
<td>0.0003</td>
</tr>
<tr>
<td>Channel length (m)</td>
<td>0.065</td>
</tr>
<tr>
<td>Number of channels</td>
<td>64</td>
</tr>
<tr>
<td>Volumetric flowrate (m³/s)</td>
<td>6.67 x 10⁻⁶</td>
</tr>
<tr>
<td>Liquid viscosity (Pa s)</td>
<td>8.57 x 10⁻⁴</td>
</tr>
<tr>
<td>Liquid density (kg/m³)</td>
<td>815</td>
</tr>
<tr>
<td>Diffusivity of hydrogen in ethanol (m²/s)</td>
<td>1.05 x 10⁻⁶</td>
</tr>
<tr>
<td>Reaction rate constant (s⁻¹)</td>
<td>4.158</td>
</tr>
<tr>
<td>Gravitational acceleration (m/s²)</td>
<td>9.81</td>
</tr>
<tr>
<td>Initial concentration of nitrobenzene (mol/m³)</td>
<td>400</td>
</tr>
<tr>
<td>System pressure (atm)</td>
<td>7</td>
</tr>
<tr>
<td>Henry's constant (mol m³/atm)</td>
<td>1.46</td>
</tr>
<tr>
<td>Residence time (s)</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Table 4.6: Falling film calculation parameters (physical constants, diffusivity, reaction rate constant obtained from Farrauto, et al, 1997)

Based on the parameters above, the amount of aniline produced would be 16.1 mol/m³ or a conversion of 4%. Hydrogen was the limiting reactant. Even though this result was rather low, it was decided to run the experiments with an initial nitrobenzene
concentration of 0.4 mol/l just to confirm the results. If the experimental conversion was as low as predicted, then further experiments would be performed using nitrobenzene concentration of 0.04 mol/l.

4.4.4 Analysis Method

Product analysis was performed using an Agilent 6890 GC with an auto-sampler. A fused silica capillary column (Rtx-5, crossbond 5% diphenyl - 95% dimethyl polysiloxane, 7 m, 0.32 mm ID, 0.25 μm df, Thames Restek) was used. Analysis was carried out using a TCD detector. The analysis recipe and calibration method can be found in Appendix 4-2 and 4-3, respectively.

4.4.5 Experimental Procedure

Experiments were conducted at 1-8 bar pressure, 60-70 °C, 0.04-1 mol nitrobenzene/l concentration and flowrates of 0.2-3 ml/min nitrobenzene solution (99.5%, Fluka, diluted in ethanol). Blank experiments carried out to test the catalytic activity of stainless steel concluded that no discernible reactions took place. In total, seven catalyst plates were examined: two each for the sputtered, impregnated and incipient wetness catalysts and one for the UV-decomposed catalyst. Nitrobenzene conversion, $X$, and aniline selectivity, $S$, were calculated by:

$$X = \frac{\text{Moles nitrobenzene reacted}}{\text{Moles nitrobenzene entering}}$$

$$S = \frac{\text{Moles aniline produced}}{\text{Moles nitrobenzene reacted}}$$
4.5 Experiments (I) - Sputtered Palladium Catalyst

Two plates were obtained pre-sputtered from IMM. They were both used without any pre-treatment. One plate was used for a set of exploratory experiments. The other plate was used after some changes were made to the experimental procedure in light of data from the initial experiments and will be reported in Section 4.7.

4.5.1 Exploratory Experiments

The effect of residence time, pressure and temperature on the conversion were determined. A series of experiments was run at 4 bar, temperature range 50-80 °C and flowrates ranging from the minimum possible (without leading to dry-out) up to 0.4 ml/min. The nitrobenzene concentration used was 0.4 mol/l. The results are shown in Figure 4.7.

![Figure 4.7: Nitrobenzene conversion as a function of flowrate at various temperatures for the sputtered palladium catalyst (1 mol NB/l, 4 bar)](image)

The conversions obtained were very low, close to the conversion estimated in Section 4.4.3. Negligible conversion was obtained at the maximum flowrate of 0.4 ml/min. There was an increase in conversion going from 50 to 70 °C. However, the
conversion obtained at 80 °C was lower than that at 70 °C, suggesting some deactivation had occurred. Subsequent reactions carried out appeared to have no conversion whatsoever, leading to the conclusion that the catalyst had been completely deactivated. A side product was detected after the first two runs.

An attempt to solve both of these problems was made by taking apart the reactor and cleaning the plate with ethanol and/or acetone. However, there was no observable recovery. The catalyst plate was then oxidised in air at 450 °C for 4 h to remove all traces of organic compounds, and then reduced in pure hydrogen at 350 °C for a further 4 h. Oxidising resulted in the structured side turning blue, while the backside turned the usual brownish colour of stainless steel. The blue colour was likely due to the formation of palladium oxide, indicating that the entire reaction-side of the plate had been covered by palladium instead of just the channel area. Note however that the channel areas covered by Teflon during operation were noticeably less blue, as shown in Figure 4.8.

![Figure 4.8: Falling film reactor plate after oxidisation](image-url)
This led to the suspicion some reaction could also be taking place outside of the reaction channels. Upon disassembly, it had been observed that the area surrounding the channels was wet, even though it had been covered over by a Teflon sheet. This may have occurred through capillary action. As such, the by-product could have been formed in those dead zones and slowly diffused out.

The entire reactor housing was also taken apart and soaked in ethanol in an attempt to remove all traces of reactants and products. After the reduction step, the reactor was re-assembled and tested. Some activity was recovered but no side-products were detected indicating that the oxidation-reduction sequence had restored activity. However, it was decided at this point to determine the deactivation characteristics of the catalyst before further parametric studies were carried out.

### 4.5.2 Deactivation Experiments

This series of experiments was conducted using the following conditions:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrobenzene concentration</td>
<td>0.4 mol/l</td>
</tr>
<tr>
<td>Liquid flowrate</td>
<td>0.2 ml/min</td>
</tr>
<tr>
<td>Hydrogen pressure</td>
<td>4 bar</td>
</tr>
<tr>
<td>Temperature</td>
<td>60 °C</td>
</tr>
</tbody>
</table>

Table 4.7: Operating conditions for deactivation experiments

The catalyst plate was oxidised in air at 450 °C for 4 h and then reduced in pure hydrogen at 350 °C for another 4 h. Samples were taken from the reactor every 1-2 h. Unfortunately, the reactor could not be operated continuously overnight. As such, it had to go through a start-up and shutdown procedure each day, which may have affected the results. The change in nitrobenzene conversion with respect to time is shown in Figure 4.9.
From the figure, the effect of successive shutdowns and start ups can be seen in the various conversion irregularities (at ca 9, 17 and 31 h of operation). However, there was a very clear sign of rapid deactivation initially followed by a slower, steady deactivation. A second attempt to reactivate the catalyst was made. However, there was no significant improvement in conversion. After 43 h, the conversion of nitrobenzene to aniline was negligible.

Selectivity was erratic (refer to Figure 4.10), but it seemed to follow the trend of conversion. After the reactivation at 36 h, only aniline was observed. However, this was followed by a sharp decrease in selectivity, i.e. side products were produced when the catalyst was not fresh. Subjecting the catalyst to another oxidation-reduction cycle failed to recover aniline production.
4.5.3 Deactivation Issues

An investigation was made into the possible causes of deactivation. It was known that palladium undergoes structural changes in the presence of hydrogen. An amorphous structure is supposedly more active than a crystalline structure (Bodnar, 1994, Yu, 2000). Also, palladium black has been known to deactivate when reduced or employed at high temperatures. This may be due to restructuring to form larger catalyst particles which are less active (Yada, 1996).

Another possible cause lay in the reactants or products. Aromatic compounds are strongly oxidising and can oxidise the catalyst (Bodnar, 1994, Kürschner, 1995). Also, at the low pressure used, hydrogen concentration in the liquid would be low. Intermediates adsorbed on the catalyst surface would be deprived of hydrogen, and could instead react to form higher molecular weight compounds which were insoluble
thus blocking the active sites (Kürschner, 1995). van Gelder, et al (1990) also shared the view that deactivation could continue while the reactor was left idle. Their catalyst was regenerated by oxidising in air at 130 °C under slightly elevated pressures for 60 h. Ammonia and ammonium bicarbonate were detected during regeneration, indicating that nitrogen-containing compounds had adsorbed on the catalyst.

Palladium can absorb up to 900 times its volume of hydrogen at room temperature. Activity for the hydrogenation of 2,4-dinitrotoluene was correlated to the formation of palladium β-hydride which acts as a reservoir of activated hydrogen (Benedetti, 1991). A later study showed that this was not true; instead, activity depends on the metal particle size: on larger particles, the aromatic ring adsorbs parallel to the surface, allowing both nitro groups to interact with the catalytic surface which increased activity. The orientation of nitrobenzene molecules on palladium is not known as it depends on the surface. For example, it adsorbs on to Mn$_3$O$_4$ and Al$_2$O$_3$ standing perpendicularly to the surface, while on MgO, it lies flat (Maltha, et al, 1994).

Hydrogen adsorption can take two forms. Below a certain temperature-dependent hydrogen concentration, a solid solution, termed the α-phase, is formed. Past this limit, a crystallographically distinct hydride phase, known as the β-hydride phase is formed. Here, hydrogen occupies interstitial positions in the metal lattice and causes it to expand by 3.6%. The absorption isotherm can be seen in Figure 4.11 (Palczewska, 1975). The same author also gave several examples illustrating the self-poisoning that occurs when palladium is transformed into its hydride. This phenomenon was also explored by Metcalfe, et al, 1971. However, this is an unclear
situation as consecutive absorption-desorption cycles can lead to the cracking of crystallites thus increasing surface area and improving activity (large crystals have been found to transform into the hydride slowly while thin films transform instantly). The deactivation effect can be explained by the electronic structure of the hydride phase: hydrogen fills the empty $d$ band of palladium with its $1s$ electron, transforming the $d$ transition metal into an $s$-$p$ metal which has a reduced ability to chemisorb and activate reactants.

Figure 4.11: Absorption isotherm for hydrogen on palladium (Palczewska, 1975)

It was also suspected that the side-product could also be playing a role in the deactivation. As such, attempts were made to determine its identity. The sample with the greatest amount of the side-product was analysed using GCMS. However, five other side products were detected as well (note: the column used in the GCMS was 30 m long, which resulted in better separation). These compounds had been produced in
much smaller quantities and had not been detected previously. It was suspected that these compounds were intermediates in the reaction route (refer to section 4.2.5).

4.5.4 Identification of Side Products

An attempt was made to determine the identity of these compounds by matching fragment mass numbers obtained using the MS with the relative molecular masses of the various possible compounds. Apart from the unknown compounds found using the GC of the GCMS, three additional sets of fragments were found using the MS. The GC trace and the various MS spectrograms can be found in Appendix 4-4 (Table 4.8 summarises the findings).

<table>
<thead>
<tr>
<th>GCMS separation time (s)</th>
<th>Detected in GC</th>
<th>Possible identity through MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.050</td>
<td>No</td>
<td>unknown</td>
</tr>
<tr>
<td>3.550</td>
<td>No</td>
<td>nitrosobenzene</td>
</tr>
<tr>
<td>4.100</td>
<td>No</td>
<td>unknown</td>
</tr>
<tr>
<td>4.300</td>
<td>Yes</td>
<td>aniline</td>
</tr>
<tr>
<td>5.517</td>
<td>Yes</td>
<td>nitrobenzene</td>
</tr>
<tr>
<td>6.217</td>
<td>Yes</td>
<td>N-ethylaniline</td>
</tr>
<tr>
<td>7.467</td>
<td>Yes</td>
<td>unknown</td>
</tr>
<tr>
<td>10.017</td>
<td>Yes</td>
<td>azobenzene</td>
</tr>
<tr>
<td>10.084</td>
<td>Yes</td>
<td>unknown</td>
</tr>
<tr>
<td>10.484</td>
<td>Yes</td>
<td>hydrazobenzene</td>
</tr>
<tr>
<td>12.734</td>
<td>Yes</td>
<td>azoxybenzene</td>
</tr>
</tbody>
</table>

Table 4.8: Detected compounds in the GCMS

The side product which was initially detected was azoxybenzene. All intermediates were detected, except phenylhydroxylamine (PHA). However, the presence of azoxybenzene, azobenzene and hydrazobenzene suggested that PHA had been produced. The absence of PHA indicates that the reduction to aniline and/or the reaction with nitrosobenzene are relatively fast reactions (refer to Figure 5 for the reaction scheme).
The relative amounts of the products based on peak sizes from the GC trace are:

- aniline > azoxybenzene > N-ethylaniline > hydrazobenzene > azobenzene > nitrosobenzene > PHA

Azoxybenzene was initially not detected after a reactivation procedure, but eventually becomes the main product (aniline concentration becomes negligible) as the run time increases. For the most part, however, the amount of azoxybenzene was comparable to that of aniline, while the rest were present in smaller amounts.

The other unknown compounds still posed a mystery. The second (t = 4.100s) and fourth (t = 10.084s) unknowns showed a clear phenyl signature while the other two were not so obvious. Also, the first (t = 3.050s) and the fourth were found to have relatively high mass fragments. Among the conjectures put forth were the possible presence of meta-nitrobenzene in the feed mixture and the possibility that ethanol could be taking part in the reaction, as suggested by the possible presence of N-ethylaniline.

Based on the reaction route and the mass spectra obtained previously, some pure samples of the suspected species were obtained: 4-aminophenol (98+%, Aldrich), azobenzene (99%, Aldrich), 1,3-dinitrobenzene (97%, Aldrich), 1,2-diphenylhydrazine (also known as hydrazobenzene, Aldrich), N-ethylaniline (98%, Aldrich), nitrosobenzene (97% Aldrich). These compounds were diluted in ethanol. Arbitrary amounts were used as the goal of this exercise was simply to compare the retention times of these compounds with those of the reaction products. The Rtx-5 column was used (see Appendix 4-5 for the analysis recipe). The chromatogram of each species is shown in Figures 4.12-4.17 in order of retention time.
Figure 4.12: Chromatogram for nitrosobenzene

Figure 4.13: Chromatogram for N-ethylaniline

Figure 4.14: Chromatogram for 4-aminophenol

Figure 4.15: Chromatogram for 1,3-dinitrobenzene

Figure 4.16: Chromatogram for azobenzene
A mixture of all these compounds was then made up and injected through the GC (see Figure 4.18). In comparison, the chromatogram of a reaction product is shown in Figure 4.19. Figure 4.20 shows the chromatogram for the same sample after 3 days.
Firstly, from Figures 4.19 and 4.20, it was clear that the product composition changes over time. From Figure 4.19, nitrosobenzene, aniline and nitrobenzene can be clearly identified. However, there remained a fourth peak with a less certain identity. The retention time of this peak (~4.06 min) is fairly close to that of N-ethylaniline (~3.69 min). However, they are reasonably different enough to be different compounds. In Figure 4.20, five peaks can be seen. As before, nitrosobenzene, aniline and nitrobenzene can be identified. However, the fourth peak in Figure 4.19 disappeared but two new peaks appeared. The latter of these two peaks matches the retention time of hydrazobenzene. Unfortunately, the former does not share the retention time (~2.78 min) of any of the samples that had been tested. Nor was it detected in the sample that was run through a GCMS.

Given that hydrazobenzene was detected after several days, some deductions can be made as to the identity of the unknown compounds. The presence of hydrazobenzene suggests that phenylhydroxylamine was present in the initial product mixture since hydrazobenzene is formed through the reduction of azoxybenzene which is produced when phenylhydroxylamine reacts with nitrosobenzene. Since the final peak in Figure 4.19 disappeared in conjunction with the appearance of the hydrazobenzene peak in Figure 4.20, it seems likely that it could be phenylhydroxylamine, which is a relatively unstable compound. The unknown peak in Figure 4.20 could be another product of phenylhydroxylamine reacting with another compound. Note that this remains as a conjecture as it is unclear how azoxybenzene could be reduced to hydrazobenzene in the absence of catalyst. One possibility is that there were traces of palladium present in the sample along with some dissolved hydrogen.
4.5.5 Discussion of Results

Without knowing whether any compounds adsorbed strongly onto the catalyst (and so were undetectable in the outlet stream), it was difficult to conclusively determine the nature of the deactivation. However, it was clear that azoxybenzene continued to be produced even when aniline production became negligible. This suggested that phenylhydroxylamine preferentially reacted with nitrosobenzene and the pathway from azoxybenzene to aniline was either blocked or required a longer residence time. Hydrazobenzene concentration was much larger than that of azobenzene, therefore it appeared that the hydrogenation of hydrazobenzene was inhibited. These observations agree with Blaser, et al (2001) who reported that nitroso, azo and azoxy intermediates adsorb strongly, and the reduction of the hydrazo compound is slow, requiring elevated temperatures and pressures.

Nitrosobenzene and phenylhydroxylamine clearly react with each other while adsorbed on the catalyst. The sputtered catalyst was a continuous layer. As such, active sites were densely packed. It seems reasonable to assume that the more densely packed the nitrosobenzene and phenylhydroxylamine molecules, the more favourable their reaction. As such, to reduce the likelihood of a reaction between them, a catalyst layer which consisted of relatively distantly spaced palladium particles would be preferable. This line of reasoning eventually led to the use of γ-alumina as catalyst carrier.

From section 4.4.3, it had already been found that the amount of nitrobenzene present in the feed was likely to be much greater than the hydrogen concentration at the surface of the catalyst. Such hydrogen-starved conditions could promote undesirable
reactions amongst adsorbed components. In addition, excess nitrobenzene could be oxidising the catalyst surface as well. Therefore, it was decided to reduce the concentration of nitrobenzene from 0.4 mol/l to 0.04 mol/l in further experiments.

Another possible cause for deactivation was an unsuitable reactivation procedure. van Gelder, et al (1990) used a temperature of only 130 °C for oxidising their catalyst in air and did not even employ a reduction cycle. It could be that the much higher temperatures that had been used (450 °C) may have adversely affected the structure of the catalyst.

Attention was also directed to the pressure and temperature when hydrogen was in contact with palladium. From Figure 4.12, the operating conditions would result in the formation of the β-hydride phase, which could be detrimental. This seemed to corroborate the suspicion that film dry-outs had led to reduction in activity. As such, the reactor could not be allowed to fill up with hydrogen alone. The method of catalyst reduction was also changed to minimise the formation of the β-hydride phase. Heating to 350 °C should result in only the α-phase forming, but in addition the chamber would be flushed of hydrogen after the reduction to prevent hydride formation as the plate cooled down to room temperature.

4.6 Experiments (II) - UV-decomposed Palladium Acetate Catalyst (UV)

This plate was used to test the ideas mentioned in the previous section (reduction in nitrobenzene concentration, reduction in reactivation temperature, change in
operational procedure to minimise catalyst exposure to hydrogen alone) to slow down catalyst deactivation and to reactivate the catalyst.

4.6.1 Experimental Results

The plate was first placed in an oven at 130 °C for 4 h to activate it. Nitrobenzene concentration was reduced to 0.04 mol/l and experiments were performed at 60 °C, 4 bar pressure and at a flowrate of 0.35 ml/min. The results are shown in Figure 4.21. With the 10-fold reduction in nitrobenzene concentration, relatively higher conversion was obtained initially (~45 %) compared to the previous catalyst. However, a stepped trend in the deactivation could be seen for the first 33 h of operation. Each step took place after the reactor was shut down for the day. The sharp rise in conversion after the 35th hour took place after the reactor was cleaned and the plate reactivated by oxidising in air at 130 °C for 4 h. Unfortunately, the plate deactivated rapidly and further reactivation attempts failed to recover activity. This was similar to the behaviour of the sputtered palladium catalyst. However, this catalyst maintained its activity for a longer period.

Figure 4.21: Nitrobenzene conversion and aniline selectivity as a function of time for the UV-decomposed palladium acetate catalyst (0.04 mol NB/l, 60 °C, 4 bar, 0.2 ml/min)
Aniline selectivity followed the same trend as conversion, except at the end when conversion was at its lowest. Selectivity became far better after the reactivation attempt, which suggested that some change to the structure of the catalyst surface had occurred. The same side-products as for the sputtered palladium plate were detected.

4.6.2 Discussion of Results

From these experiments, it seemed that deactivation occurred when the reactor was left idle overnight. This occurred even after passing ethanol through the reactor for an hour before shut-down to wash it. The plate was analysed using Raman spectroscopy and the presence of coke was detected (see Appendix 4-6). This was proof that high molecular weight compounds which were insoluble in ethanol were indeed forming on the catalyst surface and that heat treatment was required to remove them. However, these compounds were likely to have formed during the course of the experiments and did not explain the stepped behaviour in deactivation. It still seemed likely that hydrogen left in the system could also have played a role in the deactivation. As such, as a further precaution, a nitrogen line was installed to purge hydrogen from the reactor before shutdown.

This catalyst remained active for a longer period than the sputtered one. This could be due to several reasons: reduction in nitrobenzene concentration, higher palladium loading and a different catalyst structure due to a different preparation method.

The used plate was examined using an SEM (Hitachi S-570). Figure 4.22 shows several channels and Figure 4.23 shows a close-up view of one channel. A very
rough, uneven, cracked surface can be seen. The cracked surface may be the reason for the higher activity compared to that seen previously on the sputtered palladium plate as the surface area is larger. The void regions seem to indicate areas where palladium crystallites have detached. This observation led to the conclusion that one of the causes of deactivation could be palladium loss. The permanent loss of palladium from the plate would explain the irrecoverable loss of activity. It would also exacerbate deactivation due to deposition of carbonaceous species, as demonstrated by the rapid deactivation after the first reactivation attempt at 35 h. It is possible that the reactivation attempt increased the rate of palladium leaching due to the formation of cracks during the heating and cooling cycles.

Figure 4.22: SEM image of UV-deposited palladium plate (magnification: 50x)

Figure 4.23: SEM image of UV-deposited palladium plate (magnification: 500x)
4.7 Experiments (III) - Sputtered Palladium Catalyst (II) (SP2)

As mentioned in Section 4.5, this plate was obtained from IMM. It was hoped that the changes that had been implemented to the operation procedure (reduction in nitrobenzene concentration, installation of a nitrogen purge line, change in reactivation procedure) would result in a more stable catalyst and/or better recovery in activity after reactivation. In addition, a new column was installed in the GC in order to obtain better separation of products.

4.7.1 New Column

As the column used previously (Rtx-5) was lacking in product separation capability, a new capillary column was chosen, PTA-5 (poly(5% diphenyl/95% dimethylsiloxane), 30m length, 0.32 mm ID, 0.5 μm df, Supelco). This column is specifically prepared and base-deactivated to make it suitable for the analysis of amines and other basic analytes. In addition, an FID was used instead of the TCD in order to better detect any compounds present in minute quantities. The recipe used can be found in Appendix 4-7. The chromatogram of an old sample obtained using this column can be seen in Figure 4.24. The various compounds which were not found using the previous column (see section 4.5.4) were all resolved using this new column. The column was calibrated using the internal standard method (see Appendix 4-8 for details).

![Figure 4.24: Chromatogram for the reaction product using the PTA-5 column (see Figure 4.20 for comparison with Rtx-5 column)](image-url)
4.7.2 Experimental Results

This plate was first oxidised in an oven at 130 °C for 4 hours. It was then subjected to the standard test conditions (0.04 mol NB/L, 60 °C, 4 bar, 0.35 ml/min liquid flowrate). The results are shown in Figure 4.25. As can be clearly seen, there was very rapid deactivation of the catalyst.

![Figure 4.25: Nitrobenzene conversion as a function of time for the sputtered palladium catalyst SP2 (0.04 mol NB/l, 60 °C, 4 bar, 0.35 ml/min)](image)

The plate was re-oxidised at 130 °C for 4 h and then put back into the reactor. There was recovery of activity, but it was short-lived and the plate deactivated rapidly, as shown in the Figure 4.26.

![Figure 4.26: Nitrobenzene conversion as a function of time for the sputtered palladium catalyst SP2, after regeneration (0.04 mol NB/l, 60 °C, 4 bar, 0.35 ml/min)](image)
4.7.3 Discussion of Results

Prior to the reactivation, the catalyst was examined. It could be clearly seen that the surface was flaky and wrinkled. Figures 4.27-4.29 show images of the catalyst surface before and after the experiment. In Figure 4.29, a piece of palladium foil can be seen partially detached from the surface.

Figure 4.27: Optical microscope image of unused sputtered palladium plate SP2 (magnification 160x)

Figure 4.28: Image of sputtered palladium plate after reaction (confocal microscope, 200x)

Figure 4.29: Optical microscope image of flaking sputtered palladium plate SP2
It seemed likely that the deactivation was linked to the flaking of the palladium. Hence, it is reasonable to deduce that some removal of palladium had occurred during the experiments. It could be that the adhesion of palladium to stainless steel was not strong enough. It had been seen previously (Chapter 3) that when a piece of silicon bearing a thin film of silver deposited through evaporation was placed in an organic solution, the silver film detached itself. Something similar could be happening here. In addition, the sputtered palladium film had been deposited several months previously. Thin films have been observed to degrade with time, and this could have accelerated the removal of palladium.

The results showed high initial activity, both for the fresh and the reactivated catalyst. This activity was short-lived, however, with conversion reducing to less than 25% within the first hour. It was clear that the sputtered palladium catalyst was not a suitable catalyst as it did not demonstrate stable activity for long periods. It was thought that the main cause of this was the coating of active sites by heavy organic compounds. Also of concern was the removal of palladium from the reactor plate, that could have been accelerated by structural defects in the ‘continuous’ layer of deposited palladium which became larger which each reactivation cycle. The same arguments seemed to apply to the UV-deposited catalyst as well.

The simplest way of surmounting both of these factors seemed to be to increase the catalyst loading, which could be achieved by increasing the surface area of the plate. By increasing the amount of palladium, the time taken to coat a large proportion of the active sites would be increased. In addition, the effects of palladium removal would become less drastic with the greater loading.
Therefore, the wet impregnation and incipient wetness catalysts (supported on γ-alumina) were developed. In addition to higher loading, the dispersed particulate nature of the catalyst would also not be subject to the stress found in the grain boundaries of the much larger crystallites deposited using the sputtered and UV-decomposition techniques. This would prevent the large-scale removal of catalyst seen in both sputtered and UV-decomposed catalysts thus increasing lifespan as well.

4.8 Experiments (IV) - Impregnated Palladium Catalyst (IP1)

This catalyst was prepared using the procedure outlined in Section 4.3. It was used without further treatment.

4.8.1 Experimental Results

Experiments were conducted using the standard conditions (0.04 mol NB/L, 60 °C, 4 bar, 0.35 ml/min liquid flowrate) to test for catalyst stability. 100% conversion and almost 100% selectivity was achieved and maintained for 6 hours, far longer than for any of the previous catalysts (see Figure 4.30).

Figure 4.30: Nitrobenzene conversion and aniline selectivity as a function of time for the impregnated palladium catalyst IP1 (0.04 mol NB/L, 60 °C, 4 bar, 0.35 ml/min)
As such, it was decided to perform some parametric studies by altering flowrate, pressure and temperature. The runs were performed in the following manner: at each temperature (60 and 70 °C), the system pressure would be kept at 4, 5, 6 and 8 bar while the flowrates were cycled through 0.35, 1, 2 and 3 ml/min. Also, the standard run was performed at the start of each day to check the activity of the catalyst. The results are shown in Figures 4.31-4.32.

Figure 4.31: Nitrobenzene conversion as a function of flowrate at various pressure for the impregnated palladium catalyst IP1 (0.04 mol NB/l, 60 °C)

Figure 4.32: Nitrobenzene conversion as a function of flowrate at various pressure for the impregnated palladium catalyst IP1 (0.04 mol NB/l, 70 °C)
From Figure 4.30, catalyst activity decreased with time. This explained the behaviour seen in Figures 4.31-4.32, in which activity was seen to decrease with pressure. Clearly, the study had to be repeated with either a fresh or regenerated catalyst. The selectivity to aniline also decreased with time, as seen in Figure 4.30. But, as with conversion, this catalyst exhibited better characteristics compared to the previous catalysts in terms of retaining higher selectivity for a longer period and being less erratic. An important observation was that while aniline selectivity was not 100%, no side products were detected. This loss in selectivity is due to an apparent loss in the carbon balance, i.e. the number of moles of carbon entering the system was greater than that leaving. This was evidence that carbonaceous compounds were being retained in the reactor.

It was clear that this catalyst was a significant improvement over the SP and UV catalysts. However, deactivation remained a problem and could be rapid. Therefore, a viable reactivation procedure was still needed. Because it was still uncertain whether deactivation was due to the leaching of palladium or deposition of organic compounds or the formation of palladium hydride (or a combination of these), a combination of methods was attempted next.

4.8.2 Catalyst Reactivation

For the first reactivation attempt (series IP1A), the plate was cleaned in dichloromethane in an attempt to remove organic deposits. After that, the plate was baked in an oven at 130 °C for 4 h. Figure 4.33 shows the change in activity of the catalyst with time at the following conditions: nitrobenzene concentration 0.04 mol/l,
flowrate 0.35 ml/min, temperature 60 °C, pressure 4 bar. Activity was recovered. However, due to the complete conversion achieved here and previously, it was uncertain whether the initial activity exhibited by the fresh catalyst had been completely recovered. Therefore, after 3.5 h, experiments were performed at 1 bar in order to reduce conversion so that changes in initial activity could be gauged more accurately. Compared to the initial deactivation rate (see Figure 4.30), the reactivated catalyst appeared to lose its activity more quickly. This seemed to suggest that complete recovery of activity was not possible.

Figure 4.33: Nitrobenzene conversion as a function of time for the impregnated palladium catalyst after different reactivation procedures (0.04 mol NB/l, 60 °C, 1 bar, 0.35 ml/min): IP1A - dichloromethane wash and oxidation (note: 4 bar pressure used for first 3.5 h), IP1B - dichloromethane wash, IP1C - dichloromethane wash, IP1D - oxidation

The next reactivation attempt (series IP1B) was done by cleaning in dichloromethane only. The plate was tested at the same conditions as before, except that the pressure was 1 bar. As Figure 4.33 shows, there was initial recovery of activity but this was followed by rapid deactivation. To confirm these results, the catalyst was once again washed using dichloromethane and then tested (series IP1C). Initial activity was
recovered, but deactivation was even more rapid (see Figure 4.33). Note that GC analysis of the wash liquid produced no other peaks besides that of dichloromethane. However, the recovery of activity following the wash indicates that something had been removed from the surface of the catalyst. The fact that nothing else was detected yet activity recovered suggests that the removed compound(s) was either sparingly soluble in dichloromethane and/or had been present on the catalyst surface in very small amounts. But because the catalyst activity seems to decrease more quickly after each reactivation attempt, it seemed very likely that something else was affecting the palladium as well. The catalyst was then reactivated by baking at 130 °C for 4 h (series IP1D). As seen in Figure 4.33, complete conversion was obtained initially, i.e. the recovery of activity was better than when using dichloromethane alone. The activity remained stable for much longer as well.

The concentration of nitrobenzene was increased to 0.05 mol/l and the flowrate to 0.5 ml/min for the follow up experiment (series IP1E) in order to reduce the conversion. Figure 4.34 shows that activity was recovered, but deactivation was more rapid than before. It was unclear whether this was due to the increased nitrobenzene concentration or the progressive loss of initial activity from changes to the palladium. Also, two parametric studies had been conducted between 1.25-5.25 h, which may have affected the activity of the catalyst. It should be noted, however, that the loss in activity was still slower than when dichloromethane alone was used for reactivation.
The catalyst was then reactivated yet again by heating it in an oven and tested, this time with a nitrobenzene concentration of 0.1 mol/l (series IP1F). The results are shown in Figure 4.35. The initial activity was at a desirable level, i.e. less than total conversion. Again, activity decreased more rapidly than before, but slower than when only dichloromethane was used to reactivate.
These findings point out the two factors at work here:

a) deposition of organic material, possibly coke, had occurred during the reaction thus reducing activity. Upon reactivation, the deposits were removed thus restoring activity.

b) changes to the palladium had occurred, either structural or leaching. This led to overall permanent reduction in activity and catalyst lifespan.

4.8.3 Parametric Study

With the reactivation problem solved, parametric studies were conducted at various pressures (1-3 bar) and flowrates (0.5-3 ml/min). The temperature and nitrobenzene concentration were kept constant at 60 °C and 0.1 mol NB/l respectively. However, because deactivation during the course of the experiments would likely affect the results, it was decided to:

a) reactivate the catalyst after each set of experiments at a certain pressure.

b) begin and end each run with the base conditions (0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) to determine the deactivation rate.

Figure 4.36 shows the change in base case conversion for each series of runs. Series 1 corresponds to tests made during the 1 bar experiment, Series 2 the 2 bar experiment and Series 3 the 3 bar experiment. The rate of deactivation was similar.
Figure 4.36: Nitrobenzene conversion as a function of time for the impregnated palladium catalyst, base case results during parametric studies (IP1H, 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min)

Figure 4.37 shows the results of the parametric study after correction for deactivation (the correction was performed based on the assumption that the deactivation rate was linear with time. See Appendix A-9 for details). The results were a vast improvement over previous parametric studies. Figure 4.38 depicts the same results plotted to show the relationship between nitrobenzene conversion and pressure. There is a fairly linear relationship, but it is not first order with respect to hydrogen pressure as expected, instead it is somewhat more weakly dependant on hydrogen pressure.

Figure 4.37: Nitrobenzene conversion as a function of flowrate at various pressures for the impregnated palladium catalyst (IP1H, 0.1 mol NB/l, 60 °C)
Figure 4.38: Nitrobenzene conversion as a function of pressure at various flowrates for the impregnated palladium catalyst (IP1H, 0.1 mol NB/l, 60 °C)

The aniline selectivity at the standard condition for these three runs is shown in Figure 4.39. The selectivities in the first two runs were similar, but decreased in the third run. The selectivity during the parametric runs can be seen in Figure 4.40. Selectivity decreases with increasing flowrate, though the effect is reduced by increasing pressure.

Figure 4.39: Aniline selectivity as a function of time for the impregnated palladium catalyst, base case results during parametric studies (IP1H, 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min)
Figure 4.40: Aniline selectivity as a function of flowrate at various pressures (IP1H) for the impregnated palladium catalyst, base case results during parametric studies (IP1H, 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min)

4.8.4 Discussion of Results

The rate of deactivation was found to be fairly consistent throughout all three experiments (see Figure 4.36). A few observations can be made from this:

a) Pressure had no effect on the rate of deactivation. Because the hydride phase of palladium is believed to be less active, this indicated that increasing the pressure did not affect the rate of hydride formation. This suggested that practically all the hydrogen that reached the palladium surface reacted.

b) Catalyst activity was recovered by baking at 130 °C for 4 h. This suggested that loss of activity was not due to a permanent change to the catalyst.

c) Palladium content was not changing irreversibly. This differed from previous experience, suggesting that either catalyst retention had stabilised after nine runs or that improved operating procedure had preserved palladium content.
The cause of deactivation was still unclear. From the evidence obtained, it seemed to be a combination of all of the factors that have been mentioned: coking, hydride formation and palladium leaching. A short discussion of these factors follows:

a) Coke and/or high molecular weight polymers were likely to be forming in small amounts, and were readily removed by heating the catalyst to 130 °C. Given the constant rate of deactivation shown above, it seemed to be the leading and most consistent cause of deactivation.

b) From the absorption isotherm for hydrogen (refer to Figure 4.11), palladium hydride is the stable form of a palladium/hydrogen mixture at 60 °C and 1 bar, while a hydride/solid solution of hydrogen mixture exists at 130 °C. Therefore, it was possible that the hydride phase forms during the reaction and deactivates the catalyst, but is then removed upon heating to 130 °C thus restoring activity.

c) The stabilisation of the deactivation rate suggested that the palladium content was not decreasing. Therefore, leaching did not seem to be occurring. However, it was likely that there had been leaching from the fresh catalyst, but the rate had decreased till it was almost negligible.

The problem of deactivation seemed to have been solved or at least reduced with the use this catalyst. Retention of high activity remains a concern but the ability to regenerate it reproducibly is a marked improvement over the SP and UV catalysts.

4.9 Experiments (V) - Incipient Wetness Catalyst (I) (IW1)

This catalyst was prepared using the procedure outlined in Section 4.3. It was used without further treatment.
4.9.1 Experimental Results

The standard base conditions were used to test catalyst stability: 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min. The results are shown in Figure 4.41. Initial conversion was high, but this settled down to about 82 % and remained at that level for almost 9 h. This catalyst retained stable activity for a much longer period than any of the other catalysts. After 28 h, conversion was still at 75 %. Aniline selectivity was more erratic, but had an average value of 80 %. As with the IP catalyst, no side products were detected, meaning that there was a carbon balance closure problem once again.

![Figure 4.41: Nitrobenzene conversion and aniline selectivity as a function of time for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min)]

Parametric studies were performed in the liquid flowrate range 0.5-3 ml/min and at 1, 4 and 6 bar at 60 and 70 °C. Unlike the IP1 catalyst, catalyst activity remained fairly stable throughout these studies. As such, reactivation was not required between runs. The results, corrected for deactivation, are shown in Figures 4.42-4.43. The range of conversions obtained was different from that of the IP1 catalyst. The highest conversion obtained for this plate (~ 86%, Figure 4.42) was less than that obtained for the IP1 catalyst (~ 97%, Figure 4.37). But, the lowest conversion obtained for this plate (34 % at 1 bar, Figure 4.42), i.e. at the highest flowrate, was higher than that of
the IP1 plate (26% at 1 bar, Figure 4.37). Even accounting for experimental error, the conversion range for the IW plate was narrower.

![Graph](image1)

Figure 4.42: Nitrobenzene conversion as a function of flowrate at various pressures for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C)

![Graph](image2)

Figure 4.43: Nitrobenzene conversion as a function of flowrate at various pressures for the incipient wetness catalyst IW1 (0.1 mol NB/l, 70 °C)

The corresponding results for aniline selectivity are shown in Figures 4.44-4.47 below. Selectivity appeared to decrease slightly with increasing flowrate, which is likely due to the sequential nature of the reaction (i.e. nitrobenzene → nitrosobenzene → phenylhydroxylamine → aniline). The effect of pressure was not as
straightforward. The results at both temperatures indicate that selectivity reaches a maximum at about 4 bar hydrogen pressure.

Figure 4.44: Aniline selectivity as a function of flowrate at various pressures for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C)

Figure 4.45: Aniline selectivity as a function of pressure at various flowrates for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C)
Figure 4.46: Aniline selectivity as a function of flowrate at various pressures for the incipient wetness catalyst IW1 (0.1 mol NB/l, 70 °C)

Figure 4.47: Aniline selectivity as a function of pressure at various flowrates for the incipient wetness catalyst IW1 (0.1 mol NB/l, 70 °C)

4.9.2 Discussion of Results

The reactor’s performance could be examined more closely as deactivation was not a major concern. There were two differences between the IP1 and IW1 catalysts: retention of activity and range of conversion. The IW1 catalyst remained active for a longer period. This was likely due to the higher catalyst loading, which provided a larger number of active sites thus being more resilient against poisoning and leaching.
The cause for the smaller range of conversion range of the IW1 catalyst (lower maximum conversion, higher minimum conversion), however, was unclear but it seemed likely that it was due to the distribution of the catalyst. Comparison of the two fresh catalyst plates had shown that there were differences:

1) a shiny, metallic coating was clearly seen in the channels of the IW1 plate, whereas the IP1 plate had a darker colour.

2) the channels in the IW1 plate were noticeably shallower.

Therefore, it seemed very likely that the palladium had not just been deposited within the pores of the support, but also coated on top of the support. This could have led to a reduction in surface area, thus explaining the lower conversion obtained at the lowest flowrate. At the higher flowrates, it is possible that the reactants had less time to diffuse to the surface of the catalyst thus reducing the concentration at the catalyst surface. For the IP1 catalyst, this would result in reducing the concentration driving force for diffusion to the active sites located within the porous support, whereas in the case of the IW1 catalyst, palladium was already abundantly present on the surface of the support thus giving a larger conversion.

The Weisz-Prater criterion was used to determine whether there were pore diffusional resistances. For purposes of simplifying the estimation, a value was calculated for each reactant each time assuming that the reaction was first order with respect to that reactant only. For a first order system, the criterion is given by

\[ \Phi = \frac{(r_A \rho_s) L^2}{D_{el} C_s} \ll 1 \]  for no pore diffusional limitations
where \( \tau_A \) = rate of reaction (mol/kg cat s)
\( \rho_s \) = density of catalyst (kg cat/m^3 cat)
\( L \) = thickness of catalyst layer (m)
\( D_{eA} \) = effective diffusivity of A (m^2/s) = \( \frac{e_s}{\tau} D_A \)
\( C_{As} \) = concentration of A at the surface of the catalyst (mol/m^3)
\( \varepsilon_s \) = void fraction
\( \tau \) = tortuosity

The catalyst was assumed to have a density, \( \rho_s \), of 2 g/cm^3, void fraction, \( \varepsilon_s \), of 0.6 and tortuosity, \( \tau \), of \( \sqrt{3} \). The initial concentration of nitrobenzene was used (100 mol/m^3), while the concentration of hydrogen at the catalyst surface was assumed to be the same as the hydrogen concentration at 1 bar at the gas-liquid interface according to Henry's Law (3.85 mol/m^3). Calculations were made at liquid flowrates of 0.5 and 3 ml/min. Details of the calculations can be found in Appendix 4-10, the results are shown in Table 4.9 (lower values in both cases correspond to lower liquid flowrate).

From these calculations, nitrobenzene would not suffer from pore diffusional limitations. However, the case was not as clear for hydrogen as the value was not much smaller than 1. It was possible that there would be some diffusional resistance, especially at higher flowrates. This seemed to support the idea that hydrogen had less time to diffuse into the pores of the catalyst at higher flowrates which led to the observed lower conversion in the IP1 catalyst compared to the IW1 catalyst.

<table>
<thead>
<tr>
<th></th>
<th>( \Phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.3 - 0.41</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.065 - 0.09</td>
</tr>
</tbody>
</table>

Table 4.9: Weisz-Prater calculations for the reaction system

To check for external diffusional limitations, the ratio of hydrogen diffusion time through the liquid film to the residence time within the reactor was calculated at
various flowrates (see Table 4.10). The small values of $\tau_d/\tau$ indicate that interphase diffusional resistances should negligible at all flowrates.

<table>
<thead>
<tr>
<th>Flowrate (ml/min)</th>
<th>Film thickness ($\mu$m)</th>
<th>Residence time, $\tau$ (s)</th>
<th>Diffusion time, $\tau_d$ (s)</th>
<th>$\tau_d/\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>52</td>
<td>9.3</td>
<td>0.08</td>
<td>0.01</td>
</tr>
<tr>
<td>1</td>
<td>65</td>
<td>5.9</td>
<td>0.12</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>82</td>
<td>3.7</td>
<td>0.19</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>94</td>
<td>2.8</td>
<td>0.25</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 4.10: Comparison of hydrogen diffusion time across the liquid film and residence time

When the plate was removed from the reactor, several observations were evident:

a) the shiny metallic palladium coating had become duller

b) there seemed to be less palladium as the channels were noticeably deeper

c) there were black particles at the bottom end of the reactor

The particles were analysed using XPS, confirming that they were carbon-based compounds. However, it was uncertain whether they were aromatic. It is possible that these particles had formed when the catalyst was hydrogen-starved, which could have led to formation of high molecular weight carbonaceous species. It was also possible that running the reaction at 70 °C may have accelerated coke formation as the particles had never been observed in any previous experiments with the other catalyst plates. Palladium was detected in the particles as well demonstrating that catalyst had been lost during the experiments. It is uncertain how much palladium had leached out during the course of the experiments but further experimentation after reactivation brought the catalyst back to its original level of activity, suggesting that there was still sufficient palladium present to sustain activity.

Figures 4.48-4.49 were obtained through EDX analysis of the plate after removal of carbon deposits. The $\gamma$-alumina layer was observed to be cracked and patches had
detached from the surface. It is fairly clear that the palladium was deposited as a layer on top of the γ-alumina. As such, most reaction may have taken place on the surface of the catalyst layer, instead of within the pores of the support.

Figure 4.48: EDX analysis of IWI plate after reactivation to remove carbonaceous particles, (a) map view, (b) alumina content, (c) palladium content, (d) iron content. Magnification 180x.
4.10 Experiments (VI) - Impregnated Palladium Catalyst (II) (IP2)

This catalyst was prepared using the method outlined in Section 4.3, with the exception that the calcination period was 14 h, instead of 4 h.

4.10.1 Experimental Results

The catalyst was tested at the standard conditions: 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min. As shown in Figure 4.48, it demonstrated fairly stable conversion for the first 6.5 h of operation so a parametric run (changing flowrates 0.5-3 ml/min and pressures 1-4 bar) was made. Unfortunately, drastic deactivation took place, thus reducing their reliability. Unlike conversion, selectivity did not undergo massive reduction (refer to
the Figure 4.48). The average selectivity was 90%. The selectivity demonstrated by this catalyst was better and more stable than that of the IP1 catalyst (see Figure 4.30).

![Figure 4.48: Nitrobenzene conversion and aniline selectivity as a function of time for the impregnated palladium catalyst IP2 (0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min)](image)

The plate was then baked at 130 °C for 4 h but subsequent testing showed no recovery in activity. It was suspected that the catalyst had been over-oxidised during the calcination. Therefore, an attempt was made to reduce the catalyst in hydrogen within the reactor at 85 °C for 4 h. Activity was recovered but short-lived, with nitrobenzene conversion decreasing from 88% to 60% in 6 h (see Figure 4.49).
It was thought that the reduction period was not long enough. Therefore, the catalyst was reduced for a further 4 h at 80 °C. The reactivated catalyst was more stable this time, with conversion decreasing from 91 % to 75 % in 6.5 h (refer to Figure 4.50). Therefore, it was decided to perform a parametric run, the results of which are shown in Figure 4.51, after correction. Unfortunately, the catalyst deactivated severely during the 6 bar run (higher deactivation rate shown in Figure 4.50 for experiments after 6.5 h) and the results remain skewed even after applying corrections.
4.10.2 Discussion of Results

This catalyst followed the general trend exhibited by previous catalysts, but was less stable than the previous catalyst, IW1. Catalyst stability appeared to be primarily linked to the loading of the catalyst. Ignoring the effect of palladium leaching, which should happen in all the catalysts to some extent, it seemed likely that the deactivation
of the catalysts was due mainly to the reduction in the number of active sites available as time online increases. The lower the catalyst loading, the larger the proportion of active sites blocked within a given amount of time, leading to a shorter catalyst lifespan. Because the initial activity can be mostly recovered by baking the catalyst plates, it seemed reasonable to deduce that the culprits responsible for this blockage are organic in nature, possibly coke or some sort of heavy or polymeric nitrogen-containing organic compounds.

4.11 Experiments (VII) - Incipient Wetness catalyst (II) (IW2)

This plate was prepared using the same procedure as the IW1 plate. The main purpose of this experiment was to test the reproducibility of the catalyst preparation technique and the experimental results.

4.11.1 Experimental Results

The activity of this catalyst was compared to that of the IW1 catalyst at the standard conditions: 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min (refer to Figure 4.52). The stability of the IW2 catalyst was similar to that of the IW1 catalyst over the period of time investigated (the final data point of the IW2 series was taken after a series of parametric runs, which may have affected the activity). While the IW2 catalyst has a noticeably higher conversion, this was likely due to an improvement in the catalyst deposition technique from experience (less wastage of palladium nitrate solution). The selectivity towards aniline of both catalysts, however was very similar (see Figure 4.53).
The results of the parametric runs can be seen in Figure 4.54. The results follow similar trends to previous results, except for the experiments at 6 bar (see Figure 4.42 for comparison). This was likely due to a dampening of the pulsations in the flow because of a pump malfunction.
The selectivity to aniline obtained during these experiments can be seen in Figures 4.55-4.56. As with the IW1 catalyst, the selectivity decreased slightly with flowrate. Unlike the IW1 catalyst, however, the IW2 catalyst demonstrated an increase in selectivity with pressure.

Figure 4.55: Aniline selectivity as a function of flowrate at various pressures for the incipient wetness catalyst IW2 (0.1 mol NB/l, 60 °C)
Following this, a set of experiments was performed using a much higher concentration of nitrobenzene, 1 mol NB/l. The purpose of this was to determine whether higher concentrations of nitrobenzene had any deleterious effects on the catalyst, as was suspected earlier in the project. The other standard conditions were kept unchanged, and the results can be seen below (the catalyst was baked at 130 °C prior to these experiments to return it to its initial level of activity).
There appeared to be negligible change in the activity of the catalyst. It was possible that this was also due to the higher catalyst loading compared to the plates used in earlier experiments, and was therefore more resistant to the blockage of active sites by carbon compounds. The catalyst surface was noticeably darker after 8.5 hours of operation and some black particles similar to those found in a previous experiment (refer to Section 4.9.2) were found near the outlet of the plate as well, though in a smaller quantity. The selectivity towards aniline had an average value of 68 %, which was lower than that at 0.1 mol NB/l (79 %). As with all other results of the IP and IW catalysts, no side products were detected, thus bringing up the fact that some carbon was being retained within the reactor.

4.11.2 Discussion of Results

The reproducibility of this method of preparing this catalyst was shown by this set of experiments. It remained the best method of catalyst preparation, with much more stable activity than any other catalyst so far, even at higher nitrobenzene concentrations. The formation of the black particles after just 8 h of operation at elevated concentrations (compared to 28.5 h for the IW1 catalyst) suggested that nitrobenzene molecules were reacting with each other to form heavy compounds even in the presence of hydrogen.

4.12 Summary of experimental results and conclusions

4.12.1 Nitrobenzene Conversion

The IW plate is estimated to contain 140 mg of palladium. The IP plate contained a smaller amount of palladium since not all the palladium present in the impregnation
solution was allowed to deposit. Both IP and IW plates had larger catalytic surface areas than the SP and UV plates due to the presence of the γ-alumina layer. From visual observations, the UV plate is expected to have a larger amount of palladium than the SP plate, which had a 100 nm-thick layer of palladium (4.7 mg).

Catalyst longevity appeared to be dependent on palladium loading, the greater the loading, the longer the active lifespan (operation time before reactivation was required). This was likely due to the larger number of active sites, thus lessening the effect of blockage of active sites by heavy nitrogen-containing carbon compounds. Catalyst lifespans shown in Figure 4.58 (experimental conditions as noted in Table 4.11) follows the order: IW > IP > UV > SP. The IW catalyst was superior to the other catalysts, both in terms of longevity and activity. The IP catalyst had similar initial performance but demonstrated fairly drastic reduction in activity after several hours. The UV catalyst demonstrated high activity after a start-up period but which decreased to a more stable conversion of 18 %. The SP2 catalyst was the least active of all, with a very short-lived period of high activity before settling down to a conversion of about 18 %.
4.12.2 Selectivity Towards Aniline

The selectivity of the catalysts towards aniline (at the conditions shown above in Table 4.11) are presented graphically in Figures 4.49-4.60. The results for the IW and IP catalysts are shown in the Figure 4.59, while the UV catalyst is shown in Figure 4.60 due to a very different selectivity range and behaviour. The results for the SP catalyst were not included as there were some errors which skewed the results too much for comparison.
Figure 4.59: Comparison of IP and IW catalyst selectivity

Figure 4.60: Selectivity of the UV catalyst

The selectivity of the catalysts towards aniline followed a similar trend to that of nitrobenzene conversion. Both IW catalysts demonstrated similar, stable selectivity (~80 %) while the IP catalysts behaved differently. IP1 had rapid loss of selectivity (decreasing from 96 % to 58 % in 23 h) while IP2 maintained high selectivity (~ 90 %). The selectivity of the UV catalyst followed the same trend as its conversion, except at the end of the experiments where selectivity improved tremendously.
4.12.3 Carbon Balance Closure

It is obvious from the data presented above that the selectivity data is very erratic, especially for the IW and IP catalysts. The spread of data is well beyond experimental and sampling error. One of the causes of this behaviour is very likely due to a problem highlighted earlier: the fact that the carbon balance could not be closed. From the reaction scheme, 1 mol of nitrobenzene would produce 1 mol of aniline, i.e.

\[
\text{mol nitrobenzene entering} = (\text{mol nitrobenzene} + \text{mol aniline}) \text{ exiting}
\]

However, comparison of these numbers showed discrepancies, sometimes as large as 20 % (see Table 4.20). Re-examination of the data showed that, for the IW and IP catalysts, the product mixtures were made up almost entirely of ethanol, nitrobenzene, aniline and the internal standard N-ethylaniline. When other compounds were detected, they were found only in minute quantities which could not account for the missing carbon. It was suspected that this carbon could have been in the form of some heavier organic compounds which either remained on the surface of the catalyst or could not be detected using the GC (there was the possibility that heavier compounds would get stuck before entering the column or the detector).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average loss of carbon moles (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP1</td>
<td>17.3</td>
</tr>
<tr>
<td>IP2</td>
<td>8</td>
</tr>
<tr>
<td>IW1</td>
<td>14.1</td>
</tr>
<tr>
<td>IW2</td>
<td>17.5</td>
</tr>
</tbody>
</table>

Table 4.12: Discrepancy between carbon moles entering and leaving the reactor for the various catalysts

To determine the likelihood of the second possibility, a sample from the IW2B series (1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min) was analysed using thin layer chromatography (TLC). This method had been selected because heavy material present would not get 'stuck' unnoticeably as it might have in the GC. The IW2B series had been chosen as
it involved the highest concentration of nitrobenzene and seemed likely to contain the
greatest amount of undetected material. This particular sample (IW2B003) had been
chosen as it had demonstrated the lowest selectivity (55.1 %) and the carbon balance
was off by 19.9 %. The results of this experiment showed no evidence of any
compounds which had not been detected using the GC. This lent credence to the
postulate that the missing carbon had in fact adhered to the surface of the catalyst or
reactor (note that the TLC analysis had been performed by another researcher).

Some calculations were therefore made to determine whether the rate at which carbon
was being ‘lost’ was within sensible limits. The time taken for a monolayer of carbon
atoms or benzene molecules to cover the catalyst surface (i.e. the total surface area at
the bottom of all the channels on the plate) was calculated (see Appendix 4-11 for
details of the calculations). For a mole loss of 17.5 % (the average value for the IW2
plate and the highest amongst the catalysts under normal operating conditions), the
results were:

<table>
<thead>
<tr>
<th>Radius of atom/molecule</th>
<th>Carbon - 0.077 nm</th>
<th>Benzene - 0.375 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time to form a monolayer</td>
<td>190 h</td>
<td>8 h</td>
</tr>
</tbody>
</table>

Table 4.13: Time required for the formation of a monolayer

The time taken for a monolayer of benzene to form was similar to the time when the
catalyst’s activity started degrading drastically (around 7 h, see Figure 4.48).
However, the loss of activity was not catastrophic, indicating perhaps that not the
entire catalytic surface had been covered at that point. It is thought that instead of
forming a monolayer, the molecules would be more likely to form in aggregates.
The observation of black particles on both IW plates, which had been identified as carbon-containing compounds, supported this theory. While the size of these particles had not been measured, it was estimated that they were 10 - 50 μm in diameter. At the above rate, the time taken to form a layer of particles (50 μm diameter) that completely coated the geometric surface of the catalyst (i.e. the total surface area of the bottom of all channels) was estimated to be about 422 h or 0.25 % of the geometric surface per hour (1.75 % of the area after 7 h). This seemed to be the most likely 'sink' into which the carbon was disappearing.

4.12.4 Causes of Deactivation

The most compelling clues found so far with regard to the cause(s) of deactivation are:

a) the carbon particles found in the reactor
b) the disparity between carbon moles entering and leaving the reactor
c) the observed loss of palladium from the catalyst plates
d) the detection of palladium in the aforementioned carbon particles.

While the exact cause(s) of deactivation have not been pinpointed with complete confidence, the evidence obtained so far suggest that two main factors are involved:

a) High molecular weight organic deposits were likely to be forming due to the presence of nitrogen-containing compounds but could be removed by heating the catalyst to 130 °C. This agrees with the observations of van Gelder, et al (1990) for the hydrogenation of 2,4,6-trinitrotoluene. Given the constant rate of deactivation shown for the IP catalyst and the formation of carbon-based particles on the IW catalyst, it seems to be the leading cause of deactivation.
b) The inability to return the catalysts to their initial activity, the quicker deactivation after successive reactivations, observation of missing/flaking palladium and the detection of palladium in the carbonaceous particles all point to the fact that palladium loss had occurred. However, since the deactivation rate for the IP catalyst eventually became constant after several reactivations, it seemed likely that the rate of palladium loss gradually decreases for the IP and IW catalysts. While organic deposits are responsible for quicker deactivation, palladium loss leads to irrecoverable loss of activity. According to Blaser, et al (2001), metal leaching can become pronounced under hydrogen starved conditions. This could be happening in this system since hydrogen is the limiting reactant.

The mechanism responsible for causing palladium loss has not been determined as it was beyond the scope of this project. However, it seems likely to be one or more of the following: weak adhesion of palladium to the substrate, chemical leaching due to the oxidative nature of nitrobenzene or destabilisation of particle structure due to the transformation of palladium to palladium hydride (and vice versa).

4.12.5 Parametric Studies

The only catalyst with reproducible behaviour was the IW catalyst. Therefore, only parametric data from this catalyst was considered. Because there were some concerns regarding the experimental data from some of the higher flowrate experiments performed using the IW2 catalyst due to possible pump malfunctions, only the data from the IW1 catalyst will be presented.
In an attempt to determine the importance of the operating conditions (liquid flowrate, hydrogen pressure) on the conversion, the data was reinterpreted in several ways: film thickness, residence time, Reynolds number and average reaction rate. Because residence time and film thickness were inherently linked in this system, it was thought that the Reynolds number, which incorporates both of them, would be particularly important in this analysis. The average reaction rate was calculated using overall conversions and residence times. Figures 4.61-4.63 show the dependence of nitrobenzene conversion on film thickness, residence time and Reynolds number, respectively.

Figure 4.61: Nitrobenzene conversion as a function of liquid film thickness at various pressures for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C)
There appeared to be a relationship between nitrobenzene conversion, Reynolds number and pressure. The data in Figure 4.63 was re-plotted in Figure 4.64. The mesh in the figure represents the equation of best fit for this graph, which is:

\[
\text{NB conversion} = 0.95 + 0.02P - 0.27\text{Re} + 0.0001P^2 + 0.028\text{Re}^2
\]
This equation had an average difference of 3.7% from the experimental values. It can be seen from this equation that Re, which is a measure of both the film thickness and residence time, has a greater impact on the conversion than the pressure. Larger Re results in greater film thickness and lower residence time, which would lead to a corresponding decrease in conversion. The reaction system appeared to be fairly weakly dependent on hydrogen pressure.

Figure 4.64: Nitrobenzene conversion as a function of Reynolds number and hydrogen pressure for the incipient wetness catalyst IW1 (0.1 mol NB/l, 60 °C)

4.12.6 Comparison with a Batch Reactor

While it has been shown that the μ-FFR is capable of hydrogenating nitrobenzene, it is just as important to demonstrate that it can be a significant improvement to existing technology. A batch reactor was selected as a benchmark for comparison. As reported by Farrauto, et al (1997), a batch reactor (3 m³, 0.4 mol nitrobenzene/l ethanol, 20 bar H₂ pressure, 125 °C, 7.89 x 10⁻³ g cat/ml, 85% conversion) would be capable of producing 204 kmol aniline/m³ reactor daily (assuming no downtime). In
comparison, a \( \mu \)-FFR using the IW1 catalyst (0.1 mol nitrobenzene/l ethanol, 0.5 ml/min., 1 bar \( H_2 \) pressure, 60 °C, 5.4 g Pd/ml, 82% conversion) would have a daily production rate of 394 kmol aniline/m\(^3\) reactor. This represents a significant theoretical increase in the rate of production at a much lower operating pressure and temperature.

### 4.13 Conclusions

It has been shown that the microstructured falling film reactor can be used to perform a solid catalysed gas-liquid reaction. The main challenge in this project was the development of a robust catalyst that was compatible with the reactor system, in terms of incorporation, suitability for continuous use, longevity and reproducibility. Several different catalyst incorporation methods were tested (sputtering, UV-decomposition of palladium acetate, wet impregnation on \( \gamma \)-alumina, incipient wetness on \( \gamma \)-alumina) with the final method satisfying all of these requirements. In addition, semi-empirical relationships were derived to describe the behaviour of the reaction system, which will aid in future studies of the reactor.

However, this investigation was only on the proof-of-concept level. Significant hurdles (e.g. scaling/numbering up, further catalyst development) must be surpassed before the microstructured falling film reactor can be considered a true contender in hydrogenation technology.
5. Microstructured Falling Film Reactor: Hydrodynamic and Temperature Profile Investigation

The work done thus far involving the microstructured falling film reactor has been based on theoretical assumptions such as the liquid film thickness and uniformity of the temperature profile. Ideally, investigations into these fundamental aspects of the system should have been performed right at the start. However, such resources only became available towards the end of the project. Therefore, they will be presented here in the interest of completeness.

5.1 Liquid Film Thickness Measurements using Confocal Microscopy

Confocal microscopy is a widely used technique in anatomical sciences to obtain high resolution images and 3-D reconstructions of biological samples. Its main advantage is that it produces clear images of specimens at various depths. Only the region of the sample that is in-focus is detected. As such, by taking images at a series of depths, a 3-D image of the sample can be built-up.

5.1.1 Basic Working Principle of Confocal Microscopy

A laser is used to illuminate the sample (refer to Figure 5.1). The beam first has to pass through a small pinhole before being focused onto the sample using an objective lens. Because a laser is used, the beam is highly coherent and the focused spot is very specific. The light reflected from the sample passes through the objective again, then through the beamsplitter and finally through another pinhole, called the confocal pinhole, before being collected by a photomultiplier and processed into an image.
Light rays reflected from above the focal plane focus behind the confocal pinhole and are therefore mostly blocked by the pinhole. Light reflected from below the focal plane have a focus that lies before the pinhole, thus will have expanded out at the pinhole and become blocked as well. Therefore, the confocal pinhole allows only reflected light that originates from the desired depth to pass through to the detector, giving rise to sharp images. By using the laser to scan the surface at a given depth, a 2-D map of the sample at that depth can be constructed. These maps, when taken at a range of depths, can then be put together to form a 3-D model of the sample. And because the coordinate of each pixel is known, depth discrimination and optical tomography can be performed to high accuracy (Leica Microsystems, 2001, University of Waterloo, 1999, Ladic, 1995).
5.1.2 Preliminary Experiments

As most work done with confocal microscopy has been with solid or fluorescent structures, it was uncertain whether it would be possible to focus exactly on the surface of the liquid, especially when it was moving. First, dry channels were imaged using a Lasertech Corporation (1LM2W) Videorate laser scanning confocal microscope system which was an automated system linked to rudimentary analysis software. The reactor plate that was coated using UV-decomposed palladium acetate was used. The images are shown in Figure 5.2. The images are quite high quality and show good detail of the surface. The images show a very rough surface. This is due to the use of hydrochloric acid to strip the original sputtered-palladium layer. Appreciable corrosion of the stainless steel plate has occurred, and the channels are slightly shallower.

![Image](a) ![Image](b)

Figure 5.2: Confocal microscopy images of the UV-decomposed palladium acetate catalyst plate (pixel resolution 640 x 480). a) Visual view from above  b) View using analysis software (channel depth 100 μm, width 300 μm)

One problem that was encountered was sample mounting in the confocal microscope as the reactor had to be placed flat down on its back, meaning that a falling film could
not be generated. To remedy the situation, attempts were then made to see whether acceptable images could be generated with the reactor tilted upwards slightly. The images in Figure 5.3 show that there was no appreciable loss of quality. However corrections would have to be made to take the tilting into account.

![Confocal microscopy images of the tilted catalyst plate](image-url)

Figure 5.3: Confocal microscopy images of the tilted catalyst plate (bottom of image is tilted up). a) Visual view from above b) View using analysis software

Next, a droplet of water was placed in the channel. It was allowed to dry until a relatively thin film remained before an image was captured (Figure 5.4). The wetted areas are noticeably different from the un-wetted regions as they have a different reflectivity. An interesting observation was that the surface of the water was constantly in an agitated state. This may have been due to evaporation.

![Wetted areas](image-url)
Computer-processed images of the region while wet and after drying out are shown in Figure 5.5. A small difference can be observed between the two images. However, this shows that the instrument is capable of picking up the difference in depth caused by the presence of a thin film of fluid.

In order to improve the quality of the image, a stainless steel reactor plate was used in further experiments. Figure 5.6 shows an image of the edge of a droplet of liquid in the channels. Because confocal microscopy involves scanning the target layer by layer, depth data is accurately recorded. As such, changes in depth can be determined, as shown in the figure on the right. The measurement was done for the middle channel, from bottom to top. A shortcoming of this method is that there is quite a large amount of noise. However, it is quick and does not involve image processing.
Next, a dry map image of the same area was taken (Figure 5.7). Due to the relatively large difference in depth and the reflectivity of the stainless steel, the images obtained were rather noisy, and had to be smoothened out. However, the software available was not quite able to remove all noise.

Following that, one image was subtracted from the other to give the water-filled region. Again, as there was a fair amount of noise in the image, the result was somewhat noisy as well. However, the result was clearer and more useful than the previous attempt. A contour map of the result is shown in Figure 5.8. A concave profile can be seen in the middle channel (highest regions denoted by brown, lowest by green). Note: the channel walls appear to be lower (yellow) than the edges of the liquid film (brown) as they have been subtracted.
Figure 5.8: Resulting image from the subtraction of dry plate from wet plate. Colour code (highest to lowest): brown, yellow, green.

The experiment was repeated, and this time, a 3D-wireframe model of the subtracted area was obtained as well to give a clearer picture (refer to Figure 5.9, due to the resolution of the wireframe figure, details can only be seen clearly when fully enlarged on a monitor screen). Again, because of the way confocal microscopy works, all height data is stored.

Figure 5.9: Resulting image from the subtraction of dry plate from wet plate, wireframe figure on right. Colour code (highest to lowest): brown, yellow, green.

The software which had been used for these examples was fairly rudimentary. As such, it was unable to smoothen out most of the noise as confocal microscopy is generally used to examine biological specimens, which are not as reflective as stainless steel. More advanced image processing software packages are available. However,
because it was difficult to obtain measurements of vertical flow using this particular system, further experiments were conducted using a different system.

5.1.3 Liquid Film Thickness Measurements

This system (Noran Odyssey videorate laser scanning confocal microscope system) was not as automated as the previous system and was therefore more flexible. Unfortunately, this system was not linked to automated data processing packages, making it impossible to obtain data in the detailed manner of the previous system. Instead, height data had to be obtained by focusing manually on the object. However, this system was linked to a video recording system. To perform confocal microscopy on the falling film plate held vertically, a mirror was used to deflect the path of the laser beam of the microscope by 90°. The set-up was arranged such that the beam would come out horizontally through a lens extending out of the microscope. With this new arrangement, the focusing mechanism had to be changed from the usual vertical focusing of microscopes to a horizontal focusing mechanism.

Once it had been established that focusing on the dry falling film plate in this manner could be achieved, a droplet of water was placed on the channels and made to run down them to form a thin liquid layer. Again, focusing at various depths was found to be satisfactory with the rudimentary arrangement. The surface of the liquid film was readily identifiable, and there proved to be no difficulty in focusing on the bottom of the channel through the liquid film either. Therefore this method was applicable to the measurement of thin liquid films on the falling film plate. Video footage of the drying-out of the liquid film was also captured.
Because the focusing mechanism used in these experiments were fairly rough, they would not give accurate measurements of the liquid film thickness. Therefore, a new stage was designed (see Figure 5.10). It incorporated a micrometer screw that moved the plate along the focal axis, and a secondary screw that moved the plate perpendicular to this axis thus allowing the confocal beam to scan across the plate. This would allow accurate recording of height data across several channels.

Figure 5.10: Microscope stage with a horizontal focusing mechanism (to and away from the confocal beam) controlled using a screw micrometer (for depth measurements), and a secondary horizontal axis of motion perpendicular to the confocal beam

Liquid film thickness measurements were made using pure ethanol pumped through the reactor using a syringe pump (Razel A-99). A Nikon Mplan extra large working distance (0.4 ELWD) lens with 20x magnification was used. The imaging settings were: intensity 15%, brightness 40, contrast 132 and confocal pinhole 6.03 mm. Flowrates in the range 0.5-2 ml/min were studied. Measurements were taken across five adjacent channels. In each channel, the liquid film thickness was measured at five points located 0, 70, 150, 230 and 300 μm from the left wall. The averages of these measurements were then taken and plotted in Figure 5.11 below.
Figure 5.11: Average liquid film thickness profile across a channel at various flowrates

At 0.5 ml/min, the contact point between the surface of the liquid film and the side walls of the channels could not be determined as the walls were vertical and the contact point was below the top of the channels. As the flowrate was increased to 0.7 ml/min, the contact point rose to the top of the channel. Above that flowrate, the meniscus of the film became increasingly flat. As the flowrate approached 2 ml/min, very thin ‘streams’ of liquid could be seen to flow into defects on the top of the channel wall. At 2 ml/min, the channels flooded.

Table 5.1 compares the minimum and average measured liquid film thickness with those calculated using the modified Nusselt equation (Hessel, et al, 1999):

\[
\delta = \sqrt{\frac{3V \mu}{\rho bn g}}
\]

where
- \(V\) = volumetric flowrate
- \(\mu\) = liquid viscosity
- \(\rho\) = liquid density
- \(b\) = channel width
- \(n\) = number of channels
- \(g\) = gravitational acceleration
There is quite a large disparity between the values. This is most likely due to the fact that the modified Nusselt equation is inadequate in this situation as the effect of capillary forces becomes much more pronounced at such small scales. From these results, it is clear that there is a lot more work that needs to be done with regards to further understanding the fluidics of microscale structures.

### 5.2 Temperature Profile Investigation using Infra-red (IR) Spectroscopy

These experiments were performed using an Agema 880 system. Heating for the reactor was provided by a water bath (Grant W14). Because it proved to be very difficult to tell whether the infrared camera was focused on the falling film plate, the glass coverplate of the reactor was removed to allow a coin to be placed on the falling film plate to aid in focusing. The loss of the coverplate was likely to affect the temperature of the falling film plate to a certain degree, but it was deemed a necessity.

Temperature measurements were taken in the range 30-60 °C (temperature of the water bath). Prior to taking readings, the reactor was left for 30 min to allow the temperature profile to stabilise. Air currents were minimised by placing a cardboard cylinder between the lens of the IR camera and the opening of the microreactor. The camera was pre-calibrated, and was used as is due to the fact that re-calibration was a very complex procedure and the author had been advised not to attempt it. However,
A thermocouple was used to check the temperature at the centre of the falling film plate throughout the experiments. The experimental results are shown in Figures 5.12-5.15.

Figure 5.12: Temperature profile of the falling film plate at 30 °C

Figure 5.13: Temperature profile of the falling film plate at 40 °C

Figure 5.14: Temperature profile of the falling film plate at 50 °C
In general, as the temperature increased, the temperature spread also increased (see Table 5.2). The temperature profile also became less uniform. The central area of the plate was cooler than the sides, with the top and bottom the warmest. The bottom of the plate had been expected to be slightly warmer as this was where the water inlet was located. Examination of the rest of the microreactor housing showed that the temperature was higher than that of the falling film plate. It is likely that this caused the sides of the plate to be warmer than the central section. Also, with the removal of the coverplate, the central section would be expected to lose more heat than it would under experimental conditions.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Maximum temperature, $T_{\text{max}}$ (°C)</th>
<th>Minimum temperature, $T_{\text{min}}$ (°C)</th>
<th>Average temperature, $T_{\text{avg}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>29.4</td>
<td>28.5</td>
<td>28.8</td>
</tr>
<tr>
<td>40</td>
<td>37.4</td>
<td>36.3</td>
<td>36.7</td>
</tr>
<tr>
<td>50</td>
<td>45.1</td>
<td>43.0</td>
<td>43.6</td>
</tr>
<tr>
<td>60</td>
<td>55.7</td>
<td>52.8</td>
<td>53.6</td>
</tr>
</tbody>
</table>

Table 5.2: Maximum, minimum and average plate temperature at various water bath temperatures

It should be noted that the temperatures measured by the thermocouple were higher than those measured by the IR camera. This could have been due to the camera being slightly out of focus and therefore measuring the temperature just above the plate itself.
and/or a small offset to the calibration. This discrepancy increased with temperature (≈ 2 °C at 60 °C), suggesting that it may have to do with the calibration.

This set of experiments showed that the microstructured falling film reactor had a reasonably uniform temperature distribution. However, the uniformity (defined here as $(T_{\text{max}} - T_{\text{min}})/T_{\text{avg}}$) decreased slightly as the temperature increased (3 % at 30 °C, 5 % at 60 °C). As the reactor is intended for liquid phase reactions, it is unlikely that it will be used at much higher temperatures. Therefore, these variations should be acceptable. Further work in this area includes measurements during reaction and, potentially, ways of further improving the uniformity.

5.3 Conclusions

Exploration of some physical characteristics of the microstructured falling film reactor have revealed that much remains unknown or unclear about some of the basic principles governing it. The main lesson that the work presented in this chapter brings to the forefront is that assumptions used in conventional chemical engineering may not always be directly applicable to microscale chemical engineering initiatives, no matter how intuitive those assumptions may be. It was assumed that the liquid film thickness could be fairly accurately estimated using the Nusselt equation, but experimental evidence showed that this was not the case. It was thought that the temperature across the microstructured plate would be almost completely uniform, but slight variations were evident.

This shows that the development of microreactors is not an entirely straightforward process. Conventional thinking and approaches are challenged at times, and
researchers in this area should always be mindful of these pitfalls. There remains a lot of scope for fundamental studies to be done in the microscale in order to bring about greater understanding of the fluidic and material interactions at this scale. Only through such efforts will the microscale become conventional.
6. Microstructured Falling Film Reactor: Modelling of Nitrobenzene Hydrogenation

Having successfully performed the hydrogenation of nitrobenzene in the falling film reactor, an attempt was made to create a simple model of the system. The results of the parametric studies using the incipient wetness catalyst, IW1 (see Chapter 4), were used as the basis for comparison as this catalyst was the most robust and reproducible.

6.1 The Model

The system was modelled as a liquid film passing over a flat catalytic plate on one side, with the axial and radial coordinates defined as the length and height of the liquid film, respectively. Because there remained much uncertainty over the kinetics of the reaction, three different Langmuir-Hinselwood-type kinetic expressions were tested.

\[
\text{Figure 6.1: Geometry of the model}
\]

The liquid bulk was defined using the following equation:

\[
u_z \frac{\partial C_i}{\partial z} = D_i \left[ \frac{\partial^2 C_i}{\partial z^2} + \frac{\partial^2 C_i}{\partial \xi^2} \right]
\]

Assuming Henry's Law applies, the boundary conditions were defined as:

a) **Inlet:** For all \(x,\)
   \[
z = 0
   \]
   \[
   C_{NB} = C_{NB0}
   
   C_{H2} = C_{AN} = 0
   \]
b) Outlet: For all x,
\[ z = L \]
\[ \frac{\partial C_i}{\partial z} = 0 \]

c) Interface: For all z,
\[ x = \delta \]
\[ C_{H2} = \frac{P_{H2}}{H} \]
\[ \frac{\partial C_{NB}}{\partial x} = \frac{\partial C_{AN}}{\partial x} = 0 \]

d) Wall: For all z,
\[ x = 0 \]
\[ D_i \frac{\partial C_i}{\partial x} = \sigma r \]

where
- C = concentration
- P = pressure
- H = Henry's Law constant
- D = diffusivity through ethanol
- \( \sigma \) = stoichiometric coefficient
- r = rate equation
- \( u_z \) = liquid flow velocity in z direction
- NB = subscript denoting nitrobenzene
- H2 = subscript denoting hydrogen
- AN = subscript denoting aniline
- i = subscript denoting nitrobenzene, hydrogen and aniline

The equations were made dimensionless by introducing the following variables:
\[ \zeta = \frac{z}{L} \]
\[ X = \frac{x}{\delta} \]
\[ \overline{C_i} = \frac{C_i}{C_{NB0}} \]
\[ \varepsilon_i = \frac{D_i}{D_{NB}} \]
\[ Pe_{NB} = \frac{u_z L}{D_{NB}} \]
\[ \lambda = \frac{L}{\delta} \]

The dimensionless equations are:

a) Bulk: For laminar flow:
\[ 1.5 (1 - X^2) \frac{\partial \overline{C_i}}{\partial \zeta} = \frac{\varepsilon_i}{Pe_{NB}} \left[ \frac{\partial^2 \overline{C_i}}{\partial \zeta^2} + \lambda^2 \frac{\partial^2 \overline{C_i}}{\partial X^2} \right] \]
For plug flow:
\[
\frac{\partial \overline{C}_i}{\partial \zeta} = \frac{e_i}{Pe_{NB}} \left[ \frac{\partial^2 \overline{C}_i}{\partial \zeta^2} + \lambda^2 \frac{\partial^2 \overline{C}_i}{\partial X^2} \right]
\]

b) Inlet:
- \( Z = 0 \)
- \( \overline{C}_{NB} = 1 \)
- \( \overline{C}_{H_2} = \overline{C}_{AN} = 0 \)

c) Outlet:
- \( Z = 1 \)
- \( \frac{\partial \overline{C}_i}{\partial \zeta} = 0 \)

d) Interface:
- \( X = 1 \)
- \( \overline{C}_{H_2} = \frac{P_{H_2}}{HC_{NB0}} \)
- \( \frac{\partial \overline{C}_{NB}}{\partial X} = \frac{\partial \overline{C}_{AN}}{\partial Z} = 0 \)

e) Wall:

Three different Langmuir-Hinshelwood-type rate equations were tested. The first was derived by Turek, et al (1985) and matched to experimental results from a discontinuous laboratory-scale stirred autoclave (volume 0.1 l, temperature 9-45 °C, 0.11 MPa) using a nickel on alumina catalyst (catalyst loading 0.5-1.0 g, catalyst particle size 20-40 μm) and ethanol as solvent. This rate equation assumed that changes in the concentrations of aniline, ethanol and water would not affect the rate of reaction.

\[
r = \frac{kK_{NB}C_{NB}K_{H_2}C_{H_2}}{1 + K_{NB}C_{NB} + K_{H_2}C_{H_2}}
\]

(I)

\[
e_i \frac{\partial \overline{C}_i}{\partial X} = \sigma kK_{NB}K_{H_2} \frac{\overline{C}_{NB}\overline{C}_{H_2}}{(1 + K_{NB}C_{NB0}\overline{C}_{NB})(1 + K_{H_2}C_{NB0}\overline{C}_{H_2})}
\]

where
- \( k \) = reaction rate constant
- \( K_{NB} \) = adsorption coefficient for nitrobenzene
- \( K_{H_2} \) = adsorption coefficient for hydrogen

The second rate equation was derived based on Winterbottom’s postulate that the formation of nitrosobenzene on the catalyst surface is the rate determining step for nitrobenzene hydrogenation (1981):
A first order reaction (with respect to hydrogen) assuming that:

a) the second step of the mechanism is rate determining

b) hydrogen competes with nitrobenzene for active sites

c) coverage of sites by other intermediate compounds and aniline can be ignored

gives rise to the following rate equation (Hatziantoniou, et al, 1986):

\[
\begin{align*}
\dot{r} &= \frac{kK_{NB}C_{NB}K_{H2}C_{H2}}{(1 + K_{NB}C_{NB} + K_{H2}C_{H2})^3} \\
\varepsilon_i \frac{\partial C_i}{\partial x} &= \sigma_i kK_{NB}K_{H2}C_{NB0} \frac{C_{NB}C_{H2}}{(1 + K_{NB}C_{NB0}C_{NB} + K_{H2}C_{H2}C_{NB0}C_{H2})^3}
\end{align*}
\]  

(II)

This equation was matched with experimental results using a slurry reactor (inner diameter 0.06 m, mechanical stirrer at 1200 rpm) with palladium catalyst (ground monolithic catalyst, catalyst loading 3.33 kg/m^3, particle size 5 μm).

The third kinetic expression used was also derived by Hatziantoniou, et al (1986) and was based on a combination of both Langmuir-Hinshelwood and Eley-Rideal mechanisms. In this case, the assumption was that step (1) was a rapid step followed by a rate-determining step where the nitronic acid intermediate, i.e. the...
product of step (1), reacts with molecular hydrogen. Assuming hydrogen and nitrobenzene compete for the same active sites, the kinetic expression is:

\[
r = \frac{k K_{NB} C_{NB} k C_{H2}^{1/2} C_{H2}^{1/2}}{(1 + K_{NB} C_{NB} + K_{H2}^{1/2} C_{H2}^{1/2})^2}
\]

(III)

\[
e_i \frac{dC_i}{dX} = \sigma_i k K_{NB} C_{NB}^{1/2} C_{NB0}^{1/2} \frac{C_{NB} C_{H2}}{(1 + K_{NB} C_{NB0} + K_{H2}^{1/2} C_{NB0}^{1/2})^2}
\]

It was stated that such a route was unlikely. However, comparisons with experimental data found that this kinetic expression produced results that made more sense than the previous expression (even though the previous expression was found to give a better fit, the temperature-dependence of the adsorption constants was found to be erroneous).

The parameters used in the model are shown in Table 6.1. From the stoichiometry of the reaction, nitrobenzene is the excess reactant until the reaction reaches 90+ % conversion. Therefore, increasing hydrogen pressure will have an effect on the conversion provided the reaction is not zero order with respect to hydrogen concentration.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel width (m)</td>
<td>0.0003</td>
</tr>
<tr>
<td>Channel length (m)</td>
<td>0.065</td>
</tr>
<tr>
<td>Number of channels</td>
<td>64</td>
</tr>
<tr>
<td>Liquid viscosity (Pa s)</td>
<td>8.57 x 10^{-4}</td>
</tr>
<tr>
<td>Liquid density (kg/m³)</td>
<td>815</td>
</tr>
<tr>
<td>Diffusivity of hydrogen in ethanol (m²/s)</td>
<td>3.51 x 10^{-9}</td>
</tr>
<tr>
<td>Diffusivity of nitrobenzene in ethanol (m²/s)</td>
<td>2.1 x 10^{-9}</td>
</tr>
<tr>
<td>Diffusivity of aniline in ethanol (m²/s)</td>
<td>2.1 x 10^{-9}</td>
</tr>
<tr>
<td>Initial concentration of nitrobenzene (mol/m³)</td>
<td>100</td>
</tr>
<tr>
<td>Henry's constant (atm m³/mol)</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 6.1: Parameters used in the reactor model

The diffusivity of hydrogen in ethanol was calculated using the Chen-Chen formula for gases in low viscosity liquids, which is reported to have an accuracy of 6%
The diffusivity of nitrobenzene and aniline were estimated using the Wilke-Chang formula (Knudsen, et al, 1997, see Appendix 6-2).

A gPROMS program was written to solve the above equations (see Appendix 6-3 for the program) using a second order centred-finite difference method (CFDM). The effect of the number of points used was studied (see Table 6.2) and it was decided to use 30 points for all experiments.

<table>
<thead>
<tr>
<th>Number of points</th>
<th>Nitrobenzene conversion</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.846678</td>
<td>2.02</td>
</tr>
<tr>
<td>30</td>
<td>0.848075</td>
<td>4.71</td>
</tr>
<tr>
<td>50</td>
<td>0.848728</td>
<td>15.2</td>
</tr>
</tbody>
</table>

Table 6.2: Effect of the number of points used on nitrobenzene conversion and modelling time (Langmuir-Hinselwood (I), laminar flow, \( k = 0.0021 \), \( K_{NB} = 1.72 \), \( K_{H2} = 0.3 \), 1 bar, 0.5 ml/min)

The values of \( k \), \( K_{H2} \) and \( K_{NB} \) were adjusted to match the experimental conversion at the standard condition (0.5 ml/min liquid flowrate, 1 bar hydrogen pressure and 60 °C). Each kinetic expression was studied using both laminar and plug flow regimes (while the flow conditions suggest that a laminar flow profile would most applicable, plug flow profiles were briefly investigated as well). For each combination, flowrates of 0.5, 1, 2 and 3 ml/min and pressures of 1, 4 and 6 bar were used.

### 6.2 Liquid Film Thickness

The thickness of the liquid film at different flowrates was calculated based on the experimental measurements detailed in Chapter 5. Unfortunately, the channels were flooded at flowrates greater than or equal to 2 ml/min and film thickness measurements could not be performed satisfactorily. Therefore, the film thicknesses at 2 and 3 ml/min were extrapolated, as shown in Figure 6.2.
measurements could not be performed satisfactorily. Therefore, the film thicknesses at 2 and 3 ml/min were extrapolated, as shown in Figure 6.2.

A simple, linear approximation was used. It was likely that this approximation would overpredict film thicknesses above the flooding limit as the liquid would spread out over the top of the channels. The film thicknesses calculated using this expression are shown in Table 6.3.

<table>
<thead>
<tr>
<th>Flowrate (ml/min)</th>
<th>Calculated liquid film thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>82.5</td>
</tr>
<tr>
<td>1</td>
<td>96.7</td>
</tr>
<tr>
<td>2</td>
<td>125</td>
</tr>
<tr>
<td>3</td>
<td>153</td>
</tr>
</tbody>
</table>

Table 6.3: Calculated liquid film thicknesses

6.3 Langmuir-Hinshelwood Model (I)

\[
r = \frac{kK_{NB}C_{NB} \cdot K_{H_2}C_{H_2}}{1 + K_{NB}C_{NB} \cdot (1 + K_{H_2}C_{H_2})}
\]
As mentioned previously, this kinetic expression was developed for the hydrogenation of nitrobenzene over a nickel catalyst. Whilst the absorption coefficients provided were based on nickel ($K_{NB} = 1.72$, $K_{H2} = 0.3$), it was thought that they could be used as starting points in this investigation. The results can be seen in Figures 6.3-6.4.

Figure 6.3: Base case comparison of model with experimental results (Langmuir-Hinselwood (I), laminar flow, $k = 0.0021$, $K_{NB} = 1.72$, $K_{H2} = 0.3$)

Figure 6.4: Base case comparison of model with experimental results (Langmuir-Hinselwood (I), plug flow, $k = 0.013$, $K_{NB} = 1.72$, $K_{H2} = 0.3$)
The laminar flow model appeared to be a closer match than the plug flow model. Next, a series of studies was performed to optimise the values of $K_{NB}$ and $K_{H2}$. This was done by first fixing the value of $K_{H2}$ while varying the value of $K_{NB}$ for simulations at 1, 4 and 6 bar pressure under both flow regimes. The simulations were then repeated by varying $K_{H2}$ and fixing $K_{NB}$. The effect of changing $K_{H2}$ at different pressures under a laminar flow regime is shown in Figures 6.5-6.7 (see Appendix 6-4 for the other results).

Figure 6.5: Effect of varying $K_{H2}$ (Langmuir-Hinselwood (I), laminar flow, $K_{NB} = 1.72$, 1 bar)

Figure 6.6: Effect of varying $K_{H2}$ (Langmuir-Hinselwood (I), laminar flow, $K_{NB} = 1.72$, 4 bar)
It was found that:

a) When varying $K_{H2}$, the trends were similar for both laminar and plug flow. Varying $K_{NB}$ resulted in different trends under different flow regimes.

b) Changing the value of $K_{H2}$ had little effect at low pressure (i.e. 1 bar), but had much greater effect at higher pressures. Increasing the value of $K_{H2}$ increased the conversion slightly at low pressure, but had the opposite effect at high pressures. This behaviour may be due to the fact that both hydrogen and nitrobenzene compete for the same sites. At low pressures, the hydrogen concentration at the catalyst surface is low. Therefore, a larger adsorption coefficient would increase the amount absorbed thus increasing conversion. Hydrogen concentration at the catalyst, however, increases with pressure. Increasing the adsorption coefficient would lead to an inhibiting effect due to stronger adsorption of hydrogen.

c) Under laminar flow, increasing $K_{NB}$ led to lower conversions at 1 bar, most likely due to the fact that stronger adsorption of nitrobenzene would reduce the number of active sites available for hydrogen absorption. At 4 and 6 bar,
however, increasing $K_{NB}$ resulted in higher conversions at 0.5 and 1 ml/min flowrates and lower conversions at 2 and 3 ml/min. This effect may be a result of the relative concentrations of nitrobenzene and hydrogen at the catalyst surface. As flowrate increases, the ratio of hydrogen diffusion time through the liquid film to the residence time will increase. This means that an increasing portion of the reactor length will be less rich in hydrogen. So, at low flowrates, increasing $K_{NB}$ (i.e. increasing nitrobenzene adsorption) would be able to ‘take advantage’ of the increased hydrogen solubility due to increased pressure. However, at high flowrates, increasing nitrobenzene adsorption coupled with increasing catalyst bypass of hydrogen would have the net effect of reducing conversion.

d) Under plug flow, increasing $K_{NB}$ reduced conversion very slightly at 1 bar, but increased conversion at 4-6 bar. Again, this is most likely because of the reduction of the proportion of catalyst available to hydrogen at low pressures, but with increased hydrogen concentration at higher pressures an increase in nitrobenzene absorption would shift the proportions of catalyst available to each reacting species closer to stoichiometric ratios.

Figure 6.8 shows the best match between model and experiment for this kinetic expression (laminar flow mode). The model underpredicts at low pressure and at flowrates greater than or equal to 1 ml/min. However, it overpredicted at the higher pressures at the lowest flowrate of 0.5 ml/min. The model also predicted that conversions at 4 and 6 bar would be fairly similar (according to the rate equation, large concentrations of hydrogen would shift the system towards a zero-order system.
with respect to hydrogen, at low concentrations it would be first order), a fact that was not demonstrated by the experimental results.

Figure 6.8: Final comparison of model with experimental results (Langmuir-Hinselwood (I), laminar flow, \( k = 0.0042, K_{NB} = 0.01, K_{H2} = 1 \))

Figure 6.9: Final comparison of model with experimental results (Langmuir-Hinselwood (I), plug flow, \( k = 0.02, K_{NB} = 0.01, K_{H2} = 1 \))

Figure 6.9 shows the corresponding results using the plug flow mode. Deviations from experimental results were larger, as it was expected that the system was operating under laminar flow conditions. Comparing the laminar and plug flow
results, it can be seen that the plug flow model predicts lower conversions at low pressure but higher conversion at high pressure. A simple study was performed to investigate this result, using first order and zero order kinetic expressions (see Figures 6.10 and 6.11, respectively). A plug flow profile resulted in lower conversions than a laminar flow profile for a first order system, while the reverse was true for a zero order system. Recall that Model (I) approximates a first order system with respect to hydrogen at low pressures, and a zero order system at high pressures. Therefore, the plug flow profile would be expected to result in lower conversions than the laminar flow profile at low pressures and the reverse at high pressures, which shows that the results predicted by the model are consistent.

Figure 6.10: Comparison of laminar and plug flow using first order reaction kinetics ($r = kC_A$)

Figure 6.11: Comparison of laminar and plug flow using zero order reaction kinetics ($r = k$)
Examining the hydrogen concentrations at the wall, it was found that the hydrogen concentration was higher under laminar flow conditions for first order kinetics (see Figure 6.12). It was thought that this was because the surface of the liquid moved faster in laminar flow than in plug flow. This would increase the rate at which hydrogen dissolved into the liquid thus increasing the concentration driving force which in turn increased the hydrogen concentration at the wall. This would explain the higher predicted conversion using a laminar flow model. For a zero-order system, the wall hydrogen concentration was lower using plug flow as well. However, the concentration was much higher than it was using first order kinetics. Because the reaction order was zero with respect to hydrogen concentration, the concentration did not matter provided hydrogen was available for reaction. Due to higher liquid velocity at the wall, a plug flow regime would result in higher conversion.

![Figure 6.12: Comparison of laminar and plug flow wall hydrogen concentration using first and zero order kinetics (2 ml/min flowrate)](image)

6.4 Langmuir-Hinshelwood Model (II)

\[
r = \frac{kK_{NB}C_{NB}K_{H2}C_{H2}}{(1 + K_{NB}C_{NB} + K_{H2}^{\frac{1}{2}}C_{H2}^{\frac{1}{2}})^3}
\]
Figures 6.13-6.15 show the effect of varying $K_{H_2}$ using the laminar flow model. As with the previous model, increasing $K_{H_2}$ increased the predicted conversion at 1 bar, while reducing the conversion at 4 and 6 bar. At large values of $K_{H_2}$, conversion decreased with increasing pressure above 4 bar. Again, this is most likely due to the interplay of factors such as the competition between hydrogen and nitrobenzene for surface coverage and the ratio of both components on the surface.

Figure 6.13: Effect of varying $K_{H_2}$ at 1 bar (Langmuir-Hinseilwood (II), laminar flow, $K_{NB} = 0.01$)

Figure 6.14 Effect of varying $K_{H_2}$ at 4 bar (Langmuir-Hinseilwood (II), laminar flow, $K_{NB} = 0.01$)
Figure 6.15: Effect of varying $K_{H2}$ at 6 bar (Langmuir-Hinselwood (II), laminar flow, $K_{NB} = 0.01$)

The best match found is shown in Figure 6.16. It gave a result that was comparable to the first model. Figure 6.17 shows the corresponding results under the plug flow regime. As with the previous model, the laminar flow model predicted higher conversions at low pressure and lower conversions at high pressure.

Figure 6.16: Final comparison of model with experimental results (Langmuir-Hinselwood (II), laminar flow, $k = 0.036$, $K_{NB} = 0.01$, $K_{H2} = 0.3$)
Figure 6.17: Final comparison of model with experimental results (Langmuir-Hinshelwood (II), plug flow, $k = 0.2, K_{NB} = 0.01, K_{H2} = 0.3$)

6.4 Langmuir-Hinshelwood Model (III)

$$r = \frac{kK_{NB}C_{NB}K_{H2}C_{H2}}{(1 + K_{NB}C_{NB} + \frac{1}{2}K_{H2}C_{H2}^{1/2})^3}$$

This kinetic model was examined in the same way as the previous models. The best fit, based on a laminar flow profile, is shown in Figure 6.18. The corresponding results under a laminar flow pattern can be seen in Figure 6.19. Again, the laminar flow model predicted higher conversions at low pressure and lower conversions at high pressure.
6.6 Discussion and Conclusions

The best matches for all three models (laminar flow) are compared in Figures 6.20-6.22. Model (III) gave the best match overall, in-line with the observations of Hatziantoniou, et al (1986). All the models were found to give slightly better matches at higher pressure, suggesting that the hydrogen-dependence of the reaction system was not yet accurately modelled.
Figure 6.20: Comparison of all models with experimental results (1 bar)

Figure 6.221: Comparison of all models with experimental results (4 bar)

Figure 6.22: Comparison of all models with experimental results (6 bar)
There was the possibility that the method used to fit the kinetic parameters in the models, i.e. focusing on the lowest flowrate and pressure, was leaving some information out of the picture. Therefore, k values were changed in order to find solutions that matched the experimental result at 0.5 ml/min and 6 bar (the optimised $K_{H2}$ and $K_{NB}$ values were kept unchanged). Figures 6.23-6.25 show the results of these simulations.

![Graph](image)

**Figure 6.23:** Comparison of model (I) with experimental results, matched to the experimental value at 0.5 ml/min and 6 bar (laminar flow, $k = 0.00305$, $K_{NB} = 0.01$, $K_{H2} = 1$)

![Graph](image)

**Figure 6.24:** Comparison of model (II) with experimental results, matched to the experimental value at 0.5 ml/min and 6 bar (laminar flow, $k = 0.02$, $K_{NB} = 0.01$, $K_{H2} = 0.3$)
Figure 6.25 Comparison of model (III) with experimental results, matched to the experimental value at 0.5 ml/min and 6 bar (laminar flow, $k = 0.00024$, $K_{\text{fmb}} = 0.01$, $K_{\text{H2}} = 15$)

In this analysis, the models could be interpreted as underpredicting the results at high flowrates. The most likely reasons for this are:

a) the values used for the liquid film thickness were too large. Therefore, hydrogen would take longer to diffuse through the liquid film than what would happen experimentally. This would result in lower conversions. This had already been expected due to the need to extrapolate liquid film thicknesses at higher flowrates.

b) mass transfer enhancement factors which were unaccounted for in this simple model. Such enhancement is usually attributed to hydrodynamic instability at the gas-liquid interface which leads to interfacial turbulence. The most common example of this behaviour is the Marangoni effect, which describes movement in an interface caused by longitudinal variations of interfacial tension (Stemling and Scriven, 1959). Another example is hydrodynamic instability, in which secondary flow in a tangential direction to the interface due to the presence of high concentration gradients results in non-linear mass transfer that leads to
injection or suction in the boundary layer (Boyadjiev, et al, 1996). Wave formation on the surface of liquid films falling under gravity has also been known to enhance mass transfer, due to velocities normal to the interface and recirculation within waves (Wasden and Dukler, 1990).

Another observation that can be made from all the results is that there is a greater difference between the predicted values at low pressure and those at high pressure, than there is experimentally. This is most markedly obvious when comparing the results at 0.5 ml/min at all pressures: experimental values are similar at all pressures, while the theoretical value at 1 bar is often much lower than those at 4 and 6 bar (which tend to be fairly similar). The exact cause of this is uncertain at the moment, but it could be that at lower pressures, the effect of enhanced mass transfer is more evident because of there is less hydrogen available at the interfacial liquid surface. At higher pressures, the correspondingly higher concentration of hydrogen at the liquid surface masks the enhancement.

An interesting item to note is the relative magnitude of the hydrogen absorption constant compared to the nitrobenzene absorption constant. In the studies of both Turek, et al (1985) and Hatziantoniou, et al (1986), it was found that nitrobenzene had a much greater absorption coefficient than hydrogen ($K_{H2}/K_{NB}$ 0.17 for model (I), $3.4 \times 10^3$ for model (II), $1.2 \times 10^{-3}$ for model (III)). In this study, however, the theoretical data could only be fitted to experimental data provided $K_{H2}$ was larger than $K_{NB}$ ($K_{H2}/K_{NB}$ 100 for model (I), 30 for model (II), $1.5 \times 10^3$ for model (III)). The cause of this effect remains unknown, but it should be stressed that while a Langmuir-
Hinselwood-type model may appear to describe a given reaction system, it need not necessarily be mechanistically correct (Hayes and Kolaczkowski, 1997).

Clearly, much work is still required in this area, both theoretically and experimentally. More experimental data, both reaction-based and fluidics-based, will be required to produce a more accurate model. The hydrodynamics of the system are clearly not as straightforward as previously envisioned and the effect of mass enhancement factors will have to be explored and included in future models.
7. Microstructured Falling Film Reactor: Asymmetric Hydrogenation

This chapter explores the use of the microstructured falling film reactor for asymmetric hydrogenation. In this instance, it was thought that a different function of the reactor could be explored: that of evaporation in addition to reaction.

7.1 Asymmetric Transfer Hydrogenation

Unlike nitrobenzene hydrogenation, where hydrogen was supplied as a gas and had to be absorbed, a liquid phase hydrogen-donor was used here as the hydrogen source (Noyori and Hashiguchi, 1997, Zassinovich, et al, 1992). In addition, a homogeneous catalyst was used instead of a heterogeneous catalyst. The purpose of the evaporation was to remove a volatile side-product in order to shift the equilibrium of the reaction forward.

The system chosen for study was the asymmetric transfer hydrogenation of acetophenone to (S)-phenylethanol catalysed by a rhodium complex that was activated by sodium isopropoxide. Isopropanol (IPA) was used as the hydrogen source. The rhodium complex was synthesised using pentamethylcyclopentadienylrhodium chloride dimer and 1R, 2S-aminoindanol.

\[
\begin{align*}
\text{C}_{6}\text{H}_{5}\text{CO}_2\text{Me} + \text{Me}_2\text{C}-\text{OH} & \quad \text{Rh} \quad \text{Cl} \\
\text{Me}_2\text{C}-\text{H} & \quad \text{Me}_2\text{C}-\text{Me} \\
\text{C}_{6}\text{H}_{5}\text{Me} + \text{Me}_2\text{C}=\text{O}
\end{align*}
\]
Research data concerning this reaction is somewhat erratic, possibly due to the variety of catalyst complexes that can be used. For example, Gladiali, et al (1990) found that decreasing the amount of catalyst relative to the amount of substrate resulted in increases in both specific rate and enantiomeric excess (ee), while Gamez, et al (1995) observed that the specific rate increased with concentration but the ee was not. Investigation of ligand concentration led Bernard, et al (1998) to conclude that the concentration of the ligand did not affect the ee, though using too much ligand resulted in a reduction in conversion. Gladiali, et al (1990), on the other hand, found that both catalyst activity and ee increased with ligand concentration while Gamez, et al (1995) found no effect at all. The concentration of the co-catalyst required to activate the catalyst was also observed to have an effect: conversion increased with concentration, but the ee had a maximum depending on the co-catalyst/catalyst ratio (Gamez, et al, 1995). The same authors also reported that the ee decreased with increasing substrate concentration. Bellefon and Tanchoux (1998) observed that the addition of acetone at the start of the reaction could increase the ee at the cost of decreasing the reaction rate. The effect of temperature is also equally erratic. Gladiali, et al (1992) found that ee increased with increasing reaction temperature while Gamez, et al (1995) found the reverse.

Acetone is formed from isopropanol after the donation of hydrogen to acetophenone. Since this reaction is reversible, a batch reaction of this system eventually reaches an equilibrium, which limits the conversion achievable. However, acetone is relatively volatile and its removal from the system would serve to drive the reaction forward. As such, it was proposed to use the falling film reactor as a reactor-evaporator to facilitate the removal of acetone. Even though the residence time of the reactor was
not likely to be long enough to significantly improve the yield, this experiment would still provide useful exploratory information for future work in this area.

7.2 Experimental Set-up

A peristaltic pump (Cole Palmer LC-07524-55) was used to deliver the feed into the reactor. Product was removed using a water-operated suction pump. A nitrogen gas line was connected to the bottom gas interface of the reactor via a rotameter (Cole Palmer), while the top interface was left open to the atmosphere to allow removal of acetone from the system. The reactor was heated using a water bath (Grant W14). The reactor plate was a structured stainless steel plate (see Figure 7.1 for a schematic of the experimental set-up. See Chapter 3 for details of the reactor.

![Figure 7.1: Schematic of the experimental set-up](image)

7.3 Acetone Evaporation

The effect of nitrogen and liquid flowrate on the evaporation of acetone in a solution of IPA was first investigated. The proportion of acetone used was based on the batch experiments of Sun, et al (2003). 2 ml of acetone was mixed with 250 ml of IPA in a flask and kept at 0 °C by placing it in ice. This was done to minimise evaporation in the flask. However, some evaporation did occur. Therefore, samples were taken from
the flask before and after the experiments in order to determine the evaporation in the μ-FFR alone. The reactor was kept at 30 °C for these experiments. Samples were analysed using a gas chromatograph (Agilent 6890). A XXXX column and a TCD were used. The analysis procedure for acetone can be found in Appendix 7-1.

The results were quite erratic, most likely due to irregular vacuum suction rate, inconsistent nitrogen flow through the reactor and unsteady acetone evaporation rate in the feed flask. As such, three sets of experiments were performed and the average of the results was taken. The final results are shown in Figures 7.2-7.3.

![Figure 7.2: Acetone evaporation as a function of nitrogen flowrate at various liquid flowrates](image)

![Figure 7.3: Acetone evaporation as a function of liquid flowrate at various nitrogen flowrates](image)
As would be expected, higher nitrogen flowrate and lower liquid flowrate promoted evaporation (lower liquid flowrate resulted in greater residence time and smaller liquid film thickness). The greatest amount of acetone evaporated was 31% at nitrogen flowrate 150 ml/min and liquid flowrate 0.5 ml/min (theoretical residence time 9.3 s). In comparison, the batch experiments of another researcher (unpublished results) had an evaporation rate of 50% in 60 min. Therefore, the μ-FFR represents a vast improvement in evaporation rate.

7.4 Catalyst Preparation

The catalyst was prepared by mixing 11.2 mg Pentamethylcyclopentadienylrhodium chloride dimmer (Avecia), 5.6 mg 1R,2S-aminoindanol (Avecia) and 100 ml IPA (Aldrich, 99.5%) in a flask at room temperature. Nitrogen (CP grade, BOC) was bubbled through the mixture at 40 ml/min in order to keep the mixture under an inert atmosphere. The mixture was stirred overnight, resulting in a deep red catalyst solution.

7.5 Experimental Procedure

Several experiments were conducted to test the importance of the mixing order of the reactants and catalyst. The reactor was kept at 30 °C for all experiments. Samples were taken from both the reactor and the flask to compare conversions. 10 μl of acetic acid was immediately added to 0.5 ml of sample to deactivate the catalyst in order to halt the reaction. The samples were analysed using a gas chromatograph (Agilent 6890). A Cyclodex-B column was used to separate the components and detection was performed using an FID. See Appendix 7-2 for the analysis procedure.
Conversion and selectivity were calculated using the following formula (based on calibration data of a different researcher):

\[
\text{Conversion} = \frac{[R] + [S]}{[AP] + [R] + [S]}
\]

\[
\text{Selectivity} = \frac{[S] - [R]}{[S] + [R]}
\]

where \([R]\) = area of (R)-phenylethanol in chromatogram

\([S]\) = area of (S)-phenylethanol in chromatogram

\([AP]\) = area of acetophenone in chromatogram

7.5.1 Procedure 1 (P1)

1.125g acetophenone, 63 ml IPA and 25 ml catalyst solution were mixed in a flask that was pre-cooled to 0 °C using ice, after which the 0.75 ml sodium isopropoxide was added. The reactor temperature was kept at 30 °C and a flowrate of 0.5 ml/min was used. The rotameter setting was 50 ml/min. The conversion and selectivity as a function of total reaction time (i.e. total time reactants have spent in the system, from reactant mixing in the feed flask till sample collection) are shown in Figure 7.4. A not insignificant amount of reaction had already taken place in the flask even at 0 °C.

![Figure 7.4: Conversion and selectivity as a function of total reaction time (P1A, flask temperature 0 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min, nitrogen flowrate 50 ml/min)](image)

Figure 7.4: Conversion and selectivity as a function of total reaction time (P1A, flask temperature 0 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min, nitrogen flowrate 50 ml/min)
The experiment was then repeated (see Figure 7.5). This time, samples were taken from the flask at the end of the experiments as well in order to determine how much conversion had taken place within the flask during the entire period of operation.

![Graph](image)

Figure 7.5: Conversion and selectivity as a function of total reaction time for the second experiment (P1B, flask temperature 0 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min, nitrogen flowrate 50 ml/min)

The results showed that most of the reaction takes place in the flask, and that the falling film reactor only improves the conversions by about 3 % (at t = 2 h, conversion in the flask was 32 %, conversion after passing through the falling film reactor was 34.7 %). This result was not totally unexpected as this reaction was fairly slow and the falling film reactor only had a residence time of 9 s. The selectivity after passing through the reactor was lower as well, but the difference between flask and reactor product is practically negligible.

In an attempt to increase the conversion obtained, the nitrogen flowrate was increased to 150 ml/min. It was thought that this would increase the rate at which acetone evaporated. This experiment showed a drastic reduction in conversion (see Figure
However, it was believed that this was due to the deactivation of the catalyst, not the increased nitrogen flowrate because the conversion in the flask was low as well. The improvement in conversion after passing through the microreactor, however, was slightly better than in the previous experiment.

![Graph](image)

Figure 7.6: Conversion and selectivity as a function of total reaction time for the third experiment (P1C, flask temperature 0 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min, nitrogen flowrate 150 ml/min)

### 7.5.2 Procedure II (P2)

This method involved the use of two premixed solutions:

**Solution A:**
- Acetophenone: 4.5 g
- Sodium isopropoxide: 3 ml
- Isopropanol: 125 ml

**Solution B:**
- Metal precursor: 11.2 g
- Ligand: 5.6 g
- Isopropanol: 125 ml

45 ml of each solution was mixed in the feed flask that was pre-cooled to 0°C and passed through the system. The rotameter setting was 150, the reactor was kept at 30 °C and the flowrate was 0.5 ml/min. The results are shown in Figure 7.7.
The conversions obtained were slightly better than the previous experiment. However, they were still not at the level of the initial experiments (P1A and P1B). This reduction in activity was likely due to deactivation of the catalyst when exposed to the atmosphere, in line with the results of another researcher (unpublished results).

This effect was investigated further and the results of two sets of experiments using a fresh catalyst are shown in the table below. Both experiments were conducted with a flask temperature of 0 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min and nitrogen flowrate 150. Samples were taken at 15 min intervals.

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Time (min)</th>
<th>Conversion</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Flask</td>
<td>Reactor</td>
</tr>
<tr>
<td>P2DA</td>
<td>15</td>
<td>15.8</td>
<td>23.5</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>18.2</td>
<td>22.7</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>18.3</td>
<td>22.7</td>
</tr>
<tr>
<td>P2DB</td>
<td>15</td>
<td>16.9</td>
<td>23.4</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>20.3</td>
<td>24.7</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>18.8</td>
<td>23.7</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>21.1</td>
<td>23.1</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>21.6</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Table 7.1: Conversion and selectivity in reproducibility experiments (P2D, flask temperature 0 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min, nitrogen flowrate 150)
It can be seen from the results that there is still an increase in conversion after the reactants have passed through the reactor. However, it is possible that this increase is not completely attributable to the action of the falling film reactor, but could also be due to the fact that the reactants take about 1 min to flow between the flask and the falling film reactor. Because the temperature of the tubing could not be controlled, the reactants would be exposed to ambient temperature throughout this passage.

The conversion in both experiments eventually stopped increasing further at about 23%, which is quite low. It was initially thought that the reaction had reached equilibrium fairly rapidly but this explanation was ruled out by the fact that the reaction is exothermic. As such, increasing the temperature (0 °C in the flask and 30 °C in the reactor) should have resulted in a reduction in conversion. It seems more likely that the reaction rate became very retarded after about 30 min, but increasing the temperature to 30 °C increased the rate, and therefore, the conversion slightly.

From the low conversions, it was also clear that using fresh catalyst alone was not enough to obtain good conversions. Therefore, for the next experiments, a nitrogen line was connected to the feed flask in order to provide an inert atmosphere (nitrogen flowrate 50 ml/min). In addition, the feed flask was kept at 30 °C instead of 0 °C in order to rule out any ambiguities due to changes in reaction rate with temperature. Two experiments were conducted with the feed flask at 30 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min and nitrogen flowrate 150 ml/min. The results are shown in Table 7.2. Experiment P2NA used fresh catalyst, while P2NB used catalyst that had been left overnight under a nitrogen blanket.
Experiment Time Conversion Selectivity
ID (min) Flask Reactor Flask Reactor
P2NA 15 72.4 71.7 86.1 86.3
45 85.1 85.1 85.6 85.7
10 35.7 31.7 86.7 87.1
20 46.2 44.3 87.2 87.2
P2NB 30 52.0 51.8 87.1 87.2
40 55.9 56.9 87.2 86.8
60 59.4 59.8 87.1 87.1

Table 7.2: Conversion and selectivity in deactivation experiments (P2N, flask temperature 30 °C, reactor temperature 30 °C, liquid flowrate 0.5 ml/min, nitrogen flowrate 150 ml/min)

The most obvious result from these experiments was that there was negligible increase in conversion or selectivity after the reactants had passed through the reactor (the apparent reduction in conversion after passage through the falling film reactor for some of the results is most likely due to the time lag for reactant passage between the flask and the reactor outlet, the effect of which was amplified due to the increase of flask temperature to 30 °C). This shows conclusively that the reactor had no impact on the reaction at all. It had been shown in Section 7.3 that a significant amount of acetone could be removed through evaporation and had been expected that this would serve to drive the reaction forward. A possible explanation for this discrepancy is that acetone was present in amounts that were much lower than those used in the evaporation experiments. It is possible that bubbling nitrogen through the feed flask at 30 °C had removed most of the acetone produced (and served to shift the equilibrium forward as well). The much lower concentration of acetone in the liquid feed through the reactor would have reduced the evaporation rate that was achievable. Unfortunately, due to the need for an inert atmosphere in the feed flask, it was not possible to separate these effects using the current experimental set-up.
Another important observation from this experiment is that the catalyst not very stable. The day-old catalyst was exposed to air for brief periods during the setting up of both experiments. Yet there was a very significant decrease in the conversions (85 % for the fresh catalyst, 59 % for the day-old catalyst). Conversely, the selectivity improved with the reduction in conversion.

7.8 Conclusions

While it was demonstrated that the µ-FFR was much more efficient at evaporating acetone than a batch reactor (31 % at a theoretical residence time of 9.3 s vs. 50 % in 60 min for a batch reactor with nitrogen bubbling through), this did not result in improving either conversion or selectivity in the asymmetric phase transfer hydrogenation of acetophenone to (S)-phenylethanol due to intrinsic design and operational limits of the reactor (e.g. the short residence time).

The (in)stability of the catalyst introduced great difficulties and the measures put in place to surmount them need to be further refined in order to separate the effects. Ideally, the reactants should be mixed immediately before entry into the reactor, thus removing the need for the feed flask. However, doing so brings up the question of how much mixing/reaction time is required in order to produce acetone in sufficient amounts to make good use of the evaporative capabilities of the µ-FFR. Such an undertaking would have involved major changes to the experimental set-up and required optimisation experiments, which was beyond the scope of this project. A significant increase in the residence time in the reactor would likely have been required as well to make significant improvements to the conversion. Again, this was not possible at this juncture, but is a possibility for future work in this area.
8. Microreactor Design Algorithm

Based on the experience gained in this project, it became evident that the production of microreactors is a very iterative process due mainly to insufficient knowledge of the interplay of physical phenomena at the microscale. However, there is quite clearly a methodology that can be followed to produce a working microreactor, as summarized in Figure 8.1 and discussed in the following sections.

8.1 Reactor Design

In order to initiate the design process, some basic design criteria need to be known. First of all, details of the reaction that is intended to be performed using the microreactor should be determined, for example:

a) what phase(s) will be present (gas, liquid, solid, mixture of phases)?

b) is the reaction catalytic, will a heterogeneous or homogeneous catalyst be used?

c) what class of reaction(s) will be studied, e.g. inorganic or organic, hydrogenation or combustion, etc?

d) what specific reaction will the reactor be designed for?

It should be noted that microreactors are only likely to give noticeable improvements to reaction systems that are limited in some way in macroscale reactors, such as by heat transfer, mass transfer, safety limits or inaccessible chemical conditions.

Next, the most likely range of operating conditions (e.g. temperature, pressure, flowrate, pH requirements) should be found. The chemical inertness/characteristics of the most likely reactants and products need to be known as well. In addition, any other special requirements, such as optical viewing, should be decided at this point.
Reactor Design

Design Basics:
- Intended type of reaction system
- Operating conditions
- Material(s) of construction
- Unit operations required

Design Ideas
- Constraints
- Catalyst incorporation

Design suitability checks

Simple structures – basic fluidic and heat transfer calculations
Complex structures – basic CFD modelling

Reactor Fabrication

Preliminary considerations
- Survey/selection of techniques
- Fabricate tools (rigs, masks, etc.)
- Optimise fabrication techniques/recipes

Fabrication
- Microreactor and associated unit operations
- Catalyst
- Sealing
- Housing and connections

Testing
- Interface and connections
- Fluid flow and leaks

Reactor Testing

Perform test reaction(s)
Determine catalyst suitability
Parametric studies
Evaluate and improve reactor

Modelling

Calibrate sensors
Measure fluidic properties

Reactor Characterisation

Improve Throughput

Figure 8.1: Microsystem design algorithm
The materials that can/should be used to fabricate the microreaction system will depend largely on the operating conditions and chemical characteristics of the components that will pass through the reactor. Low temperature and pressure systems can be fabricated in plastics provided they are inert to the reaction material. Metals/alloys, such as stainless steel, aluminium, copper or nickel, can be used for high or very low pressure or temperature systems or systems that require greater structural or chemical robustness. For very high temperature operations (> 900 °C), silicon is one of the few microfabrication materials that can be used relatively cheaply.

The unit operations that will be required should be considered next. This includes heating/cooling, mixing, separation, fluid flow/delivery and sensors. A decision on whether to integrate all of these unit operations into a single microsystem unit or to distribute them on to different units (or some mixture of the two) should be made as well. Following this, design ideas can be generated. It should be noted that microsystem design is not necessarily always an intuitive process due to the scale involved. Any additional design constraints/requirements (e.g. aspect ratio and material limitations) should be decided upon at this point in order to winnow down the number of plausible designs. If the reaction system will be heterogeneously catalysed, it is vital that catalyst incorporation methods be considered as well.

The theoretical behaviour of the selected system(s) should be studied briefly before proceeding to the fabrication stage. For relatively simple structures, some basic calculations based on macroscale practices can be used to get an idea of the likely pressure drop that will be incurred, heat and mass transfer rates, fluid flow regime, residence time and conversion. For more complex structures or operations (e.g.
mixing) CFD modelling is required. Based on these studies channel (height, width, length) and catalyst (loading, surface area) characteristics can be determined.

8.2 Reactor Fabrication

Having decided on the materials to be used, the fabrication technique(s) need to be selected. Most materials will have several associated techniques. However, channel size, aspect ratios, equipment availability and technical expertise will affect the applicability of these techniques. For example, if silicon is chosen as the fabrication material, there are a variety of methods available for channel fabrication. However, if very deep narrow channels are required, then Deep Reactive Ion Etching (DRIE) would be the most practical technique assuming the required equipment is available. Complex microstructure architectures may require the use of more than one fabrication technique. It has to be stressed that the fabrication methods must be compatible with any catalyst incorporation technique(s) used. Otherwise, undesirable effects such as poor catalyst adhesion and distribution, blockage and inadequate sealing may result.

Once the fabrication methods have been decided, tools sometimes have to be fabricated first. For photolithography/etching-based systems, a mask would be required. For spark erosion and moulding techniques, tool inserts have to be made. These tools can usually be used to make many copies of the microsystem but it is often not possible to alter them to incorporate design changes, so they should only be made once the design is finalised. Techniques like laser machining would simply require drawing/programming the design into a CAD-based system, and are therefore
more flexible. Transparency masks can be used for photolithography systems to increase flexibility but are limited by resolution.

Most fabrication methods are fairly well-established and recipes/programmes are widely available. However, in some cases optimisation of the conditions used will be required to produce good results. This is typically the case in etching-based techniques. Once optimisation is performed, fabrication of the microsystem can proceed. Depending on the system, catalyst incorporation can be performed either before or after sealing, though there are advantages to being able to incorporate the catalyst after the reactor has been sealed as this implies that the catalyst can be changed at a later date (obviously this only applies to systems where the reactor has to be permanently sealed). It is important to realise that both catalyst incorporation and reactor sealing can be major projects in and of themselves, and can take a considerable amount of effort to optimise.

Most microreactors tend to be held within housings which provide interfaces for electrical connections (for heating/cooling and sensors), fluidic connections and insulation (heat and fluidic). In some cases, housings are used to house many microreactors in order to increase throughput. Due to the small amount of catalyst used in microreactors, the housing, connection and gasket materials have to be especially carefully selected in order to prevent contamination or poisoning of the catalyst. Testing of the microreactor and the housing for its sealing completes this phase of the microreactor production cycle. The next two phases can be performed concurrently.
8.3 Reactor Characterisation

Sensors have to be calibrated, especially if they were units that were incorporated into the reactor using microfabrication techniques. Heat profiles should also be measured to confirm theoretical predictions. Where more than one temperature zone is present, the system should be extensively tested to ensure that it is capable of maintaining structural stability while fulfilling thermal requirements over extended periods.

In some systems, particularly liquid systems, it may be important to experimentally characterise fluidic properties such as velocity, Reynolds number and mixing. This is because theoretical predictions may occasionally vary significantly from practice due to the increased importance of certain factors, such as surface tension, at the microscale. This was aptly demonstrated by disparity between measured and theoretical liquid film thicknesses in the falling film microreactor (see Chapter 5). Such measurements can be used to further refine models of the system.

8.4 Reactor Testing

In order to properly test a microreactor, the reaction system chosen has to be relevant, i.e. there has to be a good reason for performing the reaction in a microreactor rather than in a conventional reactor. Typically, microreactors are best suited for fast reactions that require a large amount of heat transfer (whether to or from the system) and/or are limited by mass transfer rates in conventional reactors.

One of the major problems encountered in heterogeneous catalytic microreactors is catalyst suitability. Often, because of small amount of catalyst used, the catalyst either
deactivates fairly rapidly or is not present in sufficient quantities to give good conversion or is rapidly poisoned thus reducing selectivity. Finding a catalyst incorporation technique that is compatible with microfabrication methods and which gives good performance is a highly iterative process, which is why a reactor design in which the catalyst can be removed and redeposited multiple times is highly desirable.

The bulk of this phase is usually taken up by catalyst development. Once a suitable catalyst has been developed, parametric studies can usually be conducted fairly rapidly due to fast process times. Based on such studies, the reactor can be evaluated through comparison with conventional reactors. Better models of the reaction system can also be developed which, in combination with experimental data and experience, can be used to design an improved microreactor system.

8.5 Improving Throughput

First generation microreactors typically have low throughputs because they are designed to be as simple as possible. Therefore, most are not suitable for industrial use. However, by running many such reactors in parallel, it is possible to increase the amount of material that can be processed. Unfortunately, this can be a very complex procedure as fluid distribution has to be controlled very accurately to a large number of reactors. In addition, if each reactor had built-in sensors, a massive network of electrical connections would be required. While achievable, such practice would inevitably be subject to an upper practical limit for the number of microreactors involved (no studies have as yet been performed to suggest what this limit would be).

Another way of improving throughput would be to redesign the microreactor system while maintaining the basic design concept. The simplest method to increase the
throughput of a single channel reactor would be to increase the number of channels operating in parallel on a single module. The next logical step would be to increase the catalytic area and catalytic activity so that residence time (i.e. channel length) can be reduced, which would allow a greater density of reaction channels. Following this, three-dimensional arrays of channels could be used perhaps. Computational modelling of such systems will be vital in order to optimise fluid flow and distribution.

8.6 Conclusions

Because microreactor design is such a new field and many of its features overturn conventional chemical engineering approaches, the experience base is still being developed. However, this is not aided by the fact that researchers throughout the world are constantly coming up with different classifications and descriptions for essentially the same concepts. It is hoped that some structure can be brought into this apparent chaos by producing a summary and guide to the basic design route.

From Figure 8.1, it is quite clear that one aspect of microreactor design is central to the rest: modelling. This is mainly because a lot remains unknown or uncertain about the way microfluidic systems behave. Reasonable assumptions and estimates can usually be applied, but never with perfect certainty that they will match experimental data. Therefore, rather than spending quite a lot of effort on something that may not ultimately work, it is far more sensible to use models to determine basic operational characteristics in order to aid in optimising microreactor design.
9. Conclusions and Future Work

In the course of this project, many aspects of microreaction technology were explored: microfabrication, catalyst development (with particular emphasis on applicability to microreactors), applications of microreactors and their operational characteristics, physical characteristics of microreactors and modelling of reaction systems. It is fairly evident that microreactor engineering is a vast multi-disciplinary topic that encompasses chemical engineering, materials science and microfabrication, amongst others, and that the surface has barely been breached.

The fabrication of a microreactor from scratch was demonstrated using the T-microreactor detailed in Chapter 3. A large amount of developmental work had to be done as the process was not straightforward. The major roadblocks were the sealing of the reactor (complicated by the fact that the reactor would be exposed to high temperatures), the deposition of silver catalyst and the development of a reactor housing that provided adequate interfaces with external equipment (pumps, heating, sensors and GC). The final product was a silicon microreactor fabricated using Deep Reactive Ion Etching or KOH etching, with silver catalyst deposited through sputtering and sealed by a Pyrex plate through anodic bonding. Another researcher has since successfully used the reactor to study the partial oxidation of methanol to formaldehyde. Future work with this reaction system mainly involves increasing throughput (by increasing the number of channels operating in parallel or enlarging the reaction channel) and investigating more methods of catalyst deposition (e.g. impregnated catalyst particles). In addition, the reactor could be used to study other reactions, such as gas-liquid nitrobenzene hydrogenation with the reactor operating in a slug flow mode.
The micro-falling film reactor was investigated in much greater detail. Through this study, it was shown that the reactor could be used to perform a solid-catalysed gas-liquid reaction, with the potential to greatly enhance the production of aniline from nitrobenzene while at the same time reducing pressure and temperature requirements. The main challenge in this project was the development of a robust catalyst that was compatible with the reactor system, in terms of incorporation, suitability for continuous use, longevity and reproducibility. Several different catalyst incorporation methods were tested (sputtering, UV-decomposition of palladium acetate, wet impregnation on γ-alumina, incipient wetness on γ-alumina) with the final method satisfying all of these requirements. Further development and optimisation of the catalyst, with emphasis on stability and in-situ reactivation, is still required in order to realise the full potential of the reactor. In addition, throughput is limited at the moment. As such, strategies have to be developed for increasing throughput, either through numbering up or through radical re-designs of the reactor while maintaining the basic concept.

However, in order to truly maximise the potential of a falling film system, the hydrodynamics need to be investigated in greater detail. It was shown in Chapter 5 that there were significant differences between experimental and theoretical liquid film thicknesses. This was most likely due to the greater effect of surface tension at the micrometer scale. In addition, there may be other physical phenomena (e.g. the Marangoni effect, hydrodynamic instability, wave formation) occurring at the gas-liquid interface, as alluded to in Chapter 6, which may be enhancing mass transfer from the gas phase to the liquid phase. All of these hydrodynamic features have to be
studied further in order to improve on the design of the micro-falling film reactor (ideally with the help of modelling).

But, due to the thus-far insufficiently developed knowledge-base, reasonable caution should be practiced when advocating the use of microreactors. Not all systems will benefit from shrinking to the microscale. The systems which are most likely to benefit are processes currently limited by heat or mass transfer constraints. And then, the reaction system itself has to be intrinsically able to take advantage of a microdevice. As shown in Chapter 7, even though the micro-falling film reactor had been demonstrated to evaporate larger amounts of acetone (in less time) than a batch reactor, no benefits were found by performing the asymmetric transfer hydrogenation of acetophenone to (S)-phenylethanol in it. Instead, the evaporation rate in the batch reactor proved to be more than adequate to bring the reaction to its limits. It is possible, however, that a more robust catalyst combined with a different microreactor architecture could bring about the desired enhancement.

At the beginning of this project, microreactors were mainly curiosities, with few working examples. In just several years, however, they have already been applied industrially (e.g. acrylate polymerisation) and commercially (e.g. biosensors). This proves that the development time for microreactor-based processes can potentially be very fast. More importantly, it also shows beyond a doubt that microreactors will become an essential part of the chemical engineer’s toolkit in the future.
10. References

3. Alépée, Ch., Maurer, R., Paratte, L., Vulpecu, L., Renaud, Ph. and Renken, A., Fast heating and cooling for high temperature chemical microreactors, Proc. 3rd Int. Conf. on Microreaction Technology, 515-525, 1999

283


35. Cao, E., Yeong, K. K., Gavriilidis, A., Cui, Z. and Jenkins, D. W. K., Microchemical reactors for oxidative dehydrogenation of methanol, Proc. 6th Int. Conf. on Microreaction Technology, 76-84, 2002


69. Ehrfeld, W., Hessel, V., Kiesewalter, S., Löwe, H., Richter, Th. and Schiewe, J., Implementation of microreaction technology in process engineering, Proc. 3rd Int. Conf. on Microreaction Technology, 14-34, 1999b
70. Ehrfeld, W., Hessel, V., Löwe, H., Extending the knowledge base in microreaction towards chemical engineering and fluid dynamic simulation, Proc. 4th Int. Conf. on Microreaction Technology, 3-22, 2000b
72. Ehrfeld, W., Hessel, V., Löwe, H., Schulz, Ch., Weber, L., Materials of LIGA technology, Microsystems Technologies, 5, 105-112, 1999c
75. Ertl, G., Knozinger, H., Weitkamp, J. (Eds.), Handbook of Heterogeneous Catalysis, Vol. 5, Wiley-VCH, Chap. 4.6, 2275, 1997
78. Fedorov, A. G. and Viskanta, R., Heat and mass transfer dynamics in the microchannel adsorption reactor, Microscale Thermophysical Engineering, 3, 111-139, 1999

285
84. Floyd, T., Jensen, K., Schmidt, M., Towards integration of chemical detection for liquid phase microchannel reactors, Proc. 4th Int. Conf. on Microreaction Technology, 461-466, 2000
85. Franz, A. J., Ajmeera, S., Firebaugh, S., Jensen, K., Schmidt, M., Expansion of microreactor capabilities through improved thermal management and catalyst deposition, Proc. 3rd Int. Conf. on Microreaction Technology, 197-206, 1999b
89. Freemantle, M., Downsizing chemistry, Chemical & Engineering News, 77(8), 27-36, 1999
90. Freitag, A., Dietrich, T., Scholz, R., Glass as a Material for Microreaction Technology, Proc. 4th Int. Conf. on Microreaction Technology, 48-54, 2000
101. Greenway, G., McCreedy, T., Microreactor technology for biological applications, Proc. 3rd Int. Conf. on Microreaction Technology, 72-79, 1999

107. Guber, A., Bacher, W., Analytical module for in-line IR spectroscopy of chemical reactions in microchannels, Proc. 3rd Int. Conf. on Microreaction Technology, 617-624, 1999


110. Hardt, S., Ehrfeld, W., Hessel, V., Vanden Bussche, K.M., Strategies for size reduction of microreactors by heat transfer enhancement effects, Proc. 4th Int. Conf. on Microreaction Technology, 432-440, 2000


118. Hessel, V., Ehrfeld, W., Golbig, K., Haverkamp, V., Löwe, H., Storz, M., Wille Ch., Guber, A., Jahnisch, K., Baerns, M., Gas/liquid microreactors for direct fluorination of aromatic compounds using elemental fluorine, Proc. 3rd Int. Conf. on Microreaction Technology, 526-540, 1999


287


133. Jones, F., Qing, D., Fang, J. and Cui, T., A fundamental study of gas-solid heterogeneous catalysis in microreactors. Proc. 4th Int. Conf. on Microreaction Technology, 400-409, 2000


146. Kulaokara, S. and Herold, K. E., HVAC&R Research, 6, 369-380, 2000


157. Lin, Y., Matson, D., Bennett, W., Thrall, K., Timchalk, C., Integrated microfluidics/electrochemical sensor systems for field-monitoring of toxic metals, Proc. 3rd Int. Conf. on Microreaction Technology, 588-596, 1999b


162. Losey, M., Schmidt, M. A. and Jensen, K. F., A micro packed-bed reactor for chemical synthesis, Proc. 3rd Int. Conf. on Microreaction Technology, 277-286, 1999


173. Martin, P., Matson, W., Bennett, W., Stewart, D., Bonham, C., Laminated ceramic microfluidic components for microreactor applications, Proc. 4th Int. Conf. on Microreaction Technology, 410-415, 2000


179. Mex, L. and Müller, J, Miniaturised direct methanol fuel cell with a plasma polymerised electrolyte membrane, Proc. 3rd Int. Conf. on Microreaction Technology, 402-408, 1999


190. Palczew ska, W., Catalytic reactivity of hydrogen on palladium and nickel hydride phases, Advances in Catalysis, 24, 245-291, 1975


211. Rinard, I., Miniplant design methodology, Proc. 2nd Int. Conf. on Microreaction Technology, 299-312, 1998


240. Štepánek, F. and Marek M., Optimization of reaction-separation networks via mass integration on the μ-scale, Proc. 3rd Int. Conf. on Microreaction Technology, 243-252, 1999


244. Stoffel, A., Kovacs, A., Kronost, W., Müller, B., LPCVD against PECVD for micromechanical applications, J. Micromech. Microeng., 8, 33-38, 1998


247. TeGrotenhuis, W. E., Cameron, R. J., Butcher, M. G., Martin, P. M. and Wegeng, R. S., Microchannel devices for efficient contacting of liquids in solvent extraction, Proc. 2nd Int. Conf. on Microreaction Technology, 329-334, 1998


292


272. Wegeng, R. S. and Drost, M. K., Opportunities for distributed processing using micro chemical systems, Proc. 2nd Int. Conf. on Microreaction Technology, 3-9, 1998


283. Woias, P., Hauser, K., Yacoub-George, E. and Hillerich, B., A silicon-based microreactor system for analytical applications, Proc. 3rd Int. Conf. on Microreaction Technology, 654-663, 1999


293
301. Zheng, A., Jones, F., Fang, J. and Cui, T., Dehydrogenation of cyclohexane to benzene in a membrane microreactor, Proc. 4th Int. Conf. on Microreaction Technology, 284-292, 2000
Appendix 3-1:

Estimation of First Order Reaction Kinetics for Methanol Oxidation
All kinetic data in this section were obtained from Robb and Harriot (1974). Because of rapid changes in catalyst activity, their reaction rate data was presented relative to the reaction rate obtained using standard conditions.

Relative rate of reaction, \( R_T = \frac{R}{R_{std}} \)

where \( R \) = reaction rate (mol CH\(_3\)OH/g cat min)

\( R_{std} \) = standard reaction rate (mol CH\(_3\)OH/g cat min)

Assuming that the system could be approximated by a CSTR,

Weight of active catalyst, \( W = \frac{FX}{R} \) g

where \( F \) = feed flowrate (m\(^3\) CH\(_3\)OH/min)

\( X \) = conversion

For the standard reaction, \( W_{std} = \frac{F_{std}X_{std}}{R_{std}} \) g

For the standard run,

\( W_{std} = 0.05 \) g

\( X_{std} = 15 \% \) (assumed average conversion)

Feed pressure, \( P = 1.72 \) atm

Partial pressure of methanol in feed, \( P_m = 0.011 \) atm

Total feed flowrate, \( Q = 500 \) cm\(^3\)/min

Feed flowrate of CH\(_3\)OH, \( Q_m = \frac{QP_m}{P} = 3.2 \times 10^{-6} \) m\(^3\) CH\(_3\)OH/min

From the ideal gas law, \( PQ = FR \)

where \( R \) = ideal gas constant = 0.082 m\(^3\) atm/kmol K

\( T \) = temperature (K) = 695 K

\( F_{std} = \frac{PQ_m}{RT} = 9.6 \times 10^{-5} \) mol CH\(_3\)OH/min

\( \therefore R_{std} = \frac{F_{std}X_{std}}{W_{std}} \)

\( = 2.88 \times 10^{-4} \) mol CH\(_3\)OH/g cat min

The reactor consisted of a hollow glass tube (9 mm diameter) with a glass thermowell (6 mm diameter) in the centre. The catalyst was packed into the annulus between the two glass tubes, length of the catalyst bed was 1.2-4 cm.

Weight of catalyst per reactor volume, \( W_v = \frac{0.05}{\pi[(45-3) \times 10^{-3}]^2(0.04)} = 1.77 \times 10^5 \) g cat/m\(^3\)

reactor

\( R_{std} = 2.88 \times 10^{-4} \) mol CH\(_3\)OH/g cat min

\( = (2.88 \times 10^{-4})(1.77 \times 10^5) \) mol CH\(_3\)OH/m\(^3\) reactor min

\( = 0.85 \) mol CH\(_3\)OH/m\(^3\) reactor s
The reaction system used here has a very different silver surface area per reactor volume than that of the microreactor. Therefore, $R_{\text{std}}$ had to be corrected to approximate the reaction rate that would be obtained in the microreactor assuming these kinetics were remotely applicable.

For this reactor:

- Average crystallite size of Ag = $5.5 \times 10^{-9}$ m
- Amount of Ag in catalyst = 1.25 wt% of $W_{\text{std}} = 6.25 \times 10^4$ g
- Assume catalyst surface area is covered by hemispherical Ag crystallites of radius, $r = 2.75 \times 10^{-9}$ m

**Volume of 1 hemisphere =**

$$
\frac{2}{3} \pi r^3 = 4.36 \times 10^{-20} \text{ cm}^3
$$

**Density of Ag, $\rho_{\text{Ag}}$ = 10.49 g/cm$^3$**

**Weight of 1 hemisphere =**

$$(4.36 \times 10^{-20})(10.49) = 4.57 \times 10^{-19}$ g

∴ Number of Ag hemispheres =

$$\frac{6.25 \times 10^4}{4.57 \times 10^{-19}} = 1.37 \times 10^{15}
$$

**Surface area of 1 hemisphere =**

$$2\pi r^2 = 4.75 \times 10^{-17} \text{ m}^2
$$

∴ Total surface area of Ag hemispheres =

$$(1.37 \times 10^{15})(4.75 \times 10^{-17}) = 0.065 \text{ m}^2
$$

Specific surface area of Ag in catalyst =

$$\frac{0.065}{0.05} = 1.3 \text{ m}^2 \text{ Ag/g cat}
$$

Surface area of Ag per reactor volume =

$$1.3 \left(1.77 \times 10^5\right) = 2.3 \times 10^5 \text{ m}^2 \text{ Ag/m}^3 \text{ reactor}
$$

For the microreactor,

- Surface area of catalyst = 0.015 ($6 \times 10^{-4}$) = $9 \times 10^{-6}$ m$^2$
- Volume of reaction channel = 0.015 ($6 \times 10^{-4}$)($3 \times 10^{-4}$) = $2.7 \times 10^{-9}$ m$^3$

Surface area of Ag per reactor volume =

$$\frac{9 \times 10^{-6}}{2.7 \times 10^{-9}} = 3333 \text{ m}^2 \text{ Ag/m}^3 \text{ microreactor}
$$

∴ The silver surface area per reactor volume in this reactor is 69 times greater than that in the microreactor.

$$R_{\text{stdm}} = \frac{R_{\text{std}}}{69} = 0.012 \text{ mol CH}_3\text{OH/m}^3 \text{ reactor s}
$$

The initial slope of the graph of $R_T$ against average methanol partial pressure was used to estimate the first order rate constant,

$$k = 1.53 \text{ m}^3 \text{ reactor/mol CH}_3\text{OH}
$$

$$R_T = kC_M
$$

$$\frac{R}{R_{\text{std}} = kC_M}
$$

∴ Reaction rate, $R_{\text{stdm}} = k \cdot R_{\text{stdm}}C_M$

$$= KC_M
$$

Estimated first order rate constant for the microreactor, $K = 1.53(0.012) = 0.018 \text{ s}^{-1}$
Appendix 3-2:

Calculations for the Pre-Heat Channels
Heating with no phase change

\[ Q = M \cdot C_p \cdot \Delta T \quad \text{W} \]

where
- \( M \) = Mass flowrate of reactant (kg/s)
- \( C_p \) = Specific heat capacity of reactant (J/kg K)
- \( \Delta T \) = Change in temperature of reactant (K)
  \( = T_2 - T_1 \)

Assume that the flow pattern can be approximated by co-current flow.

\[ \Delta T_1 = t_1 - T_1 \]
\[ \Delta T_2 = t_2 - T_2 \]

\[
\text{LMTD, } \Delta T_{LM} = \frac{\Delta T_2 - \Delta T_1}{\ln\left(\frac{\Delta T_2}{\Delta T_1}\right)}
\]

Channel width = \( a \) m
Channel height = \( b \) m
Cross-sectional area for flow, \( A = ab \) m²
Perimeter, \( P = 2(a + b) \) m
Hydraulic diameter, \( D_h = \frac{4A}{P} \) m

Assume overall heat transfer coefficient \( U_a \) W/m²°K

From Newton’s Law of cooling, \( Q = U_a \cdot A_T \cdot \Delta T_{LM} \) W

\( \therefore \) Total area for heat transfer (m²), \( A_T = \frac{Q}{U \Delta T_{LM}} \) m²

Giving channel length, \( L = \frac{A_T}{a} \) m

Linear velocity of fluid, \( u = \frac{M}{\rho A} \) m/s
Reynolds number, \( Re = \frac{\rho u D_H}{\mu} \)

where \( \rho \) = density of reactant (kg/m\(^3\))
\( \mu \) = viscosity of reactant (Pa s)

For laminar flow, friction factor in a pipe, \( C_f \approx \frac{64}{Re} \)

(this is an approximation as the friction factor varies with shape of the cross-sectional area for flow. \( 57 < C_f Re < 73 \) for rectangular cross-sections)

Pressure drop, \( \Delta P = \frac{u C_f L \mu}{2 D_h^2} \) (N/m\(^2\))

Prandtl number, \( Pr = \frac{\mu C_p}{k} \)

where \( k \) = thermal conductivity of reactant (W/m K)

Assuming that the channel can be approximated by a pipe, Nusselt number (Edwards, 1979),

\[
Nu = \frac{h D_H}{k} = 3.66 + \frac{0.065 \left( \frac{D_H}{L} \right) Re Pr}{1 + 0.04 \left[ \left( \frac{D_H}{L} \right) Re Pr \right]^{\frac{3}{5}}}
\]

.: Heat transfer coefficient in channel,

\[
h_i = \frac{k}{D_H} \left\{ 3.66 + \frac{0.065 \left( \frac{D_H}{L} \right) Re Pr}{1 + 0.04 \left[ \left( \frac{D_H}{L} \right) Re Pr \right]^{\frac{3}{5}}} \right\}
\]

If the heating side is fluid based, the heat transfer coefficient on the heating side, \( h_o \), is calculated from the corresponding \( Re \), \( Pr \) and \( Nu \) numbers, using the same formulae as above.

The overall heat transfer coefficient, \( U = \frac{1}{1/h_i + 1/h_o} \) W/m\(^2\) K

(wall resistance was omitted as it was insignificant)

If the heating side is electrical,
resistance of wall, \( r_w = \frac{t_w}{k_w} \, \text{m}^2 \text{K}/\text{W} \)

where \( t_w = \) channel wall thickness (m)
\( k_w = \) channel wall thermal conductivity (W/m K)

The overall heat transfer coefficient, \( U = \frac{1}{\frac{1}{h_i} + r_w} \, \text{W/m}^2 \text{K} \)

This calculated overall heat transfer coefficient is then compared to the assumed value, \( U_A \). The process is repeated until both numbers become equal. A summary of the process algorithm is shown below.
**Boiling**

Determining the length of the boiling section requires a different approach. The total boiling length has to be discretised into sections before being totalled, as the existing correlations are based on the vapour fraction, which continually changes throughout the boiling process.

As such, the channel is divided into 10 sections, where the vapour fraction increases by 0.1 in each section (except for the final one, which has been set to a vapour fraction of 0.99 to avoid division by zero).

![Division of boiling section](image)

Figure A3-2.2: Division of boiling section

The linear velocity of the fluid entering the boiling section will be same as that leaving the liquid heating section, i.e. it will be determined by the cross-sectional area of the channel. However, once boiling starts, progressively more of the fluid will exist in the vapour phase and the linear velocity will change. As such, the heat transfer coefficient will gradually change.

At the same time, unlike in heating, two boiling processes will occur simultaneously: convection boiling and nucleate boiling. The latter occurs in pool boiling when bubbling takes place, causing agitation and an increase in heat transfer while the former occurs in flowing boiling mixtures, giving rise to annular flow. It should be noted, however, that it is not known whether boiling will occur in this way in sub-millimeter scales. It is also not known whether the flow pattern can be classified as laminar or turbulent.

As things stand, it was assumed that macroscale fluidic laws and correlations will be applicable to this case as well, or, at the very least, give a reasonable solution. The Reynolds number will also be used to determine the flow regime based on macroscopic systems.

The liquid velocity (assuming only liquid in the tube), \( u_{lx} = (1 - x) u_L \)

where
\[
\begin{align*}
x & = \text{Fraction of vapour} \\
u_L & = \text{Velocity of liquid entering the boiling section (m/s)} \\
L & = \text{Subscript denoting liquid}
\end{align*}
\]

\[
Re_{lx} = \frac{\rho_L u_L D_H}{\mu_L}
\]

Using this value of \( Re_{lx} \), a heat transfer factor, \( j_{hx} \), can be found from a correlation given by Sinnott, 1996.
The heat transfer coefficient for convective boiling can then be determined.

\[ h_{fcx} = \frac{k_L}{\frac{D_H}{2}} \frac{j_{nx}}{Re_L Pr_L^{0.33}} \text{ W/m}^2 \text{ K} \]

This value is for the case when liquid flows alone in the tube. For two-phase flow, a correction factor, \( f_c \), has to be introduced. This can be done by first calculating the Lockhart-Martinelli two phase-flow parameter, \( 1/X_u \). Note also that this parameter is for turbulent flow. However, since boiling generally results in turbulent conditions and the correlations used tend to include turbulence, it was assumed it would be acceptable for a simplified calculation.

\[ \frac{1}{X_u} = \left[ \frac{x}{1 - x} \right]^{0.9} \left[ \frac{\rho_L}{\rho_v} \right]^{0.5} \left[ \frac{\mu_r}{\mu_L} \right]^{0.1} \]

Referring to the convective boiling enhancement factor chart (Sinnott, 1996), gives the convective boiling factor.

Convective boiling coefficient, \( h_{fcx} = h_{fcx} f_c \text{ W/m}^2 \text{ K} \)

Mostinski’s correlation was used to determine the nucleate boiling coefficient (Sinnott, 1996):

\[ h_{nb} = 0.104 P_C^{0.69} q^{0.7} \left[ 1.8 \left( \frac{P}{P_C} \right)^{0.17} + 4 \left( \frac{P}{P_C} \right)^{1.2} + 10 \left( \frac{P}{P_C} \right)^{10} \right] \]

where \( P_C = \text{Critical pressure (bar)} \)
\( P = \text{Operating pressure (bar)} \)
\( q = \text{heat flux (W/m}^2) \)
\( = h_{nb} (t_2 - T_2) \)

Therefore,

\[ h_{nb} = \left\{ 0.104 P_C^{0.69} (t_2 - T_2)^{0.7} \left[ 1.8 \left( \frac{P}{P_C} \right)^{0.17} + 4 \left( \frac{P}{P_C} \right)^{1.2} + 10 \left( \frac{P}{P_C} \right)^{10} \right] \right\}^{0.3} \]

Because nucleate boiling is more difficult in a flowing fluid, this coefficient needs to be reduced. To determine the suppression factor, \( f_s \), the value, \( Re_{Lx} f_c^{1.25} \) has to be calculated. \( f_s \) can then be determined from the nucleate boiling suppression factor chart (Sinnott, 1996).

The corrected nucleate boiling heat transfer coefficient, \( h_{nb} = h_{nb} f_s \text{ W/m}^2 \text{ K} \)
The forced convective boiling heat transfer coefficient, \( h_{cx} = h_{fcx}' + h_{nb}' \) W/m\(^2\) K

The heat required to boil each additional 0.1 vapour fraction of vapour will be constant, and given by

\[ Q_{0.1} = x M_L h_{vap} = 0.1 M_L h_{vap} \text{ W} \]

where \( h_{vap} = \text{latent heat of vaporisation (J/kg)} \)

The forced convective boiling heat transfer coefficient calculated above is only that at the point where the vapour fraction is \( x \). However, as mentioned previously, the value of this coefficient changes continuously. For an approximation, however, it was assumed that the average heat transfer coefficient over this range would be accurate enough to describe the section. This was required for the calculation of the length of each section in which 0.1 mass fraction of the liquid was vaporised.

Average forced convective boiling heat transfer coefficient, \( h_{cbavg} = (h_{cx} + h_{cx+0.1})/2 \)

From Newton’s Law of cooling,

\[ Q_{0.1} = h_{cbavg} A_{Tx} (t_2 - T_2) \]

giving \( A_{Tx} = \frac{Q_{0.1}}{h_{cbavg} (t_2 - T_2)} \text{ m}^2 \)

Section length, \( L_x = \frac{A_{Tx}}{a} \text{ m} \)

The total length of the boiling section is then given by the sum of the lengths of each section.

The pressure gradient in a horizontal tube is given by (Mills, 1999)

\[ \frac{dP}{dz} = \frac{dP_w}{dz} + \frac{dP_M}{dz} \]

where \( \frac{dP_w}{dz} = \text{Pressure gradient due to wall friction (N/m}^3\) \)

\[ \frac{dP_M}{dz} = \text{Pressure gradient due to momentum change (N/m}^3\) \]

Due to the changing vapour fraction, both viscosity and density will not remain constant. As such, a reference viscosity is used:
\[
\frac{1}{\mu_r} = \frac{x}{\mu_v} + \frac{1-x}{\mu_L} \quad \text{m}^2/\text{N s}
\]

where \( V \) = subscript denoting vapour

The Reynolds number at this reference viscosity, \( \text{Re}_r = \frac{GD_{hi}}{\mu_r} \)

where \( G \) = mass flowrate of inlet liquid per unit area of flow (kg/m\(^2\) s)

The flow density at each point studied is given by \( \rho = x \rho_v + (1 - x) \rho_L \)

Friction factor for laminar flow in a pipe, \( C_f = \frac{64}{\text{Re}} \)

Pressure gradient due to wall friction, \( \frac{dP_w}{dz} = -\frac{C_f G^2}{2D_{hi} \rho} \quad \text{N/m}^3 \)

Pressure gradient due to momentum change, \( \frac{dP_M}{dz} = \left( \frac{G}{\rho} \right)^2 \frac{d\rho}{dz} \)

\[
= \left( \frac{G}{\rho} \right)^2 \frac{d}{dz} \left[ x \rho_v + (1 - x) \rho_L \right]
\]

\[
= \left( \frac{G}{\rho} \right)^2 \left[ \rho_v \frac{dx}{dz} - \rho_L \frac{dx}{dz} \right]
\]

\[
= \left( \frac{G}{\rho} \right)^2 \left[ (\rho_v - \rho_L) \frac{dx}{dz} \right]
\]

An energy balance gives \( \frac{dx}{dz} = \frac{Q_{0\ell}}{L_s M_L h_{wp}} = \frac{x}{L_s} = 0.1 \frac{L_s}{L_s} \)

\[
\therefore \quad \frac{dP_M}{dz} = \left( \frac{G}{\rho} \right)^2 (\rho_v - \rho_L) 0.1 \frac{L_s}{L_s} \quad \text{N/m}^2
\]

And the pressure drop in one section, \( \Delta P_x = L_s \frac{dP}{dz} \)
The total pressure drop in the boiling section will be the sum of the pressure drops in each section.

\[ L_x \left( \frac{dP_w}{dz} + \frac{dP_M}{dz} \right) \text{ N/m}^2 \]
Appendix 3-3:

Mask Design for the Basic T-Microreactor
Appendix 3-4:

Mask Design for the T-Microreactor
Appendix 3-5:

Empirical Etch Rate Chart for KOH Etching
Empirically calculated etch rates for <100> Si in KOH solution
(Rai-choudhuri, P., 1997)
Appendix 3-6:

Schematic of the Reactor Rig
ALL MEASUREMENTS IN CM
EXCEPT WHERE STATED

STAINLESS STEEL
ALL MEASUREMENTS IN CM EXCEPT WHERE STATED

STAINLESS STEEL

GASKETS: TFEFLON

1 SET (2 SEPARATE SHEETS) EACH FOR PORTS A & B

SAME DIMENSIONS EXCEPT: SMALL HOLES WITH DIAMETER 4MM INSTEAD OF 3/16"

THICKNESS OF AVAILABLE THICK TFEFLON TAPE
Appendix 3-7:

Schematic of the Second Reactor Rig
ALL MEASUREMENTS IN MM EXCEPT WHERE STATED

STAINLESS STEEL EXCEPT WHERE SPECIFIED OTHERWISE

CROSS-SECTION X-X
Appendix 4-1:

Estimation of Reactant Concentration
Assuming the reaction is first order with respect to hydrogen and flow is laminar, a
model which satisfies this reaction system was proposed by Gobby, et al (2001). The
dimensionless concentration, $\theta_a$, is given by

$$\theta_a = \exp(-\lambda_a \zeta)$$

where $\zeta$ = dimensionless distance in the flow direction $= \frac{z}{L}$
$z$ = distance along the direction of flow
$L$ = total length

Provided $Pe/R < 1$, $\lambda_a$ is defined as:

$$\frac{\lambda_a Pe}{R} = \begin{cases} 
3 \left( \frac{Da}{2} + 1 \right) - \frac{\sqrt{9Da^2 + 3Da + 9}}{4}, & Da < 2.0 \\
\left( \frac{\pi Da}{2(Da + 1)} \right)^2, & Da > 2.0
\end{cases}$$

where $Pe = $ Peclet no. $= \frac{Uh}{D}$
$R = \frac{L}{h}$
$Da = $ Damkohler no. $= \frac{kh}{D}$
$U = $ liquid velocity (m/s)
$h = $ liquid film thickness (m) $= \frac{3V\mu}{\rho bhng}$
$D = $ diffusivity of hydrogen in ethanol (m$^2$/s)
$k = $ reaction rate constant (s$^{-1}$)
$V = $ volumetric flowrate (m$^3$/s)
$\mu = $ liquid viscosity (Pa s)
$\rho = $ liquid density (kg/m$^3$)
$b = $ channel width (m)
$n = $ number of channels
$g = $ gravitational acceleration (m/s$^2$)

At the same time, $\theta_a = \frac{C_a}{C_{ao}}$

where $C_a = $ concentration of hydrogen (mol/m$^3$)
$C_{ao} = $ initial concentration of hydrogen (mol/m$^3$) $= \frac{P}{H}$
$P = $ system pressure (atm)
H = Henry's constant (atm m³/mol)

Therefore, conversion, \( X_a = \frac{C_{eo} - C_a}{C_{eo}} = 1 - \frac{C_a}{C_{eo}} = 1 - \theta_a \)

The reactor was divided into blocks of equal size, \( \zeta \), ranging from 0.1 to 1 \times 10^{-7}. Accuracy would increase with a reduction in block size. Because the initial concentration of hydrogen at the gas-liquid interface of each block is exactly the same, the conversion obtained in each block will be the same. Therefore, the total amount of product made will be the sum of the product obtained in each block.

The reaction has the following equation:

\[ 3H_2 + NB \rightarrow AN + 2H_2O \]

Therefore, the amount of aniline produced in each block will be a third of the hydrogen used up, and is given by

\[ C_{An} = \frac{C_{eo} \cdot X}{3} \]

and the total aniline production,

\[ C_{Tan} = \frac{C_{An}}{\zeta} \]

The parameters used for the calculation are shown below.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel width (m)</td>
<td>0.0003</td>
</tr>
<tr>
<td>Channel length (m)</td>
<td>0.065</td>
</tr>
<tr>
<td>Number of channels</td>
<td>64</td>
</tr>
<tr>
<td>Volumetric flowrate (m³/s)</td>
<td>6.67 \times 10^4</td>
</tr>
<tr>
<td>Liquid viscosity (Pa s)</td>
<td>8.57 \times 10^{-4}</td>
</tr>
<tr>
<td>Liquid density (kg/m³)</td>
<td>815</td>
</tr>
<tr>
<td>Diffusivity of hydrogen in ethanol (m²/s)</td>
<td>1.05 \times 10^{-9}</td>
</tr>
<tr>
<td>Reaction rate constant (s⁻¹)</td>
<td>4.158</td>
</tr>
<tr>
<td>Gravitational acceleration (m/s²)</td>
<td>9.82</td>
</tr>
<tr>
<td>Initial concentration of nitrobenzene (mol/m³)</td>
<td>400</td>
</tr>
<tr>
<td>System pressure (atm)</td>
<td>7</td>
</tr>
<tr>
<td>Henry's constant (mol m³/atm)</td>
<td>1.46</td>
</tr>
<tr>
<td>Residence time (s)</td>
<td>9.3</td>
</tr>
</tbody>
</table>

The results from the calculations are as follows:

<table>
<thead>
<tr>
<th>Block size, ( \zeta )</th>
<th>0.1</th>
<th>0.01</th>
<th>0.001</th>
<th>0.0001</th>
<th>1 \times 10^{-5}</th>
<th>1 \times 10^{-6}</th>
<th>1 \times 10^{-7}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total aniline production (mol/m³)</td>
<td>10.1</td>
<td>15.3</td>
<td>16.0</td>
<td>16.1</td>
<td>16.1</td>
<td>16.1</td>
<td>16.1</td>
</tr>
</tbody>
</table>

Based on the parameters above, the amount of aniline produced would be 16.1 mol/m³ or a conversion of 4%.
Appendix 4-2:

Analysis Recipe for the Rtx-5 Capillary Column
<table>
<thead>
<tr>
<th><strong>Oven</strong></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temperature</td>
<td>75 °C</td>
<td></td>
</tr>
<tr>
<td>Initial time</td>
<td>0.5 min</td>
<td></td>
</tr>
<tr>
<td>Ramp:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate</td>
<td>50 °C/min</td>
<td></td>
</tr>
<tr>
<td>Final temperature</td>
<td>100 °C</td>
<td></td>
</tr>
<tr>
<td>Hold time</td>
<td>2 min</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Inlet</strong></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>Split</td>
<td></td>
</tr>
<tr>
<td>Initial temperature</td>
<td>200 °C</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>20.9 kPa</td>
<td></td>
</tr>
<tr>
<td>Split ratio</td>
<td>15:1</td>
<td></td>
</tr>
<tr>
<td>Split flow</td>
<td>30 ml/min</td>
<td></td>
</tr>
<tr>
<td>Total flow</td>
<td>35.2 ml/min</td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>Helium</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Column</strong></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>Constant flow</td>
<td></td>
</tr>
<tr>
<td>Initial flow</td>
<td>2 ml/min</td>
<td></td>
</tr>
<tr>
<td>Nominal initial pressure</td>
<td>20.9 kPa</td>
<td></td>
</tr>
<tr>
<td>Average velocity</td>
<td>44 cm/s</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Injector</strong></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample washes</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Sample pumps</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Injection volume</td>
<td>1 μl</td>
<td></td>
</tr>
<tr>
<td>Syringe size</td>
<td>10 ml</td>
<td></td>
</tr>
<tr>
<td>Post injection washes</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Detector integration</strong></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope sensitivity</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Peak width</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Area reject</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Height reject</td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>
Appendix 4-3:

Calibration Data for the Rtx-5 Capillary Column
For calibration, the following mixture of the three compounds was prepared:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>89.6244</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>9.6474</td>
</tr>
<tr>
<td>Aniline</td>
<td>0.7282</td>
</tr>
</tbody>
</table>

From this mixture, 1 ml was taken and added to 0.25 ml of ethanol. This mixture was then injected into the GC and the results recorded. Successive mixtures were prepared by decreasing the amount of the initial calibration mixture by 0.1 ml each time while increasing the amount of ethanol added so that the total volume was always 1.25 ml. Each mixture was then run through the GC three times to obtain an average.

Calibration graph for nitrobenzene

Calibration graph for aniline
Appendix 4-4:

GC traces and MS spectrograms of side products for the SP1 catalyst
Fisons Instruments TRIO-1000 LAB BASE Data System

Kay Kim  MBAD27  Instrument: Trio-1

3885RC04'33 (3.550) COMBINE: (28 to 33) - (((10 to 13) + (20 to 22)) * 1.000)

%FS

51.0

50.0

40.0

52.0

63.0

74.0

78.0

93.0

108.0

m/z 40 50 60 70 80 90 100 110 120 130 140 150

77.0

25856
Fisons Instruments TRI0-1000 LAB BASE Data System

Kay Kim  MBAD27

3005RC04'78 (4.300)  COMBINE: ((74 to 79)-((105 to 107)+(116 to 117)))*1.000

Instrument: Trio-1

%FS

100

66.0

65.0

40.0

47.0

41.0

63.0

67.0

92.0

94.0

m/z 40 60 80 100 120 140 160 180 200

93.0

782336
NITROBENZENE
Fisons Instruments TRIO-1000 LAB BASE Data System

Kay Kim MBAD27

Instrument: Trio-1

3005RC04'193 (6.217) COMBINE:((192 to 194)-((183 to 184)+(202 to 204))*1.000)

106.0

120.0

122.0

m/z 40 50 60 70 80 90 100 110 120 130 140 150

%FS 40.0 41.0 -53.0 59.0 65.0 -66.0 78.0 91.0 103.0 107.0 118.0 122.0

100.0

25088
Fisons Instruments TRIO-1000 LAB BASE Data System
Kay Kim MBAD27 Instrument: Trio-1
3095RC04' 421 (18.017) COMBINE: (419 to 421) - ((399 to 403) + (439 to 441)) × 1.000

%FS - 51.0 - 50.0 - 40.0 - 63.0 - 78.0 - 105.0 - 182.0

m/z 40 60 80 100 120 140 160 180 200

A20 BEnZEN3
Fisons Instruments TRIO-1000 LAB BASE Data System

Kay Kim NBAD27

Instrument: Trio-1

3005RC04 '449 (10.484) COMBINE: (448 to 450) - (((438 to 440) + (462 to 465)) * 1.000)

109.0

160.0

63.0, 69.0, 75.0, 145.0, 172.0, 185.0

-40.0, -89.0, -186.0, 262.0

m/z 50 100 150 200 250 300 350

30208
Fisons Instruments TRIO-1000 LAB BASE Data System

Instrument: Trio-1

Kay Kim MBAD27

3005RC04'584 (12.734) COMBINE: (583 to 586) - (((564 to 566) + (599 to 605)) * 1.000) * 1.000

y.FS

50.0 65.0 91.0 105.0 115.0 141.0 169.0 170.0 198.0

%FS

m/z 40 60 80 100 120 140 160 180 200 220 240
Fisons Instruments TRIO-1000 LAB BASE Data System

Kay Kin NBAD27 Instrument: Trio-1

3005RC04'3 (3.050) COMBINE: (3 to 4) - (((11 to 12) + (14 to 16)) x 1.000)
Fisons Instruments TRIO-1000 LAB BASE Data System

Kay Kim  MBAD27

3805RC04'66 (4.100)  COMBINE:(64 to 69)-((102 to 104)+(105 to 106))*1.000

145.0  173.0  34816

174.0

175.0
Fisons Instruments TRIO-1000 LAB BASE Data System

Kay Kim NBAD27

Instrument: Trio-1

3005RC04'268 (7.467) COMBINE: (268 to 269) - ((249 to 251) + (288 to 290)) * 1.000

%FS

m/z 40 60 80 100 120 140 160 180 200

100

115.0

128.0

142.0

144.0

40.0 51.0 62.0 63.0 75.0 89.0 101.0 90.0
Fisons Instruments TRIO-1000 LAB BASE Data System

Kay Kim MBAD27 Instrument: Trio-1

50054CO4'425 (10.884) COMBINE: (423 to 427)-(406 to 408)+(438 to 440)*1.000

\[5632\]

- 51.0
- 69.0
- 77.0
- 104.0
- 78.0
- 249.0

M/2: 50 100 150 200 250 300
Appendix 4-5:

Analysis Recipe for the Rtx-5 Capillary Column
(Comparison Analysis of Side Products)
<table>
<thead>
<tr>
<th><strong>Oven</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temperature</td>
<td>75 °C</td>
</tr>
<tr>
<td>Initial time</td>
<td>2 min</td>
</tr>
<tr>
<td>Ramp:</td>
<td></td>
</tr>
<tr>
<td>Rate</td>
<td>20 °C/min</td>
</tr>
<tr>
<td>Final temperature</td>
<td>200 °C</td>
</tr>
<tr>
<td>Hold time</td>
<td>1.75 min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Inlet</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>Split</td>
</tr>
<tr>
<td>Initial temperature</td>
<td>200 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>10.9 kPa</td>
</tr>
<tr>
<td>Split ratio</td>
<td>15:1</td>
</tr>
<tr>
<td>Split flow</td>
<td>15.0 ml/min</td>
</tr>
<tr>
<td>Total flow</td>
<td>19.2 ml/min</td>
</tr>
<tr>
<td>Gas</td>
<td>Helium</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Column</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>Constant flow</td>
</tr>
<tr>
<td>Initial flow</td>
<td>1.0 ml/min</td>
</tr>
<tr>
<td>Nominal initial pressure</td>
<td>10.9 kPa</td>
</tr>
<tr>
<td>Average velocity</td>
<td>23 cm/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Injector</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample pumps</td>
<td>6</td>
</tr>
<tr>
<td>Injection volume</td>
<td>2 μl</td>
</tr>
<tr>
<td>Syringe size</td>
<td>10 μl</td>
</tr>
<tr>
<td>Post injection washes</td>
<td>3</td>
</tr>
</tbody>
</table>
Appendix 4-6:

Raman Spectroscopy Analysis of the UV-decomposed Palladium Acetate Catalyst
UV deposit - in valley

Raman wavenumber shift / cm$^{-1}$
UV deposition - on ridge

Graph showing intensity (arb. units) versus Raman wavenumber shift (cm⁻¹) for UV deposition on a ridge.
substrate - microscope uncovered

Raman wavenumber shift / cm$^{-1}$

Intensity (arb. units)
Appendix 4-7:

Analysis Recipe for the PTA-5 Capillary Column
<table>
<thead>
<tr>
<th><strong>Oven</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temperature</td>
<td>75 °C</td>
</tr>
<tr>
<td>Initial time</td>
<td>9 min</td>
</tr>
<tr>
<td>Ramp 1:</td>
<td></td>
</tr>
<tr>
<td>Rate</td>
<td>20 °C/min</td>
</tr>
<tr>
<td>Final temperature</td>
<td>200 °C</td>
</tr>
<tr>
<td>Hold time</td>
<td>3.75 min</td>
</tr>
<tr>
<td>Ramp 2:</td>
<td></td>
</tr>
<tr>
<td>Rate</td>
<td>20 °C/min</td>
</tr>
<tr>
<td>Final temperature</td>
<td>225 °C</td>
</tr>
<tr>
<td>Hold time</td>
<td>14.75 min</td>
</tr>
<tr>
<td>Total run time</td>
<td>35 min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Inlet</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>Split</td>
</tr>
<tr>
<td>Initial temperature</td>
<td>250 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>2.71 psi</td>
</tr>
<tr>
<td>Split ratio</td>
<td>35.63:1</td>
</tr>
<tr>
<td>Split flow</td>
<td>14.6 ml/min</td>
</tr>
<tr>
<td>Total flow</td>
<td>18 ml/min</td>
</tr>
<tr>
<td>Gas</td>
<td>Helium</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Column</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>Constant flow</td>
</tr>
<tr>
<td>Initial flow</td>
<td>0.4 ml/min</td>
</tr>
<tr>
<td>Nominal initial pressure</td>
<td>2.71 psi</td>
</tr>
<tr>
<td>Average velocity</td>
<td>9 cm/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Injector</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample washes</td>
<td>3</td>
</tr>
<tr>
<td>Sample pumps</td>
<td>3</td>
</tr>
<tr>
<td>Injection volume</td>
<td>1 μl</td>
</tr>
<tr>
<td>Syringe size</td>
<td>10 μl</td>
</tr>
<tr>
<td>Post injection washes</td>
<td>3</td>
</tr>
</tbody>
</table>
Appendix 4-8:

Calibration Method for the PTA-5 Capillary Column
The internal standard method was chosen to help improve calibration. In this method, a compound is added to the GC sample in a known concentration. The relative response of the sample compounds to the internal standard can then be used to accurately determine their concentrations, without worry about inconsistent sample sizes and instrument instability. The principle is as follows. Assuming that there is a linear relationship between the peak area of a compound and its concentration, then

\[ C_i = K_i A_i \]

where \( C \) = concentration of compound \( i \)
\( K \) = absolute response factor of compound \( i \)
\( A \) = peak area of compound \( i \)

Since the absolute response factor for each component is constant within a given concentration range, the relative response factor of two components will also be constant, i.e.

\[ K_{1/2} = \frac{K_1}{K_2} = \frac{C_1 A_2}{C_2 A_1} \]

is constant. If all concentrations are known, then \( K_{1/2} \) can be determined. If a known concentration of the internal standard is then added to an unknown sample, the amount of the components present in the sample can then be determined from the relative response factor:

\[ C'_1 = C'_2 K_{1/2} \frac{A'_1}{A'_2} \]

The choice of internal standard is restricted by several criteria (Rouessac et al, 2000):

a) it must not be present initially in the sample
b) the peak must be well resolved from the other components of the sample
c) its retention time must be close to that of the other components
d) its concentration must be close to or greater than the concentration of the components to be measured to obtain a linear response
e) it must not react with the other components

It was decided to test out a compound which had previously been suspected to be a side product, but which had turned out not to be the case: N-ethylaniline. This compound had a retention time which was just slightly longer than that of nitrobenzene. To test out chemical inertness, equal amounts of N-ethylaniline,
nitrobenzene and aniline were mixed together in ethanol and sampled over a few days. No other products were found in those samples and the concentration of the 3 compounds remained constant. Therefore, it was determined that N-ethylaniline was suitable for use as an internal standard (spot checks of experimental samples were also conducted at random in later experiments and confirmed the absence of N-ethylaniline in the reaction product).

Solution A, containing nitrobenzene (1.54 wt%), aniline (1.24 wt%) and ethanol was made up. Five calibration samples with a range of concentrations were prepared from solution A by adding ethanol to decreasing amounts of solution A such that the total volume was 1 ml. A 5 vol% solution of N-ethylaniline in ethanol (solution B) was made up as well. 0.2 ml of solution B was then added to each calibration sample. Each sample was put through the GC three times in order to obtain an average relative response factor for nitrobenzene/N-ethylaniline ($K_{\text{NB/NEAN}}$) and aniline/N-ethylaniline ($K_{\text{AN/NEAN}}$).

<table>
<thead>
<tr>
<th></th>
<th>Relative response factor, $K_{\text{NEAN}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrobenzene</td>
<td>1.245</td>
</tr>
<tr>
<td>Aniline</td>
<td>0.95</td>
</tr>
</tbody>
</table>
Appendix 4-9:

Method of Correcting Nitrobenzene Conversion for Deactivation
First, the overall trend of deactivation was determined from experiments performed using the base conditions. For the

a) IP catalysts, this was done before and after each set of parametric runs as the catalyst was reactivated between each run (see Figure A-9.1)

b) IW catalysts, this was done throughout the active lifespan of the catalyst, i.e. without any reactivation at all (see Figure A-9.2)

The deactivation trend was assumed to be linear in both cases, resulting in a line with equation

\[ NB = mT + c \]

where

- \( NB \) = experimental nitrobenzene conversion
- \( T \) = time onstream (h)
- \( m \) = gradient
- \( c \) = intercept

![Figure A4-9.1: Nitrobenzene conversion as a function of time for the impregnated palladium catalyst, base case results during parametric studies (IP1H, 0.1 mol NB/l, 60 °C, 1 bar, 0.5 ml/min)](image)
The experimental values obtained during the parametric runs were then corrected as follows:

\[ NB_{\text{act}} = \text{experimental conversion (at } T) \times \text{base case conversion of fresh catalyst/base case conversion (at } T) \]

\[ NB_{\text{act}} = \frac{NB_{\text{exp}}N_{B0}}{mT + c} \]

where \( NB_{\text{act}} \) = corrected nitrobenzene conversion
\( NB_{\text{exp}} \) = experimental conversion
\( T \) = time onstream (h)
\( m \) = gradient of deactivation line
\( c \) = intercept of deactivation line
Appendix 4-10:

Calculation of the Weisz-Prater Criterion
For a first order system, the Weisz-Prater criterion for no pore diffusional limitations is given by:

$$\Phi = \frac{r_A \rho_s h^2}{D_{eA} C_{As}} << 1 \text{ for no pore diffusional limitations}$$

where $r_A$ = rate of reaction (mol/kg cat s)
$\rho_s$ = density of catalyst (kg cat/m$^3$ cat)
$h$ = thickness of catalyst layer (m) = $1 \times 10^{-5}$ m

$D_{eA}$ = effective diffusivity of A (m$^2$/s) = $\frac{D_a}{8s}$

$C_{As}$ = concentration of A at the surface of the catalyst (mol/m$^3$)
$\varepsilon_s$ = void fraction = 0.6
$\tau$ = tortuosity = $\sqrt{3}$

$D_A$ = diffusivity of A (m$^2$/s), calculated using the Wilke-Chang method (see Appendix 6-2)

Effective diffusivity of hydrogen in ethanol = $1.22 \times 10^{-8}$ m$^2$/s
Effective diffusivity of nitrobenzene in ethanol = $7.27 \times 10^{-10}$ m$^2$/s

At flowrate 0.5 ml/min (residence time 9.3 s), nitrobenzene conversion, $X_{NB} = 85\%$
Initial concentration of nitrobenzene, $C_{NB0} = 100$ mol/m$^3$
Moles nitrobenzene reacted = 85 mol/m$^3$
Overall rate of reaction of nitrobenzene = $85/9.3 = 9.14$ mol NB/m$^3$s
Overall rate of reaction of hydrogen = $(9.14)(3) = 27.4$ mol H$\_2$/m$^3$s

Volume of catalyst = $bh \ln m^3$
Volume of reactor (i.e. reacting volume) = $b \delta \ln m^3$

Volume of reactor/volume of catalyst = $\frac{\delta}{h}$ m$^3$/m$^3$ catalyst

where $b$ = channel width (m)
$l$ = channel length (m)
$n$ = number of channels
$\delta$ = liquid film thickness (m)

Liquid film thickness (at 0.5 ml/min flowrate) = $5.18 \times 10^{-5}$ m
Volume of reactor/volume of catalyst = $5.18$ m$^3$/m$^3$ catalyst

$\therefore r_{NB} \rho_s = 9.14 \times 5.18 = 47.3$ mol NB/m$^3$ cat s
$r_{H2} \rho_s = 27.4 \times 5.18 = 142$ mol H$\_2$/M$^3$ cat s
$\Phi_{NB} = 0.065$
$\Phi_{H2} = 0.3$

Since $\Phi_{NB}$ and $\Phi_{H2} < 1$, there are no pore diffusional limitations

Repeating the calculations at a flowrate of 3 ml/min (residence time 2.8 s, nitrobenzene conversion 0.35) yielded:

$\Phi_{NB} = 0.09$
$\Phi_{H2} = 0.41$

Again, since $\Phi_{NB}$ and $\Phi_{H2} < 1$, there are no pore diffusional limitations
Appendix 4-11:

Calculations for Surface Coverage by Carbon/Organic Deposits
Coverage of catalytic surface area through the formation of a monolayer

For the IW2 catalyst, % loss of moles = 17.5 %
Assume flowrate of 0.5 ml/min (residence time 9.3 s)
Concentration of nitrobenzene per pass = 0.1 mol/l
Amount lost per pass = 1.75 x 10^{-5} mol/ml
Number of moles lost per pass = 1.74 x 10^{-9} mol
Number of molecules lost per pass = (1.74 x 10^{-9})(6.02 x 10^{23}) = 1.05 x 10^{15}

Using molecules the size of benzene as an example,
Radius of a benzene molecule = 3.75 x 10^{-10} m
Cross sectional surface area of a benzene molecule = 4.42 x 10^{-19} m^2
Area covered by benzene molecules per pass
= (4.42 x 10^{-19})(1.05 x 10^{15}) = 4.64 x 10^{-4} m^2

Catalyst surface area = 58 m^2/g
Catalyst density = 2 g/cm^3
Catalyst area per volume = 1.16 x 10^8 m^2/m^3
Volume of catalyst = 1.25 x 10^{-8} m^3
Catalyst surface area = 1.45 m^2

Number of passes for the entire catalytic surface to be covered by benzene = 3125
Time per pass = 9.3 s
Time taken to cover the entire catalytic surface area = 8 h
Coverage of geometric catalyst surface area through the formation of aggregates

Particle radius = $2.5 \times 10^{-5}$ m
Cross sectional area of particle = $1.96 \times 10^{-9}$ m$^2$
Volume of particle = $6.54 \times 10^{-14}$ m$^3$

Volume of a benzene particle (radius $3.75 \times 10^{-10}$ m) = $2.21 \times 10^{-28}$ m$^3$
Number of benzene molecules in each particle = $2.96 \times 10^{14}$

At a mole loss of 17.5 % per pass,
Number of benzene molecules lost per pass = $1.05 \times 10^{15}$
:. Number of particles formed per pass = 3.9
Total cross sectional area of particles per pass = $(3.9)(1.96 \times 10^{-9})$ m$^2$
Total cross sectional area of particles per hour = $(3.9)(1.96 \times 10^{-9})(3600)/9.3 = 2.96 \times 10^6$ m$^2$

Geometric catalyst surface area = $(3 \times 10^{-4})(6.5 \times 10^2)(64) = 1.25 \times 10^{-3}$ m$^2$
Rate of catalyst geometric area coverage = 0.25 %/h
Time taken to cover the entire geometric catalyst area = 422 h
Appendix 6-1:

Estimation of the Diffusivity of Gases in Low Viscosity Liquids
The Chen-Chen formula for diffusivity of gases in low viscosity liquids is reported to have an accuracy of 6% (Knudsen, et al, 1997)

\[
D_{AB} = 2.018 \times 10^{-9} \left( \frac{\beta V_{CB}}{M_A \sqrt{\pi}} \right)^{3/2} \left( \frac{R T_{CB}}{M_B V_{CA}} \right)^{1/2} \left( \frac{V_R - 1}{T_{CB}} \right)^{1/2} 
\]

\[
V_R = \frac{V_B}{0.9742 (V_{mIB} + 0.04765)} 
\]

where \( \beta \) = parameter accounting for hydrogen bonding of the solvent = 2.31

\( V_C \) = critical volume
\( V_B \) = molar volume of B at boiling point
\( V_{mIB} \) = molar volume of B at melting point
\( T_C \) = critical temperature
\( M \) = relative molecular mass
\( R \) = gas constant

\( V_B \) and \( V_{mIB} \) were in turn estimated from the modified Rackett equation (Liley, et al, 1997):

\[
V_{sat} = \left( \frac{RT_C}{P_C} \right)^n \]

\[
n = 1.0 + \left( 1.0 - T_r \right)^{3/2} 
\]

where \( P_C \) = critical pressure
\( Z_{RA} \) = experimental parameter = 0.2523
\( T_r = \frac{T}{T_C} \)
Appendix 6-2:

Estimation of the Diffusivity of Liquids in Liquids
The Wilke-Chang formula for the diffusivity of general mixtures was used (Knudsen, et al, 1997):

$$D_{AB} = \frac{7.4 \times 10^{-8} (\phi_B M_B)^{0.5} T}{\mu_B V_A^{0.6}}$$

where
- $\phi_B$ = association factor for B = 1.5 for ethanol
- $M_B$ = molecular weight of B (ethanol) = 46
- $T$ = absolute temperature (K) = 333 K
- $\mu_B$ = viscosity of B (ethanol) = 0.65 cP
- $V_A$ = specific volume of A (cm$^3$/mol)
Appendix 6-3:

gPROMS Program
### MODEL LIQUID

#### PARAMETER

- \( n \) AS REAL *number of channels
- \( b \) AS REAL *channel width
- \( h \) AS REAL *channel height
- \( L \) AS REAL *channel length
- \( \nu \) AS REAL *liquid viscosity
- \( \rho \) AS REAL *liquid density
- \( \eta \) AS REAL *prevalitional/acceleration
- \( \nu_b \) AS REAL *inlet conc of NB
- \( \nu_d \) AS REAL *diffusivity of NB
- \( \nu_n \) AS REAL *diffusivity of AN
- \( V_\text{eth} \) AS REAL *parameter
- \( V_\text{ch} \) AS REAL *critical molar volume of ethanol
- \( V_\text{h2} \) AS REAL *critical molar volume of H2
- \( T \) AS REAL *Temperature
- \( T_{\text{eth}} \) AS REAL *critical temperature of ethanol
- \( \beta \) AS REAL *critical temperature of ethanol
- \( \phi \) AS REAL *Gas constant
- \( \mu_\text{h2} \) AS REAL *H2 viscosity
- \( \mu_\text{meth} \) AS REAL *H2 molar/pressure
- \( \mu_\text{eth} \) AS REAL *ethanol pressure
- \( \nu_\text{h2} \) AS REAL *rate constant molH2 + e
- \( \nu_\text{ch} \) AS REAL *rate constant molH2 + e
- \( \nu_\text{sig} \) AS REAL *stoichiometric coefficient for H2
- \( \nu_\text{eta} \) AS REAL *stoichiometric coefficient for AN

#### DISTRIBUTION_DOMAIN

- \( Axial \) AS \((0:1)\)
- \( Radial \) AS \((0:1)\)

#### VARIABLE

- \( \delta \) AS \( \delta \)
- \( u \) AS \( U \)
- \( \nu_b \) AS \( \nu_b \)
- \( \nu_n \) AS \( \nu_n \)
- \( \tau_\text{b} \) AS \( \tau_\text{b} \)
- \( \tau_\text{n} \) AS \( \tau_\text{n} \)
- \( \nu_\text{ch} \) AS \( \nu_\text{ch} \)
- \( \nu_\text{h2} \) AS \( \nu_\text{h2} \)
- \( \nu_\text{sig} \) AS \( \nu_\text{sig} \)
- \( \nu_\text{eta} \) AS \( \nu_\text{eta} \)
restoration of model

end

**Model Liquid**

---

**MODEL**

**INIT**

**AS Liquid**

**SET**

**WITHIN**

**Axial**:

Axial = (CFDM, 2, 50); Radial = (CFDM, 2, 50); N = 64; n = 3E-4; L = 6.5E-2; CVeth = 0.0000761; dens = 792.5813; g = 9.82; Cnb0 = 100; Dnb = 2.1E-9; Den = 2.1E-9; Vr = 1.316; Vceth = 168; VcH2 = 64; T = 333; TEeth = 513.92; beta = 2.31; M = 9.3144E7; Mh2 = 2; Meth = 46; pH2 = 1; HC = 0.26; V = 8.33E-9; k = 0.0021; sigh2 = 1; signb = 0.3333; signa = -0.3333;

end

**PRESET**

**RESTORE** "FFR85"

**SOLUTION PARAMETERS**

OutputLevel := 2; gRMS := ON; MaxInitIterations := 1000; BLOCKDECOMPOSITION := ON; AbsoluteAccuracy := 1E-10; RelativeAccuracy := 1E-10; RelativeAccuracy := 1E-10;

end

**SCHEDULE**

**SAVE** "FFR81214"
Appendix 6-4:

Optimisation of $K_{NB}$ and $K_{H2}$ for Model (I)
Figure A6-4.1: Comparison of model with experimental results (Langmuir-Hinselwood (I), plug flow, $K_{NB} = 1.72$, 1 bar)

Figure A6-4.2: Comparison of model with experimental results (Langmuir-Hinselwood (I), plug flow, $K_{NB} = 1.72$, 4 bar)

Figure A6-4.3: Comparison of model with experimental results (Langmuir-Hinselwood (I), plug flow, $K_{NB} = 1.72$, 6 bar)
Figure A6-4.4: Comparison of model with experimental results (Langmuir-Hinselwood (I), laminar flow, $K_{H2} = 0.3$, 1 bar)

Figure A6-4.5: Comparison of model with experimental results (Langmuir-Hinselwood (I), laminar flow, $K_{H2} = 0.3$, 4 bar)

Figure A6-4.6: Comparison of model with experimental results (Langmuir-Hinselwood (I), laminar flow, $K_{H2} = 0.3$, 6 bar)
Figure A6-4.7: Comparison of model with experimental results (Langmuir-Hinselwood (I), plug flow, \( K_{H2} = 0.3, 1 \text{ bar} \))

Figure A6-4.8: Comparison of model with experimental results (Langmuir-Hinselwood (I), plug flow, \( K_{H2} = 0.3, 4 \text{ bar} \))

Figure A6-4.9: Comparison of model with experimental results (Langmuir-Hinselwood (I), plug flow, \( K_{H2} = 0.3, 6 \text{ bar} \))
Appendix 7-1:

Analysis Recipe for the Cyclodex-B Capillary Column
<table>
<thead>
<tr>
<th><strong>Oven</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Inlet</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
</tr>
<tr>
<td>Initial temperature</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Split ratio</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Column</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
</tr>
<tr>
<td>Initial flow</td>
</tr>
<tr>
<td>Nominal initial pressure</td>
</tr>
<tr>
<td>Average velocity</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Detector</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Flowrate: H2</td>
</tr>
<tr>
<td>Air</td>
</tr>
<tr>
<td>Makeup</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Injector</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample washes</td>
</tr>
<tr>
<td>Sample pumps</td>
</tr>
<tr>
<td>Injection volume</td>
</tr>
<tr>
<td>Syringe size</td>
</tr>
<tr>
<td>Post injection washes</td>
</tr>
</tbody>
</table>
Appendix 7-2:

Analysis Recipe for the DB-624 Capillary Column
<table>
<thead>
<tr>
<th><strong>Oven</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>250 °C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Inlet</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>Split</td>
</tr>
<tr>
<td>Initial temp</td>
<td>250 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>20 psi</td>
</tr>
<tr>
<td>Split ratio</td>
<td>200:1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Column</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>Constant pressure</td>
</tr>
<tr>
<td>Initial flow</td>
<td>2 ml/min</td>
</tr>
<tr>
<td>Nominal initial pressure</td>
<td>20.9 kPa</td>
</tr>
<tr>
<td>Average velocity</td>
<td>44 cm/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Detector</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>250 °C</td>
</tr>
<tr>
<td>Flowrate: H2</td>
<td>40 ml/min</td>
</tr>
<tr>
<td>Air</td>
<td>450 ml/min</td>
</tr>
<tr>
<td>Makeup</td>
<td>45 ml/min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Injector</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample washes</td>
<td>3</td>
</tr>
<tr>
<td>Sample pumps</td>
<td>3</td>
</tr>
<tr>
<td>Injection volume</td>
<td>0.2 μl</td>
</tr>
<tr>
<td>Syringe size</td>
<td>1 μl</td>
</tr>
<tr>
<td>Post injection washes</td>
<td>3</td>
</tr>
</tbody>
</table>