MODELING AND DEMONSTRATION OF A SUB-WATT SCALE METHANOL REFORMER

By

JAMELYN DAVIS HOLLADAY

A dissertation submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

WASHINGTON STATE UNIVERSITY
The Gene and Linda Voiland School of Chemical Engineering and Bioengineering

MAY 2015
To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of JAMELYN DAVIS HOLLADAY find it satisfactory and recommend that it be accepted.

Yong Wang, Ph.D., Chair

James N. Petersen, Ph.D.

Cornelius F. Ivory, Ph.D.

Su Ha, Ph.D.
ACKNOWLEDGEMENT

I would like to begin by thanking Dr. Yong Wang, my committee chair, for his encouragement, instruction, support, and friendship. I could not have done this without him. In conjunction with Dr. Wang, I would like to thank my committee members Dr. James Petersen, Dr. Cornelius Ivory, and Dr. Su Ha for their patience and guidance. I would like to extend a special thanks to Dr. Paul Humble for the many useful conversations. In addition, I would like to show my appreciation to my colleagues and managers at the Pacific Northwest National Laboratory for their support and encouragement. I also express my indebtedness to my Heavenly Father for the gifts He has given me.

This work has taken quite a considerable amount of my time over the last few years. So I give a special thanks to his wife and family for support, encouragement, and understanding as for the many days and nights of not being as available as I would have liked in order to complete this project.
A micro-scale methanol fuel processor was designed, modeled, built and tested for the production of hydrogen for a small fuel cell (<1W). Methanol was selected due to the low reforming temperature. The fuel processor included the methanol-water vaporizer, preheater, catalytic methanol steam reformer, catalytic combustor, a vaporizer/preheater for the combustion fuel and oxidant, and in one embodiment a CO selective methanation reactor. The fuel processor had a novel radial flow design with the methanol reformer and catalytic combustor separated by a thin shim and a volume less than 0.5 cm$^3$. A highly active non-pyrophoric PdZnO/Al$_2$O$_3$ catalyst was used in the methanol reformer. In the CO methanation reactor, a Ru/Al$_2$O$_3$ catalyst was used. A rate equation for the Pd/ZnO/Al$_2$O$_3$ catalyst was determined to be: 

$$(-r_A) (mmol / kgcat \cdot s) = 2.9047 \times 10^{10} e^{\frac{94800}{RT}} p_{MeOH}^{0.715} p_{H_2O}^{-0.088}.$$
Three fuel processor generations were built and tested. The first generation had the smallest reformer, was able to produce up to approximately 1.1 sccm of hydrogen with a thermal efficiency of up to 9 wt%. The second generation expanded the methanol reformer reactor and increased the hydrogen production to ~3.5 sccm and the thermal efficiency to ~33%. The third variation included the selective methanation reactor which reduced the CO content to less than 100ppm.

A three dimensional model of the reactor was developed to explore design variations to improve the reactor performance. Two variations were examined, the first included multiple outlets rather than the single outlet in the baseline designs on the methanol steam reformer side which did not improve performance. The second explored the use of three fins or baffles in the reformer section. This increased the gas residence time in the hottest portion of the reactor allowing a temperature reduction of almost 30°C at the equivalent inlet flow rate to achieve >99.5% conversion. In addition, the inlet flow rate could be increased by 2.7x at approximately equivalent temperatures. Finally, the model clearly showed the reactor was heat transfer limited. Therefore a new design which had the combustor exhaust envelope the steam reformer. This would not only better insulate the methanol reformer, but the exhaust gases could heat the sides of the reactor.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>III</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>IV</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>X</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>XII</td>
</tr>
<tr>
<td>CHAPTER 1 OVERALL INTRODUCTION AND RESEARCH OBJECTIVE</td>
<td>1</td>
</tr>
<tr>
<td>1.1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.2 BACKGROUND INFORMATION</td>
<td>3</td>
</tr>
<tr>
<td>1.2.1 Fuel reforming approaches</td>
<td>3</td>
</tr>
<tr>
<td>1.2.2 Methanol fuel selection</td>
<td>10</td>
</tr>
<tr>
<td>1.2.3 Materials of construction and micro-reactor design</td>
<td>13</td>
</tr>
<tr>
<td>1.3 RESEARCH OBJECTIVE</td>
<td>23</td>
</tr>
<tr>
<td>1.4 DISSERTATION STRUCTURE</td>
<td>26</td>
</tr>
<tr>
<td>1.5 PUBLICATIONS FROM THIS WORK</td>
<td>27</td>
</tr>
<tr>
<td>1.5.1 Journal articles</td>
<td>27</td>
</tr>
<tr>
<td>1.5.2 Book and book chapters</td>
<td>29</td>
</tr>
<tr>
<td>1.5.3 Conference publications</td>
<td>29</td>
</tr>
<tr>
<td>1.7 REFERENCES</td>
<td>31</td>
</tr>
<tr>
<td>CHAPTER 2 A REVIEW OF –RECENT ADVANCES IN NUMERICAL SIMULATIONS OF MICROSCALE FUEL PROCESSORS FOR HYDROGEN PRODUCTION</td>
<td>39</td>
</tr>
<tr>
<td>CHAPTER 3 3-D MODEL OF A RADIAL FLOW SUB-WATT METHANOL FUEL PROCESSOR</td>
<td>106</td>
</tr>
</tbody>
</table>
APPENDIX B. HIGH EFFICIENCY AND LOW CARBON MONOXIDE MICRO-SCALE METHANOL PROCESSORS 182

B.1. INTRODUCTION 183

B.2. EXPERIMENTAL 185

B.2.1. High thermal efficiency micro-scale methanol processor 185

B.2.2. Carbon monoxide reduction 186

B.3. RESULTS AND DISCUSSION 187

B.1. High thermal efficiency micro-scale methanol processor 187

B.2. Carbon monoxide reduction 189

B.4. CONCLUSIONS 192

B.5 REFERENCES 193

APPENDIX C. KINETIC STUDIES OF METHANOL-STEAM REFORMING OVER PD/ZNO CATALYST USING A MICROCHANNEL REACTOR 195

C.1. INTRODUCTION 196

C.2. EXPERIMENTAL 199

C.3. RESULTS AND DISCUSSION 203

C.3.1 Kinetics of steam reforming of methanol 203

C.3.2 Performance comparison between the microchannel reactor and a conventional fixed bed reactor—Evaluate catalyst at isothermal conditions 211

C.4. CONCLUSIONS 219

C.7 NOMENCLATURE 220

C.5 REFERENCES 222

APPENDIX D. COMBUSTION CATALYST FABRICATION 224
APPENDIX E. MESO-SCALE FUEL CELL AND MICRO-SCALE FUEL PROCESSOR TESTING .................................................. 226

APPENDIX F. CALCULATIONS ......................................................................................................................................... 229
  F.1 MEAR’S CRITERION ............................................................................................................................................... 229
  F.2 THIELE MODULUS ............................................................................................................................................... 230

APPENDIX G. DEVICE DESIGNS .................................................................................................................................... 235

APPENDIX H. NSF PROPOSAL: INTEGRATED PULSATING HEAT PIPE MULTIFERROIC DEVICE ................................. 239
LIST OF TABLES

Table 1.1. Advantages and disadvantages of three common fuel processing technologies
(Adapted from Holladay et al. (17) ........................................................................................................ 5

Table 1.2 Microreactor material benefits and drawbacks (adapted from\textsuperscript{54,55}) ................. 15

Table 2.1. Fuel and Fuel-Water mix energy density for several common fuels. ................................. 43

Table 2.2. Comparison of reforming technologies (adapted from\textsuperscript{[2, 12, 25, 26]}) ..................... 44

Table 2.3. Microreactor material advantages and challenges (adapted from \textsuperscript{[12]}) .................. 46

Table 3.1 Model Parameters............................................................................................................. 119

Table 4.1 Pd/ZnO Advantages and disadvantages............................................................................. 150

Table A.2. Fuel processor feed energy density (hydrocarbon + water) ............................................. 168

Table A.3. Typical reformate dry gas composition from Battelle’s Pd/ZnO catalyst and Cu/Zn catalysts with water + methanol (S:C 1.8:1) as fuel ................................................................. 173

Table B.1. Fuel Processor Performance at >99% methanol conversion....................................... 190

Table B.2. Methanol processor with integrated carbon monoxide reactor performance.............. 191

Table C.1. Measured Reaction Rate of Steam Reforming of Methanol on Pd/ZnO Catalyst ....... 207
Table C.2. Parameters of the Rate Equation............................................................................ 209

Table F.1  Thiele modulus parameters ....................................................................................... 233
LIST OF FIGURES

Figure 1.1 Energy density of fuels with and without water. MeOH is 1.2:1 S:C and C8-C12 is ~3:1 S:C. .......................................................... 13

Figure 1.2. Schematic of the basic design. “Vap” identifies where in the inlet tube vaporization may occur. “Preheat” identifies where in the inlet tube preheating occurs. “Recup” shows where heat recuperation from the products to the incoming reactants occurs. ......................... 23

Figure 2.1. Isothermal packed bed performance compared to experimental data at 503 K [27]. W = catalyst weight in kg and F = methanol flow in mol s^{-1}. .......................................................... 53

Figure 2.2. Modeling predictions for wall coated reactors at 503 K. Unlike the packed bed reactor, no heat transfer limitations were predicted[27]. W = catalyst weight in kg and F = methanol flow in mol s^{-1}. The numbers in parenthesis represent the catalyst coating thickness. .................................................................................. 53

Figure 2.3. Schematic figure of zigzag and straight catalytic wall microchannel reactor configurations. [32] (used with permission). .......................................................... 54

Figure 2.4. Dimensions used in microreactor model. TOX is the total oxidation or combustion side[32] (used with permission). .......................................................... 55

Figure 2.5. Zigzag configuration has a higher (a) hydrogen production (mole fraction) and a lower CO selectivity (b) than the straight configuration [32] (used with permission)............. 57
Figure 2.6. Annular reformer with hot gas in the outer tube and packed bed reformer with incline and fishbone-shaped baffle plates inside the reformer from reference [36] Reprinted with permission from Energy and Fuels reference 35. Copyright (2012) American Chemical Society.

Figure 2.7. Physical domain of the annulus design methanol reformer with methanol air combustor proposed by Chen et al. [38]. $Q_{in,R}$ is reformer inlet volumetric flow rate ($m^3 s^{-1}$), $T_{in}$ is inlet temperature (K), $R_b$ is reformer radius (m), $R_c$ is combustor radius (m), $t_c$ is combustion wall thickness (m), $t_r$ is reformer wall thickness (m), $L$ is the inlet and outlet length (m), and $L_b$ is the reformer length (m).

Figure 2.8. Microchannel cross section. This drawing shows the dimensions, location of coordinate axes and direction of flow[28].

Figure 2.9. Top view of microchannel plate reactor modeled by Chen et al.[34]. The dimensions are in mm and the channel depth is 0.5 mm.

Figure 2.10. Methanol conversion at three different temperatures. Notice the differences in methanol conversion between the channels illustrating the non-uniform reaction rates [40].

Figure 2.11. Schematic diagram used by Hseuh et al.[41]. H is the microchannel height (m), W is the microchannel width (m), L is the microchannel length (m), $T_w$ is the wall temperature (°C), x, y, and z are coordinates, $?_1$ is the open channel height (m), and $?_2$ is the catalyst thickness (m).
Figure 2.12. Effect of microchannel aspect ratio ($\gamma = H/W$) and wall temperature on methanol conversion ($\eta$) and CO concentration at channel outlet[41].

Figure 2.13. Schematic of Hseuh et al. 2010 serpentine microreactor design[43]. $T_w$ is the wall temperature ($^\circ$C), $H$ is the channel height (m), $W_s$ is the solids width in the channel (m), $x_w$ is the open portion of the channel (m), $\delta_1$ is the catalyst thickness (m), $\delta_2$ is the open channel height (m), and $x$, $y$, and $z$ are coordinates (m).

Figure 2.14 Local temperature distribution ($\theta$) and methanol conversion predicted results with and without wall conduction. This shows that wall conduction must be considered[43]. $T_w$ is the wall temperature ($^\circ$C), $T_0$ is the inlet temperature ($^\circ$C), Re is the Reynolds number, S/C is the steam to carbon ratio, $X$ is the dimensionless distance from the flow channel inlet to outlet, $M_{\text{CH}_3\text{OH}}$ is the mole fraction of methanol.

Figure 2.15. Methanol conversion (circles) and mean channel temperatures at the outlet (triangles) as a function of the GHSV in the 4 channel arrangement[44]. The 1.40 mm, 0.70 mm and 0.35 mm refer to the channel size. SRM is the steam reforming of methanol to distinguish from combustion reactions.

Figure 2.16. Temperature distribution in the co flow, counter flow and cross flow configurations $d=0.7$mm, reforming 28,224 hr$^{-1}$, and combustion at 75,263 hr$^{-1}$ [44].

Figure 2.17. An array of microchannels forming a complete reactor and the reactor specifications for the baseline case[1].
Figure 2.18. Microchannel plate reactor by Jang et al.[48]......................................................... 84

Figure 2.19. Inlet and outlet configurations considered by Jang et al. [48]11. ............................. 86

Figure 2.20. Methanol conversion and mole fraction of CO with different configurations and
over a range of flow rates. The Central inlet/two outlets had the best performance[48]11...... 87

Figure 2.21. Flow velocity in the channels[48] 11. ......................................................................... 87

Figure 2.22. Microchannel plates with two different manifold structures[52]. ........................... 88

Figure 2.23. Velocity Distribution (a) without reaction and (b) with reaction. MPOM is oblique
manifold and MPRM is the right angle manifold[52]12. ............................................................... 90

Figure 2.24. (a) Comparison of velocity degree of uniformity and (b) methanol conversion in the
MPOM and MPRM with reaction[52]12. ....................................................................................... 91

Figure 2.25. Micro-pin-fin methanol reformer design. a) is the 2-D diagram, b) fabricated
catalyst support, and c) completed microreactor[7]. ................................................................... 92

Figure 2.26. Schematic of disc reactor with tree shaped network (a) compared to microreactor
with parallel flow pattern (b) [55]. ............................................................................................... 93

Figure 2.27. Hydrogen mole fraction distribution at T=503 K, V_in=0.3 m s^{-1}, and steam to carbon
ratio of 1.3 for the (a) tree shaped network and (b) parallel flow channel14[55]. ......................... 94
Figure 2.28. Methanol conversion of the tree shaped (Constructal) and parallel channel reactors\textsuperscript{14}[55]. ........................................................................................................................................................................ 95

Figure 3.1. Schematic of baseline reactor design ................................................................................................. 111

Figure 3.2. Enthalpy change of the water-methanol mixture (1.2:1 molar). This was used to calculate a \(C_p\) over the vaporization range to simulate vaporization in the reformer. ............. 117

Figure 3.3. Density change of the water-methanol mixture (1.2:1 molar). .......................................................... 117

Figure 3.4. Reformer system projected temperature isotherm (temperature in K) contours with 0.2 ml hr\textsuperscript{-1} methanol water mix flow and a >99.5% methanol conversion. The steam reformer is the upper reactor and the combustor is in the lower section. ................................................................. 121

Figure 3.5. Baseline methanol steam reformer system projected reaction rate in kg methanol converted m\textsuperscript{-3} s\textsuperscript{-1} at >99.5% methanol conversion.................................................................................................................. 122

Figure 3.6. Predicted methanol conversion (solid line) compared to experimental results at 0.15 ml hr\textsuperscript{-1} and 0.2 ml hr\textsuperscript{-1} methanol-water mixture flow rates. Temperature corresponds to the thermocouple temperature in the experiments and the temperature at approximate location of the thermocouple in the model (Tcr). ................................................................................................................. 123

Figure 3.7. Predicted velocity profiles (velocity in m s\textsuperscript{-1}) at inlet fluid flow for 0.2 ml hr\textsuperscript{-1} methanol water mixture feed and >99.5% methanol conversion. A) shows the cross-cross section and B) shows the outside. The methanol reformer is the top reactor and the combustor

xvi
is the bottom reactor. The maximum velocity of the methanol section was \( \approx 3.1 \text{ m s}^{-1} \), but a finer scale was used in order to see the velocity profile in the reactor sections more clearly. 

Figure 3.8. Predicted velocity profiles (velocity in m s\(^{-1}\)) for the reactor design with 4 outlets at inlet fluid flow for 0.2 ml hr\(^{-1}\) methanol water mixture feed and >99.5% methanol conversion. A) shows the cross-cross section and B) shows the outside. The methanol reformer is the top reactor and the combustor is the bottom reactor. The maximum velocity of the methanol section was \( \approx 3.1 \text{ m s}^{-1} \), but a finer scale was used in order to see the velocity profile in the reactor sections more clearly.

Figure 3.9. Predicted baseline methanol conversion and predicted methanol conversion with multiple outlets. No significant improvement was predicted in the numerical simulation. Temperature corresponds to the thermocouple temperature in the experiments and the temperature at approximate location of the thermocouple in the model (Tcr).

Figure 3.10. Predicted velocity profiles (velocity in m s\(^{-1}\)) for the finned reactor design at inlet fluid flow for 0.2 ml hr\(^{-1}\) methanol water mixture feed and >99.5% methanol conversion. A) shows the cross-cross section view and B) shows the outside view. The methanol reformer is the top reactor and the combustor is the bottom reactor. The maximum velocity of the methanol section was \( \approx 3 \text{ m s}^{-1} \), but a finer scale was used in order to see the velocity profile in the reactor sections more clearly.
Figure 3.11. Velocity streamlines (velocity in m s\(^{-1}\)) in the methanol reformer section only of the A) baseline reactor, B) multi-exit reactor design and C) finned reactor design. Inlet flow was 0.2 ml hr\(^{-1}\) and >99.5% methanol conversion. The maximum flow was ~3.1 m s\(^{-1}\). ........................ 128

Figure 3.12. Predicted temperature distribution (temperature in K) in finned reformer at 0.2 ml hr\(^{-1}\) inlet rate and >99.5% methanol conversion. The top portion is the steam reformer reactor and the bottom section is the combustor. ........................................................... 129

Figure 3.13. Predicted methanol conversion for 0.2 ml hr\(^{-1}\) methanol water mix inlet flow for the original reactor design (blue line) and the finned reactor (dotted red line). Temperature corresponds to the thermocouple temperature in the experiments and the temperature at approximate location of the thermocouple in the model (Tcr). .................................................. 131

Figure 3.14 Methanol mass fraction (wt% methanol) in (A) the baseline reactor, 0.2 ml hr\(^{-1}\) inlet feed and >99.5% methanol conversion, (B) finned reactor, 0.2 ml hr\(^{-1}\) inlet feed, and >99.5% methanol conversion, and (C) finned reactor, 0.54 ml hr\(^{-1}\) inlet feed, and >99.5% methanol conversion................................................................. 132

Figure 3.15 Methanol mass fraction (wt% methanol) in the reactors with finer scale. (A) the baseline reactor, 0.2 ml hr\(^{-1}\) inlet feed and >99.5% methanol conversion, (B) finned reactor, 0.2 ml hr\(^{-1}\) inlet feed, and >99.5% methanol conversion, and (C) finned reactor, 0.54 ml hr\(^{-1}\) inlet feed, and >99.5% methanol conversion............................ 132
Figure 3.16 Fuel processor with the combustor exhaust flowing around the methanol reformer. ................................................................. 135

Figure 4.1. A) Radial methane steam reformer reactor with recuperative heat exchanger. B) Plate with catalyst inserts. ................................................................. 155

Figure 4.2 Jacketed reactor design. Notice the combustion exhaust gas wraps around the steam reformer providing heat and insulation ........................................... 156

Figure A.3. Fuel processor schematic. ......................................................................................................................................................... 166

Figure A.2. Effect of steam to carbon ratio on the Pd/ZnO catalyst performance. The steam to carbon ratio of 1.8:1 appeared to give the best results. (See footnote 2)... 172

Figure A.3. Effect of contact time on methanol reforming with the Pd/ZnO. As expected, longer contact times allowed lower processing temperatures. (See footnote 2)........ 173

Figure A.4. Comparison of Pd/ZnO (Battelle's catalyst) with Cu/Zn on alumina (commercial) catalyst at steam to carbon ratio of 1.8:1 and 300 ms contact time. Lower temperature was required to achieve 100% methanol conversion on the Battelle catalyst compared to the commercial catalyst tested......................................................... 174

Figure A.5. Integrated fuel processor system. It is 0.15” in diameter and 0.25” in length (Appendix G). ......................................................................................................................................................... 177

Figure A.6. Testing equipment schematic. ......................................................................................................................................................... 178
Figure B.1. Second generation micro-scale fuel processor—high efficiency. The diameter is 0.25” and the length is 0.38” (Appendix D). Volume is < 0.4cm³ ........................................................................................................... 186

Figure B.2. Second generation micro-scale fuel processor with CO removal reactor. The methanation section adds 0.075” in length and is 0.028” in diameter (Appendix G). The total volume is <0.5 cm³ ........................................................................................................................................ 187

Figure B.3. High efficiency reactor performance ........................................................................................................ 188

Figure B.4. Low carbon monoxide fuel processor performance² .............................................................................. 191

Figure C.1. Reactor assembly ................................................................................................................................. 200

Figure C.2. Schematic of reactor system process diagram ............................................................................................. 201

Figure C.3. Catalytic performance of Pd/ZnO catalyst in a microchannel reactor .............................................. 204

Figure C.4. Isothermal lines of the microchannel reactor with Pd/ZnO catalyst .......................................................... 206

Figure C.5. Comparison between predicted rate and measured rate ................................................................. 209

Figure C.6. Steam partial pressure effect on MSR reaction rate in a differential reactor (T=210°C, PMeOH=34.2 kPa) .................................................................................................................. 211

Figure C.7. Performance comparison of the tubular and the microchannel reactors (WHSV=4.53 gMeOH/gcat/hr) .................................................................................................................... 213
Figure C.8. 3D pseudo-homogenous model simulation sequence for methanol steam reformation. ................................................................. 215

Figure C.9. Temperature profiles of the tubular reactor and the microchannel catalyst slab bed. (wall temperature at 220°C, WHSV=4.53 gMeOH/gcat/hr). ............................................................... 216

Figure C.10. Temperature profiles of the tubular reactor at different furnace temperatures (WHSV=4.53 gMeOH/gcat/hr) ......................................................................................... 217

Figure C.11. Temperature profile of the microchannel reactor at high methanol conversion (WHSV=4.53 gMeOH/gcat/hr). ......................................................................................... 218

Figure C.12. Temperature distribution along the catalytic bed in the microchannel reactor. ... 218

Figure E.1. Assembly of mesoscale fuel cell components. Membrane/electrode assembly (not shown) goes between the two current collector plates. Only one current collector is shown; the other cannot be seen in this view. It is located on the lower side of the first current collector plate. For air-breathing operation, only one manifold is used..................................................... 227

Figure E.2. PBI meso-scale fuel cell ....................................................................................... 228

Figure E.3. Bread-boarded fuel processor fuel cell performance................................................. 228

Figure H.1. Magnetization change in Ni_{45}Co_{5}Mn_{40}Sn_{10} with changing temperature^{(5)} ............ 249

Figure H.2. Multiferroic material with embedded heat transfer mechanism.............................. 250
Figure H.3 Multiferroic material with embedded heat transfer mechanism.............................. 251

Figure H.4 PHP schematic showing the main sections: evaporator, adiabatic and condenser . 253

Figure H.5 A singular MFP (2) and proposed array of MFP integrated with PHP. ....................... 254

Figure H.6. Critical diameter of 3 common working fluids.......................................................... 255

Figure H.7 Film thickness variations with Capillary number using Aussilous and Quere correlation with the typical Ca range for a PHP shown in the grey box. This Ca range is approximately 0.007 to 7 m/s for a water film........................................................................... 260

Figure H.8. Test stand set-up. Thermocouples will be connected to each loop at the condenser, adiabatic, and evaporator sections. .......................................................... 264

Figure H.9. PHP-MFD device integration for circular pipe............................................................. 267

Figure H.10. PHP-MFD device integration for rectangular pipe....................................................... 267

Figure H.11. MFD-PHP integrated device test stand set-up. Thermocouples will be connected to each loop at the condenser, adiabatic, and evaporator sections. The MFD will be connected to a load (resistor) and voltmeter to measure power veneration .................................................... 268
Dedication

This dissertation is dedicated to my wife and family without whose support and patience it would not have been possible.
CHAPTER 1 OVERALL INTRODUCTION AND RESEARCH OBJECTIVE

1.1 Introduction

Remarkable achievements in microelectronics have increased functionality of personal electronic devices and other electronics while making such devices smaller. However, as new capabilities have been added, power consumption has risen alarmingly. The US military is particularly interested in microsensors that operate on less than 500 mW_e of electric power*. Batteries have been the energy storage solution for these devices, but new approaches, such as micro-scale rotary engines and thermal electric generators, are being developed to generate electric power from hydrocarbon fuels. Since hydrocarbon fuels have thermal energy density of 10x greater than batteries, even at a thermal to electrical efficiency of 5%, would have a greater energy density than Li-ion batteries at <0.2 kW_e/kg^{(1,2)}.

Numerous micro-scale power devices have been proposed for sub-watt power production, but few have been successfully demonstrated. One attempt was a micro-scale wankel engine, a rotary engine^{(1,3)}, which was suitable for power generation in the 10’s of watt range, but could not be scaled down further. The rotary engines suffered from stiction. Stiction is a phenomenon where objects in the micrometer range adhere together due to electrostatic, Van der Waals and/or hydrogen bonding forces. Stiction limits how close moving objects can come together, which causes problems for creating the compression required for the engines

* To distinguish between thermal and electric a subscript “e” will designate electric and “t” thermal.
to have the torque necessary for efficient electric power generation\(^3\). To avoid stiction devices without moving parts are desired. Thermoelectric generators (TEG) are an option that does not require moving parts\(^{2,4}\). Unfortunately TEG’s operate at high temperatures making thermal management difficult. Various architectures and insulation have been explored. Marton et al.’s device, which burned butane and used vacuum insulation, was only 2.5% efficient\(^4\). An alternative was a 3-D Swiss roll reactor which has the advantage of, in theory, being able to recuperate heat in all directions\(^5\). While this was a clever design, it was ultimately not successful due to challenges in controlling the catalyst deposition process for the catalytic combustor, TEG integration, and scaling down the device\(^{5,6}\).

Fuel cells coupled with hydrogen produced from hydrocarbon fuel processors was another approach\(^{7-16}\). A micro-scale fuel processor would convert he paraffinic hydrocarbon to a hydrogen rich stream. The fuel cell would then electrochemically react hydrogen with oxygen from the air to make water and electric power. This direct conversion from chemical energy to electrical power is a great advantage over the microengine and TEG systems that were proposed. For both the microengine and TEG systems, the first step in electric power generation is chemical energy conversion to thermal power. For the microengines, the thermal power is then converted to mechanical power and finally to electrical power. However, since the first step is conversion to thermal power, this limits their efficiency to what is achievable in the Carnot Cycle. The conversion steps to transform the thermal power to mechanical power and then from mechanical power to electrical power each introduce inefficiencies into the system making desirable efficiencies difficult to attain. The TEG systems are not quite as
complicated, as the thermal power can be converted directly to electrical power. However, low temperature TEG efficiencies are quite low due to the low ZT’s of the available materials. ZT is the figure of merit for TEGs. It takes into consideration of the thermal and electrical conductivities of the materials used and represents the ability to produce power. For both the microengines and the TEGs to have reasonable efficiencies, a high temperature differential is required. However, high temperatures for small devices create thermal management challenges\(^{(2,4)}\). Since a fuel cell is an electrochemical conversion of chemical energy to electrical power, it is not a heat engine and its efficiency is not limited by the Carnot Cycle. It avoids the need for a high temperature differential and, potentially, is a much simpler system. We hypothesize that a micro-scale methanol fuel processor which produces less than 500 mW\(_t\) hydrogen equivalent with a thermal efficiency > 10% can be scaled to a volume less than 0.5 cm\(^3\).

1.2 Background information

1.2.1 Fuel reforming approaches

Fuel processing technologies convert a hydrogen containing chemicals such as methane, paraffinic hydrocarbons, ammonia, or methanol into a hydrogen rich stream called reformate\(^{(17)}\). The reformate gas is composed primarily of hydrogen, carbon monoxide and carbon dioxide. Depending on the ultimate application of the reformate, further processing may be required. Fuel reforming is the most common hydrogen production method in commercial use.
today. Most hydrocarbon fuels contain at least some amount of sulfur which poisons catalyst and presents perhaps the biggest challenge to reforming. For microscale reformers, it is assumed that a sulfur free fuel will be utilized. This brief review will cover only vapor phase fuel reforming which is the most commonly used reforming technology for microscale reformers, so desulfurization, plasma reforming, aqueous reforming, and pyrolysis will not be discussed. An overview of these technologies as well as other hydrogen production techniques is available by Holladay et al. in reference (17).

There are three primary vapor phase techniques used to produce hydrogen from hydrocarbon fuels: steam reforming, partial oxidation (POX), and autothermal reforming (ATR). A summary of the advantages and disadvantages of these processes is contained in Table 1.

Steam reforming is an endothermic process and therefore requires an external heat source. However, unlike POX and ATR, steam reforming does not require oxygen, has a lower operating, and the reformate product has a \( \text{H}_2/\text{CO} \) ratio (~3:1) which is the highest of the three technologies. Due to the highly endothermic nature of the steam reforming reactions, there is often heat and mass transfer limitations which for conventional designs require a larger reactor than POX and ATR (17). Furthermore, steam reforming requires excess water (typically 3:1 steam to carbon ratio or higher), which is much larger than ATR (typically 50% of what is required by steam reforming) and POX which doesn’t require any water. POX partially oxidizes (combusts) the hydrocarbon with oxygen to produce the reformate (17). The “controlled” combustion provides the heat for reforming, so no external heat source is required.
Table 1.1. Advantages and disadvantages of three common fuel processing technologies

(Adapted from Holladay et al. (17)

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Reforming</td>
<td>• Most extensive industrial experience</td>
<td>• Largest reactor size</td>
</tr>
<tr>
<td></td>
<td>• Oxygen not required</td>
<td>• Requires a large amount of water</td>
</tr>
<tr>
<td></td>
<td>• Lowest process temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Best H₂/CO ratio for H₂ production</td>
<td></td>
</tr>
<tr>
<td>Autothermal Reforming</td>
<td>• Lower process temperature than POX</td>
<td>• Limited commercial experience</td>
</tr>
<tr>
<td></td>
<td>• Low methane slip</td>
<td>• Requires air or oxygen</td>
</tr>
<tr>
<td>Partial Oxidation</td>
<td>• Decreased desulfurization requirement</td>
<td>• Low H₂/CO ratio</td>
</tr>
<tr>
<td></td>
<td>• No catalyst required</td>
<td>• Very high processing temperatures</td>
</tr>
<tr>
<td></td>
<td>• Low methane slip</td>
<td>• Soot formation/handling adds process complexity</td>
</tr>
</tbody>
</table>

Other advantages include: no catalyst requirement (although a catalyst is sometimes used), low methane slip, and has the highest sulfur tolerance of the three processes. The process occurs at high temperatures (>700°C) with some soot formation. The H₂/CO ratio in the reformate product varies from 1:1 to 2:1 depending on how the reactor is operated. These H₂/CO ratios are favored for synthesis reactors such as Fischer-Tropsch\(^{17}\). Autothermal reforming combines POX and steam reforming to try and gain the advantages of each process with the objective of a thermally neutral process with high hydrogen content product. Partial oxidation is used to provide the heat, while endothermic steam reforming process increases the hydrogen content\(^{17}\). Autothermal reforming is typically conducted at lower pressure than POX and steam reforming reactors and has a low methane slip. Both the POX and ATR require an expensive and
complex oxygen separation unit in order to feed pure oxygen to the reactor or the product gas is diluted with nitrogen. In addition, if there is nitrogen in the reactant stream, a small amount of ammonia may be produced \(^{(17)}\). Steam reforming is typically the preferred process for hydrogen production in industry \(^{(18-22)}\).

For hydrogen production, one or more water-gas-shift (WGS) reactors - typically a high temperature reactor and low temperature reactor - are used to convert CO and water to CO\(_2\) and H\(_2\). The high temperature (310-450°C) reactor has fast kinetics, but thermodynamics limits the CO shift. Therefore, a lower temperature reactor (210-250°C) is used to polish off the carbon monoxide to a lower level typically to less than 1% \(^{(18-22)}\). Since the temperatures are lower than that of the reformers, multiple heat exchangers are required. TeGrotenhuis et al. \(^{(23,24)}\) have demonstrated the potential of using microchannel reactors to build a gradient temperature WGS reactor that contains the high temperature WGS and low temperature WGS in a single unit for >2-3 kW\(_e\) units. Smaller units have never been demonstrated.

To further reduce the carbon monoxide, a preferential oxidation reactor or a carbon monoxide selective methanation reactor can be used \(^{(17,21,25,26)}\). For preferential oxidation sometimes the term selective oxidation is used, but this is misleading. Selective oxidation refers to carbon monoxide reduction within a fuel cell, typically a PEMFC; whereas preferential oxidation occurs in a reactor external to the fuel cell \(^{(17,25)}\). The PrOx and methanation reactors each have their advantages and challenges. The preferential oxidation reactor increases the system complexity because carefully measured concentrations of air must be added to the system \(^{(17,21,25,26)}\). However these reactors are compact and if excessive air is introduced, some
hydrogen is burned. Methanation reactors are simpler in that no air is required; however, for every carbon monoxide reacted, three hydrogen molecules are consumed. Also, the carbon dioxide reacts with the hydrogen, so careful control of the reactor conditions need to be maintained in order to minimize unnecessary consumption of hydrogen. Currently, preferential oxidation is the primary technique being developed\textsuperscript{(17,25)}. Alternatively, a membrane (ceramic or more commonly a palladium alloy) or pressure swing adsorption can be used to produce high purity (>99.999%) hydrogen\textsuperscript{(17)}. The challenge with PrOx and selective oxidation is that additional air must be metered into the reactor. For a micro-scale device this would significantly increase the complexity of the system. Membrane separation would necessitate high temperature and pressures which are not desirable for this system\textsuperscript{(17)}.

The reforming, WGS, and oxidation reactions can be generalized as follows for hydrocarbon and methanol fuels\textsuperscript{(17,25,27,28)}:

Steam reforming

\begin{align}
C_m H_n + m H_2 O &= m C O + (m + (\frac{1}{2})n) H_2 \\
\Delta H &= \text{hydrocarbon dependent} \quad (1.1)
\end{align}

\begin{align}
CH_3 OH + H_2 O &= CO_2 + 3H_2 \\
\Delta H &= +49 \text{ kJmol}^{-1} \quad (1.2)
\end{align}

Partial oxidation

\begin{align}
C_m H_n + (\frac{1}{2})m O_2 &= m C O + (\frac{1}{2})H_2 \\
\Delta H &= \text{hydrocarbon dependent} \quad (1.3)
\end{align}

\begin{align}
CH_3 OH + (\frac{1}{2})O_2 &= CO_2 + 2H_2 \\
\Delta H &= -193.2 \text{ kJmol}^{-1} \quad (1.4)
\end{align}
Autothermal reforming

\[ C_mH_n + (\frac{1}{2})mH_2O + (\frac{1}{4})mO_2 = mCO + ((\frac{1}{2})m + (\frac{1}{4})n)H_2 \quad \Delta H = \text{hydrocarbon dependent} \quad (1.5) \]

\[ 4\text{CH}_3\text{OH} + (3)\text{H}_2\text{O} + (\frac{5}{2})\text{O}_2 = 4\text{CO}_2 + 11\text{H}_2 \quad \Delta H = 0 \quad (1.6) \]

Carbon (coke) formation

\[ C_mH_n = xC + C_{m-x}H_{n-2x} + xH_2 \quad \Delta H = \text{hydrocarbon dependent} \quad (1.7) \]

\[ 2\text{CO} = \text{C} + \text{CO}_2 \quad \Delta H = +172.4 \text{ kJmol}^{-1} \quad (1.8) \]

\[ \text{CO} + \text{H}_2 = \text{C} + \text{H}_2\text{O} \quad (1.9) \]

Water-gas-shift

\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \quad \Delta H = -41.1 \text{ kJmol}^{-1} \quad (1.10) \]

\[ \text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O} \quad \text{RWGS} \quad (1.11) \]

CO oxidation

\[ \text{CO} + \text{O}_2 = \text{CO}_2 \quad \Delta H = +283 \text{ kJmol}^{-1} \quad (1.12) \]

\[ \text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O} \quad \Delta H = -242 \text{ kJ/mol}^{-1} \quad (1.13) \]

The enthalpies are reported at ambient temperature and pressure with reactants and products in the gas phase\(^{(17)}\).
There are three primary metals used as catalysts for steam reforming: nickel (non-precious metal), platinum or rhodium with the Pt and Rh being Group VIII precious metals. Due to severe mass and heat transfer limitations, conventional steam reformers are limited to an effectiveness factor of catalyst which is typically less than 5% \(^{(17,29)}\). Therefore, kinetics and thus the activity of the catalyst, are rarely the limiting factor with conventional steam reformer reactors \(^{(20)}\), so less expensive nickel catalysts are used almost universally in industry. The mass and heat transfer limitations have been shown to be overcome by employing microchannel based reactors enabling intrinsic kinetics of steam reforming to be exploited\(^{(19,30)}\). In these systems, the noble Group VIII metals, particularly Rh \(^{(31)}\), are preferred since they exhibit much higher specific activities than nickel catalysts \(^{(20,32,33)}\). However, the high cost of Rh is driving some researchers to develop alternative catalysts such as Co based catalysts \(^{(34,35)}\). Intermediate and high temperatures required for steam reforming may promote carbon formation, and steam to carbon ratios (≈2.5 or higher) higher than stoichiometry are required to gasify coke when a nickel based catalyst is used. Coke formation is much less over the noble Group VIII metals. Promoter, such as magnesia or potassium or other alkaline components, are added to the catalyst support to minimize the coke formation \(^{(36)}\). Steam reforming is commonly used in industry for the production of hydrogen from methane where high thermal efficiencies of up to approximately 85%, based on the higher heating values, have been achieved\(^{(21)}\).

For methanol reforming CuO/ZnO/Al\(_2\)O\(_3\) based catalysts are the primary materials. It is generally agreed that the active component on the CuO/ZnO/Al\(_2\)O\(_3\) catalyst for steam reforming (as well as methanol synthesis) is copper. While extremely active, CuO/ZnO based catalysts are
susceptible to sintering at temperatures >300°C and are highly pyrophoric when exposed to air at any temperature\(^{(37)}\). Another option are precious metal alloys, not containing copper, with Pd/ZnO being the most active and selective for this type of catalyst.\(^{(38)}\) Iwasa et. al were the first to report that Pd supported on ZnO and reduced at >300 °C has exceptional high activity and selectivity to CO\(_2\) and H\(_2\)\(^{(39-43)}\), although not as high as CuO/ZnO. In addition, the Pd/ZnO catalyst is not as prone to sintering at temperatures >300°C and is not pyrophoric\(^{(44)}\). Due to its higher stability and the fact it is not pyrophoric, Pd/ZnO was selected as the catalyst for the steam reformer.

In order to keep the system as simple as possible, steam reforming was selected as the primary reforming technology. The POX and ATR both require air or oxygen to be metered into the system which would require additional controls, perhaps a second blower (with its associated parasitic power), and would dilute the hydrogen stream. The WGS reactors were avoided by the selection of methanol as the fuel. Further discussion on fuel selection is in the following section. For the low CO reactors, preferential CO methanation with a Ru/Al\(_2\)O\(_3\) catalyst\(^{(45)}\) was selected.

### 1.2.2 Methanol fuel selection

The ideal fuel characteristics for micro-scale fuel processor would include\(^{(44)}\):

- High energy density
- No contaminants (sulfur, siloxanes, etc.)
• Low reforming temperature
• Low carbon monoxide and other contaminants.

Upon initial consideration, methane, ammonia, and paraffinic hydrocarbon fuels seem to be superior to methanol due to their higher energy density (>12 kWt-hr/kg) compared to methanol (~5.6 kWt-hr/kg). However, there are several other considerations that need to be addressed. First, methanol typically does not contain other contaminants such as sulfur which are common in paraffinic fuels and methane. Ammonia itself is a contaminant in fuel cells and causes irreversible damage to the PEM membranes even at sub 10 ppm levels. Therefore, when ammonia is used as a fuel for fuel processors, a scrubber must be included to decrease the ammonia content to acceptable levels. Despite this concern, there are several literature articles on ammonia reformers for automotive and portable hydrogen generators. Whereas, if any methanol slips through, a PEM fuel cell can tolerate low levels of methanol and any impact is reversible and the performance can be recovered with removal of the methanol.

Methanol has the lowest fuel steam reforming temperature compared to other fuels. For micro-scale systems this is a significant advantage as thermal management is a major challenge. Methanol can be reformed at temperatures <400°C whereas, methane, most paraffinic, and ammonia require temperatures in excess of 700°C. In addition, during methanol steam reforming there is a low likelihood of coke formation, which is a significant problem at low temperature fuel processing for paraffinic hydrocarbons. Of course, if ATR or
POX is being used, methanol’s reforming temperature increases to be comparable to that of other fuels. The low temperature advantage is only for steam reforming (17).

Minimizing carbon monoxide production is an important consideration for fuel and reforming technology selection. PEM fuel cells can only tolerate low levels (<100 ppm) CO (51). The CO tolerance increases to a couple of percent for medium temperature such as polybenzimidazole (PBI) fuel cells (52). For high temperature fuel cells, such as solid oxide fuel cells, high CO levels are acceptable. However, for high efficiency and relatively easy thermal integration, lower temperature operation is desirable (51). For methane and paraffinic hydrocarbon reforming (steam reforming, POX, or ATR) the CO production is an order of magnitude higher than that of methanol steam reforming (17,44). Therefore in order to minimize CO and maximize H2 one or more WGS reactors plus additional CO cleanup are required as discussed above.

Finally, water management is a very important consideration in fuel selection. For steam reforming water requirements range from 1.2:1 steam to carbon ratio (S:C) for methanol, to 4:1 S:C for methane and paraffinic hydrocarbons (17). In conventional reactors, water, if needed, can be captured from the reformate or fuel cell cathode exhaust (17,44). For micro-scale systems water recovery becomes difficult since most condensors are orientation dependent, add additional unit operations to the system increasing the size and complexity, and would require a pump or other mechanism to provide the water to the reformer. Therefore, it is necessary to carry the water. In this scenario, methanol, unlike paraffinic hydrocarbons, is miscible in water.
making it easy to co-feed it to the reformer. Furthermore, if water is included in the fuel energy density calculations, the gravimetric advantages of the other fuels is negated (Figure 1.1).

![Figure 1.1 Energy density of fuels with and without water. MeOH is 1.2:1 S:C and C8-C12 is ~3:1 S:C.](image)

In conclusion, due to methanol’s low reforming temperature, the fact that it does not contain poisons like sulfur, it produces a lower amount of CO compared to the other fuels, and the fact that it does not require as much water as other fuels, it was selected as the fuel for the micro-scale reformer system.

1.2.3 Materials of construction and micro-reactor design

To build an efficient and compact microreactor, the fabrication technique must allow for three-dimensional structures and the use of the appropriate materials, and should be low cost.\(^{(53)}\) Since reactants and products must flow in and out of the device, traditional standard

---

\(^{(53)}\) This section is from Holladay, J. D., Y. Wang, and E. O. Jones, "Review of developments in portable hydrogen production using microreactor technology," Chem. Rev. 104, 4767-4790 (2004). The table number was updated to fit in this dissertation.
thin film techniques are not suitable for the reactor framework. However, thin film techniques are very useful for integration, surface preparation, sensor integration, and finishing or packaging. Fortunately, traditional thin film techniques can be modified for microreactor fabrication; other techniques, which will be discussed below, are also available.

Materials

The fabrication materials chosen must be chemically compatible, have the appropriate thermal properties, and be structurally sound. Table 1 lists the benefits and drawbacks of some common materials used in microreactor fabrication. The materials are divided into four general categories: metals, silicon (which includes materials containing silicon or that are processed with semiconductor fabrication techniques), low-temperature co-fired ceramics (LTCC), and plastics. Polymeric materials would be of great interest in microreactors; however, no hydrogen generating microreactors built of polymers were reported in the literature at the time of this review. It would be an interesting area of development; although the thermal and chemical compatibility may be an issue. The material selection process is complicated by the fabrication process; i.e., will the fabrication process alter the material properties and, if so, how? Microreactors have the potential to be manufactured using high-volume, low-cost techniques, but the design, material, and fabrication selections should take cost into account to avoid developing a laboratory curiosity rather than a commercially viable device.
Table 1.2 Microreactor material benefits and drawbacks (adapted from (54,55))

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Benefits</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>Standard fabrication techniques</td>
<td>High thermal conductivity</td>
</tr>
<tr>
<td></td>
<td>Durable</td>
<td>Poor compatibility with ceramics and glass</td>
</tr>
<tr>
<td></td>
<td>Low to modest costs</td>
<td></td>
</tr>
<tr>
<td></td>
<td>No clean room required</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>Well characterized silicon fabrication techniques</td>
<td>Modest thermal conductivity</td>
</tr>
<tr>
<td></td>
<td>High precision</td>
<td>Fragile</td>
</tr>
<tr>
<td></td>
<td>Low cost</td>
<td>Requires a clean room</td>
</tr>
<tr>
<td>LTCC</td>
<td>Flexible fabrication</td>
<td>Non-standard fabrication</td>
</tr>
<tr>
<td></td>
<td>Refractory and durable</td>
<td>Low thermal conductivity</td>
</tr>
<tr>
<td></td>
<td>Low cost</td>
<td>Sealing</td>
</tr>
<tr>
<td></td>
<td>No clean room required</td>
<td></td>
</tr>
<tr>
<td>Polymer²</td>
<td>Low thermal conductivity</td>
<td>Chemical compatibility</td>
</tr>
<tr>
<td></td>
<td>Low cost</td>
<td>Thermal compatibility</td>
</tr>
<tr>
<td></td>
<td>Fabrication</td>
<td></td>
</tr>
</tbody>
</table>

Fabrication techniques

A number of fabrication techniques meet the general requirements for constructing an efficient and compact microreactor. Popular methods include LIGA, wet and dry etching processes, micromachining, lamination, and soft lithography.

LIGA

The LIGA technique was primarily developed by researchers in Germany, with Forschungszentrum Karlsruhe and the Institute for Microtechnology Mainz (IMM) being the primary drivers. This process combines deep lithography, electroplating, and molding

² The polymer portion was not included in the original article. It was added here.
(lithographie, galvanoformung, abformtechnik - LIGA)\textsuperscript{(53,56)} using three general steps. The first step is the pattern transfer using a serial beam writing process or mask into a photoresist or a special photosensitive epoxy, such as SU8, deposited on an electrically conductive substrate.\textsuperscript{(53)} After any undesirable material is removed (e.g., the mask is developed), a relief structure is formed by electroplating onto the exposed substrate areas. Once the metallic structure is formed, the resist or epoxy is removed. In some instances, this metallic structure may be the final product; however, usually it is used as a master tool for a replication process (such as injection molding, casting, or embossing), which is the final step in the process.\textsuperscript{(53,56)}

\textit{Wet and dry etching processes}

Wet and dry etching processes have largely been developed for the semiconductor industry. Wet etching uses a liquid etch solution (such as potassium hydroxide to etch silicon) to remove unwanted material from the substrate anisotropically, whereas dry etching tends to use plasmas or reactive plasmas and may be anisotropic or isotropic, depending on the plasma source.\textsuperscript{(53)} Similar to dry etching is deep reactive ion etching (DRIE), which is often used in the fabrication of microelectromechanical systems (MEMS).\textsuperscript{(56)} Since wet etching is an anisotropic process, it has strong restrictions on the geometries that can be made. Isotropic dry etching enables a wider variety of geometries, but is more limited in the materials that can be etched. The initial step in the process is the same as that of LIGA; specifically, a pattern is transferred into a photoresist or other protective layer. The unprotected substrate areas are etched using
either technique. Next, the protective layer is removed. To make the final device several substrates fabricated using this method are stacked on top of each other.\textsuperscript{(53)}

\textit{Micromachining}

In contrast to LIGA and wet/dry etching, the three main processes for micromachining shapes typically do not need the initial deposition of a resist, epoxy, or other protective layers. The equipment also tends to be less expensive for purchasing and maintenance. While not required, these processes are often computer controlled. The first technique involves traditional milling, turning, and grinding, but with ultra-precision machines that produce small features.\textsuperscript{(53,56)} The feature sizes are not as small as those constructed from LIGA and other fabrication processes; however, almost any material can be used. The second technique uses laser radiation to remove material or, in some situations, to build up material.\textsuperscript{(53)} The most common procedure is to remove material by melting, evaporation, decomposition, photoablation, or a combination of these removal techniques. Some development involves building structures by photochemically cross-linking in organic compounds or powder solidification by laser sintering. Both processes can be used to make devices down to critical dimensions of approximately 10 $\mu$m; however, the surfaces tend to be rough, which may cause problems in some cases.\textsuperscript{(53)} The third technique is electro discharge machining (EDM), also called micro-electro discharge machining. This technique is limited to electrically conductive work pieces. Material is removed by small sparks in a dielectric fluid, such as deionized water or oil, between the work piece and an electrode. The main disadvantages of this type of machining are
relatively rough surfaces; limitations in miniaturization to the size of the electrodes and spark; and relatively long machining times, which may limit the technology to prototyping and manufacture of mold inserts.\(^{(53)}\)

**Lamination**

In a lamination process, several sheets with different patterns are stacked, then brazed or bonded together. In a MEMS-based approach, DRIE is used to make patterns in silicon or other materials. The substrates are then stacked and bonded together using silicon bonding methods developed for MEMS. Another approach, used by researchers at Pacific Northwest National Laboratory (PNNL),\(^{(56)}\) is the fabrication of thin metal laminates using stamping, embossing, or processes described previously. These laminates are then stacked and brazed or diffusion bonded into a single device.\(^{(56-58)}\) Lamination is also particularly well suited for fabricating ceramic devices. Ceramic tapes, in the soft, pliable “green state,” are cut, molded, laser cut, etc., to the desired design and stacked. After curing in high-temperature furnaces, the laminates are bonded into a single structure.\(^{(56)}\)

**Soft lithography**

Whitesides and coworkers developed a collection of lithographic techniques referred to as soft lithography.\(^{(58)}\) An elastomer, often poly(dimethylsiloxane), with a pattern embossed on its surface, is used to transfer the pattern onto the substrate (often by stamping). This
technique is use in biological applications, but can be combined with other polymers, electroplating techniques, or molding of ceramics for low-cost, fast prototyping of devices."^{56,58}

**Design strategies**

Various reactor types have been used as the foundation for microreactor designs, including coated wall reactors, packed-bed reactors, structured catalyst reactors, and membrane reactors.

*Coated wall reactors*

Techniques for depositing catalyst onto the reactor walls include wash coating, ink jet printing, aerosol sprays, and thin film deposition by chemical or physical vapor deposition."^{56} Wash coating techniques, similar to those used in conventional auto converter manufacturing, can form a thin layer of catalyst with high surface area on reactor walls which results in more efficient utilization of catalysts compared to their conventional counterparts such as pellets or extrudates. Unfortunately, due to non-uniform surface tension, the wash coating solutions tend to collect in the corners of the reactors."^{56} However, in some cases, the surface tension phenomenon can be an advantage, as demonstrated, for example, by the innovative work of Arana et al."^{59}, who used surface tension to make a stop valve to control catalyst deposition.

With aerosol sprays, the catalyst is deposited directly on the reactor substrate, and the sprays can be used to coat already-formed channels."^{56} Ink jet catalyst ink deposition allows precise placement of the catalyst, but at the cost of having to seal the system after deposition,
which eliminates some fabrication options such as diffusion bonding. Additionally, the choice of
catalyst composition allowed by ink deposition is limited. Physical or chemical vapor deposition
techniques place thin catalyst layers with low surface areas. Examples of these techniques
include electron beam deposition, radio frequency (RF) sputtering, thermal vaporization,
chemical vapor deposition (CVD), and reactive chemical vapor deposition. These resulting
smooth surfaces can be roughened by thermal activation to increase their surface area, but
surface areas similar to wash coating generally cannot be attained. Physical deposition like
sputtering is difficult to achieve uniform coating on non-planar surfaces. Additionally, both
methods are typically limited to metals and simple oxides due to the availability of precursors.

Packed-bed microreactors

Packed-bed microreactors simply insert conventional powder catalysts in microreactors.
The advantages of using conventional catalysts include decreased cost, increased catalyst
availability and reproducibility, and greater understanding of catalyst performance. The high
heat and mass transfer rates in microreactors tend to boost the performance of these
catalysts.\(^{56}\) The disadvantages of the packed-bed reactors include high-pressure drop and
potential channeling at high throughput, and the possibility of channel plugging.\(^{56}\)

Structured catalyst reactors

The powder used in packed-bed reactors can be integrated onto a foam or felt substrate
to be used in microreactors.\(^{60}\) By supporting the catalyst on structured substrates, plugging
can be avoided and pressure drop can be reduced due to the large opening pores in the foams or felt (typically 100 to 300 μm in diameter). Additionally, conventional catalysts typically used in packed-bed reactors can be used which offers much wider range of catalyst availability with high reproducibility. This type of reactor often consists of narrow microchannels, where the supported catalysts are placed. Problems associated with “channeling” can be mitigated by designing channel geometries such that the laminar average residence time is longer than the radial diffusion time. Fast mass transfer rates can be achieved with this design.\(^{(61)}\)

A variation of this technique was developed by Wan et al.\(^{(62)}\) to grow zeolites in microchannels. The first step was to place seed in the channel(s) where the zeolite was desired. Once the seed was in place, zeolites could be grown using conventional techniques, with the deposition steps repeated a number of times to obtain the desired thickness. These zeolites could be coated, or further patterned with photoresist and buffered oxide etch. Once the desired pattern was achieved, the photoresist was stripped using acetone. Freestanding zeolite membranes were also fabricated using this technique with the additional step of silicon etching using tetramethylammonium hydroxide. Wan et al.\(^{(62)}\) fabricated films of ZSM-5 and titanium silicate-1.

Membrane reactors

Membrane separation techniques are a common way of obtaining high-purity (often \(\geq 99.99\%\)) hydrogen in industry. For small reactors, it is appealing to combine the hydrogen
purification step with the generation reactors to make compact devices.\(^{(56)}\) Metal membranes, typically palladium or palladium alloys, are used in these reactors. In conventional systems, high pressures (often greater than 250 psi) and temperatures of 300°C or more are required for high hydrogen recovery.\(^{(25)}\) The small feature sizes and complex geometries possible in microreactors have enabled extremely thin metal membranes to be fabricated that allow high hydrogen recovery at relatively low pressures.\(^{(56)}\)

*Materials and design strategy for this work.*

For this work a radial packed bed design fabricated from stainless steel was chosen (Figure 1.2). The design allows the methanol steam reformer is in direct contact with a catalytic combustor. This design was chosen since it focuses the heat from the combustor directly to the entry point of the steam reformer where the reaction is highest. It is believed that this would enable high efficiency even at the micro-scale.
Initially, ceramics material was considered, but the thin ceramic materials were brittle and difficult to seal. Polyimide was also tested. This material was stable up to 400°C\textsuperscript{(63)}, but the epoxy used for assembly were only stable to 200°C\textsuperscript{(64)}. The initial tests with this reactor were moderately successful, but the reactor was not thermally stable. It was believed the epoxy failed at the higher temperature. Stainless steel was successfully used for the construction and testing as reported in the next sections.

1.3 Research objective

Several micro-scale reactors using the impinging architecture in Figure 1.2 have been demonstrated by the author. Details of this work can be found in Appendixes A-C which contain
3 published journal articles describing the experimental work. The integrated micro-scale fuel processor was fabricated from stainless steel and included the catalytic combustor, vaporizers, heat exchangers and catalytic steam reformer. For the steam reformer catalyst, 8.9% Pd/ZnO/Al₂O₃ catalyst (see Appendix C) was chosen for its high durability and tolerance to air. The combustor catalyst was 10 wt% Pd on Al₂O₃. The first generation reactor was a proof of concept and had a volume of ~0.1 cm³, was able to produce up to 250 t of hydrogen, operated up to 450°C, and used a water-methanol mixture (1.8:1 molar ratio). The exit dry gas composition was:

- H₂: 73-74%
- CO₂: 25-26%
- CO: 1-2%

The first generation reactor had a thermal efficiency up to 13%. The thermal efficiency was calculated using equation 1.14

\[
Efficiency = \frac{\Delta H_{c\text{\,hydrogen}}}{\Delta H_{c\text{\,reformer+combustor fuel}}} \quad [1.14]
\]

where \( \Delta H_{c\text{\,hydrogen}} \) is the lower heating value of the produced hydrogen and \( \Delta H_{c\text{\,reformer}} \) and \( \Delta H_{c\text{\,combustor fuel}} \) refers to the lower heating value of the methanol fed to the reformer and the lower heating value of the fuel fed to the combustor which is methanol in this case. The details of this work are in Appendix A.
The second generation reactors were designed to increase the efficiency and decrease the CO production. Two types of reactors were built: a high efficiency version and a low CO version. For both reactors, the amount of water in the steam reformer feed was decreased to 1.2:1 molar ratio (or 60 wt% methanol). In addition, the reformer volume was increased to approximately 0.3 cm³. Finally, in the first generation reactor the reformer bed was limited to the area between the inlet plunger and the shim separating the reformer from the combustor (~0.25mm). In the second generation reactor the entire volume in the reformer section was packed with catalyst powder. For the low CO reactor a selective CO methanation reactor was added using a 3 wt% Ru/Al₂O₃ methanation catalyst. The reactor volumes were ~0.3cm³ for the high efficiency reactor and ~0.5cm³ for the reformer plus the methanation reactor. The high efficiency reactor was able to achieve up to 33% efficiency, lowered the reformer temperature to a maximum of ~345°C and produced up to ~630mWt. The low CO reactor was able to achieve 100-300ppm CO with an efficiency of 9.5 – 19%. See Appendix B for more details.

It is obvious that the methanol reformer design of the second generation reactor does not efficiently use all of the available catalyst. With a single exit the gas flow will preferentially travel on one side of the reactor. In addition, while the packed bed has some tortuosity which will cause some mixing, by changing the reactor design the gases would be forced to take a longer route through the catalyst bed better utilizing the catalyst and improving reactor performance. Therefore, the objective was to develop a numerical model of the reformer and to show the model can be used as a tool to quickly identify and assess design perturbations
with the intent to improve efficiency. The design perturbations selected include increasing the number of exit streams from 1 to 4 and a separate model for evaluating the impact of fins or baffles in the packed bed. Both of these simple design changes should increase the flow distribution in the catalyst bed. Modeling was used to determine the impact.

1.4 Dissertation structure

This dissertation is composed of mixture of standalone manuscripts with a not previously published introduction and conclusion section. The first chapter introduces the research area and provides a background on the fuel processing, materials and fabrication techniques for micro-scale production, fuel selection rationale, and a description of the overall research objectives. Chapter 2 provides a thorough literature review of numerical models for micro-scale fuel processors. The next section, Chapter 3, describes the 3D numerical model of the reactor. The model is used to explore and evaluate several design variations which could improve the methanol steam reformer’s performance. The final Chapter, Chapter 6, comprises of overall conclusions and potential future research direction. Appendix A-C contain the journal articles of (A) the proof of concept reactor, (B) the high efficiency and low CO reactors, and (C) the PdZnO/Al₂O₃ catalyst development including kinetic rate expression. Appendix D details the fabrication of the combustion catalyst, while Appendix E summarizes the experimental results of some test of the proof-of-concept reactor with a micro-scale fuel cell. Analysis of Mear’s criterion and Thiele modulus are located in Appendix F. Appendix G has the detail drawings of
the device designs. The final Appendix, Appendix H, includes the narrative section of the NSF proposal for potential future work using microchannel architecture.

1.5 Publications from this work

1.5.1 Journal articles


1.5.2 Book and book chapters


1.5.3 Conference publications


1.7. References


CHAPTER 2 A REVIEW OF –RECENT ADVANCES IN NUMERICAL SIMULATIONS OF MICROSCALE FUEL PROCESSORS FOR HYDROGEN PRODUCTION

J.D. Holladay\textsuperscript{a,4} and Y. Wang\textsuperscript{b}

\textsuperscript{a}Pacific Northwest National Laboratory, 902 Battelle Blvd. Richland WA. 99352 USA
\textsuperscript{b} The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman WA. 99164-6515.

Abstract

Microscale (<5 W) reformers for hydrogen production have been investigated for over a decade. These devices are intended to provide hydrogen for small fuel cells. Due to the reformer’s small size, numerical simulations are critical to understand heat and mass transfer phenomena occurring in the systems and help guide the further improvements. This paper reviews the development of the numerical codes and details the reaction equations used. The majority of the devices utilized methanol as the fuel due to methanol’s low reforming temperature and high conversion, although, there are several methane fueled systems. The

\textsuperscript{3} This is the review article referenced in Chapter 5. It was published in Journal of Power Sources 2015, volume 282 pp 602-621.
\textsuperscript{4} Corresponding author. Tel/fax 509-371-6692/509-375-2323. email: jamie.holladay@pnnl.gov
increased computational power and more complex codes have led to improved accuracy of numerical simulations. Initial models focused on the reformer, while more recently, the simulations began including other unit operations such as vaporizers, inlet manifolds, and combustors. These codes are critical for developing the next generation systems. The systems reviewed included plate reactors, microchannel reactors, and annulus reactors for both wash-coated and packed bed systems.

Keywords: hydrogen production, microchannel, microreformer, methanol reformer, methane reformer, fuel cells.

2.1 Introduction

Over the past decade we have witnessed an unprecedented increase in the use and functionality of small personal electronic devices such as smart phones and tablet computers. With each generation, the power demand of these devices has increased. While there has been substantial improvement in batteries over the recent years, batteries still fail to yield the desired energy density for long duration usage. Fuel cells have been proposed to meet the increasing power demands[1]. The primary challenge for a small scale fuel cell is how to safely store hydrogen fuel. To this end many groups have developed microscale fuel processors which can convert a hydrocarbon or ammonia based fuel to a hydrogen rich stream for use in proton
exchange membrane (PEM) or solid oxide fuel cells [1-12]. As part of the microscale fuel processor research, various models have been developed as design tools and to better understand the system physics. This paper reviews the microreactor models developed for small scale (<5 W) hydrogen production suitable to power low power personal electronic devices.

2.1.1 Microreactor general characteristics

The main factors in considering the microreactor design include: fuel cell choice, fuel choice, fuel processing approach, operating temperature, catalysts, reactor architecture and materials of fabrication. Fuel cell choice determines constraints on gas constituents to the fuel cell. A polymer electrolyte membrane (PEM) fuel cell (FC) operates at low temperatures, typically less than 363 K. The low temperature operation causes the fuel cells to be very sensitive to carbon monoxide poisoning. Therefore fuel processing systems for PEMFC must produce a hydrogen rich gas stream with less than 100 ppm CO, or preferably less than 10 ppm CO[12]. Several higher temperature fuel cells have been proposed for small scale power supplies including phosphoric acid doped polybenzimidazole (PBI), which operates at 388-423 K and solid oxide fuel cells (SOFC), which typically operate >973 K [13-15]. PBI FC and SOFC both can tolerate CO at higher concentrations (>1% and >10% respectively), making the fuel processing requirements less stringent[13-15]; however, PBI FC and SOFC have some loss in
performance compared to PEMFC and the higher temperature operation makes thermal management much harder.

By far the most popular fuel for small scale hydrogen production is methanol. While lacking the high energy density compared to paraffinic hydrocarbons, methanol can be reformed to hydrogen at lower temperatures than paraffinic hydrocarbons; 473-573 K compared to greater than 775 K[2]. The low temperatures have two advantages, first the lower temperatures make thermal management easier and second the lower temperatures favor higher hydrogen production due to thermodynamic equilibrium. For steam reforming there is an added benefit for methanol compared to other hydrocarbon fuels. Steam reforming requires water. Ideally, water produced by the fuel cell can be recycled for use in the reformer. This works for larger applications, but for these miniature applications, the added balance of plant may become problematic. Therefore it is likely that the water will be carried. Methanol steam reforming requires significantly less water than paraffinic hydrocarbons (1.2:1 steam: carbon compared to 3:1 or more) to mitigate coke formation on the catalysts. If water is included in the energy density, methanol actually has a slightly higher energy density than other hydrocarbons, and is only slightly less than that of methane. Other fuels of interest include: ammonia[16], methane[17-19], butane[14], and ethanol[20-22].
### Table 2.1. Fuel and Fuel-Water mix energy density for several common fuels.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Fuel Energy Density (kW-hr kg⁻¹)</th>
<th>Fuel-Water Energy Density (kW-hr kg⁻¹)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>13.9</td>
<td>3.8</td>
</tr>
<tr>
<td>Propane</td>
<td>12.7</td>
<td>3.2</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>12.3</td>
<td>3.05</td>
</tr>
<tr>
<td>Methanol</td>
<td>5.6</td>
<td>3.7</td>
</tr>
</tbody>
</table>

*Fuel-water mix represents the stoichiometric requirement for steam reforming, defined as a molar S/C of 3.0 for paraffinic hydrocarbons and 1.2 for methanol. Fuel-water energy density is based upon the lower heating value of the hydrogen produced from reforming the mixture with 100% conversion to CO₂ and H₂. (i.e. CH₄ + 2H₂O → CO₂ + 4H₂).

For reformers producing less than 5 W equivalent hydrogen there are three main classes of fuel processing used: steam reforming (SR), partial oxidation (POx), and autothermal reforming (ATR). Steam reforming is an endothermic process where the fuel mixed with water is decomposed over a catalyst to produce a hydrogen rich product gas. In partial oxidation, the fuel is mixed with oxygen and, as the name indicates, is oxidized. The partial oxidation rips apart the molecule producing mostly hydrogen, methane, CO, CO₂, and water. POx can be done with or without a catalyst. ATR is a combination of the two processes where the POx reaction provides heat for the endothermic SR. Table 2.2 lists some advantages and disadvantages for each of the reforming approaches. More details on the reforming approaches, including catalysts, can be found in review articles by Holladay et al.[2], Song[23], and Bartholomew and Farrauto[24].
Table 2.2. Comparison of reforming technologies (adapted from[2, 12, 25, 26])

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Reforming</td>
<td>Most extensive industrial experience</td>
<td>Highly endothermic</td>
</tr>
<tr>
<td></td>
<td>Oxygen not required</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lowest processing temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Best H₂/CO ratio for H₂ production</td>
<td></td>
</tr>
<tr>
<td>Autothermal reforming</td>
<td>Lower process temperature than POX</td>
<td>Limited commercial experience</td>
</tr>
<tr>
<td></td>
<td>Low fuel slip</td>
<td>Requires air or oxygen</td>
</tr>
<tr>
<td>Partial oxidation</td>
<td>Decreased desulfurization requirement</td>
<td>Low H₂/CO ratio</td>
</tr>
<tr>
<td></td>
<td>No catalyst required (although sometimes used)</td>
<td>Requires air or oxygen</td>
</tr>
<tr>
<td></td>
<td>Low fuel slip</td>
<td>Very high processing temperatures</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Soot formation / handling adds process</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Complexity</td>
</tr>
</tbody>
</table>
The small nature of low power reactors lends itself to a microchannel or plate architecture; however, small packed bed reactors and membrane reactors have also been examined\cite{12, 27, 28}. Microchannel and plate architectures have high heat and mass transfer rates with the potential to enable high thermal integration and therefore higher efficiencies. Membrane reactors allow for process intensification by integrating multiple unit operations into one reactor. While a packed bed is simplistic in design and fabrication, it must be combined with other approaches, a membrane, microchannels or both, for implementation. Initially, the main material for construction was silicon due to ease of fabrication, or ceramics since they have a low thermal conductivity. However, more designs based on metals are appearing. Table 2.3 lists advantages and challenges for various classes of materials.

Due to the small nature of these reactors, models (one-dimensional, two-dimensional and three-dimensional) have been developed to aid in understanding the performance and to aid in design. This paper reviews the modeling work that has been reported on this scale of microreformer. While there has been great interest and many papers involved with modeling microchannel and small reactors, there are relatively few reported results from modeling reactors at the low power (<5 W range).
Table 2.3. Microreactor material advantages and challenges (adapted from [12])

<table>
<thead>
<tr>
<th>Material</th>
<th>Advantages</th>
<th>Challenges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>Conventional fabrication techniques</td>
<td>Poor compatibility with ceramics and glass</td>
</tr>
<tr>
<td></td>
<td>Durable</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low to modest costs</td>
<td></td>
</tr>
<tr>
<td></td>
<td>No clean room required</td>
<td></td>
</tr>
<tr>
<td>Silicon and silicon type of</td>
<td>Well characterized silicon fabrication</td>
<td>Fragile material</td>
</tr>
<tr>
<td>materials</td>
<td>techniques</td>
<td>Requires a clean room</td>
</tr>
<tr>
<td></td>
<td>High precision manufacturing</td>
<td></td>
</tr>
<tr>
<td>Low Temperature Co-Fired Ceramics</td>
<td>Low cost, high volume manufacturing</td>
<td>Non-standard fabrication</td>
</tr>
<tr>
<td></td>
<td>Flexible fabrication</td>
<td>Sealing</td>
</tr>
<tr>
<td>Polymers</td>
<td>Low cost</td>
<td>Chemical compatibility</td>
</tr>
<tr>
<td></td>
<td>Flexible Fabrication</td>
<td>Thermal stability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sealing</td>
</tr>
</tbody>
</table>

2.2.0 One Dimensional Models. One dimensional models are the simplest models to develop and require less computational power. They can be useful to determine trends in performance. However, many assumptions are required for one dimensional models. For example, they assume that variables such as concentration, velocity, temperature, etc., change predominantly in one defined direction. In most real world situations, this is not the case. There are only two significant papers using a one-dimensional (1-D) model to analyze a microreformer of this
In 2006 Kawamura et al. [29] reported the use of 1-D model to aid in their design of a Si-based methanol reformer suitable for powering 1 W class devices when connected to a PEM fuel cell. They correctly identified the thermal management challenge when building a device at such a small scale, and used their 1-D model to optimize the heat and mass flow in their design. They reported a serpentine reactor that was 25 mm long, 17 mm wide, and 1.3 mm thick. The reactor was constructed on silicon and glass substrates using common silicon processing techniques. The reactor was heated by building in a Ta-Si-O-N electrical resistance heater built into the device. The channels were wash coated with a Cu/ZnO/Al₂O₃ catalyst. This catalyst was chosen since it can operate at relatively low temperatures (typically <523 K) with high conversion [29]. The challenge with Cu/ZnO based catalysts is that they are pyrophoric and water sensitive, making the system design challenging for practical applications [13, 30]. A steam to carbon ratio (steam to methanol) ratio of 2 on a molar basis was used. The rate equation used was:

\[ r_{SR} = \frac{\eta \rho_{cat} \delta (w + 2h + 2\delta)}{wh} k_0 \exp \left( \frac{-E_a}{RT} \right)(RT)^{0.09} \text{C}_{\text{methanol}}^{0.26} \text{C}_{\text{H}_2\text{O}}^{0.03} \text{C}_{\text{H}_2}^{-0.2} \]  

(2.1)

Where \(\eta\) is the effectiveness factor of the catalyst, \(\rho_{cat}\) is the catalyst’s bulk density (1600 kg m\(^{-3}\)), \(\delta\) is the thickness of the catalyst layer, \(w\) and \(h\) are the cross-sectional width and depth of the microchannel catalyst layer, \(E_a\) is the activation energy (114.5 kJ mol\(^{-1}\)), and \(k_0\) is the pre-exponential factor of \(1.63 \times 10^{10}\) mol kg\(^{-1}\) s\(^{-1}\) Pa\(^{-0.09}\) respectively. This reaction equation was
determined at methanol partial pressures in excess of 5 kPa. Knudsen diffusion was assumed to dominate in the catalyst layer and the effective diffusion coefficient of methanol ($D_{e\text{meoh}}$) was calculated using equation 2.2:

$$D_{e\text{meoh}} = 3.067r_e \frac{\varepsilon}{\tau} \sqrt{\frac{T}{M_{\text{meoh}}}}$$  \hspace{1cm} (2.2)

Where $\varepsilon$ is the catalyst void volume, $\tau$ the tortuosity, $r_e$ the pore radius, $M_{\text{meoh}}$ methanol molecular mass, and $T$ is temperature. They used the standard equations for an incompressible fluid for the heat, mass and momentum. The model results were used to design a microreactor which was built and tested. During operation the reactor temperature was fairly well predicted by the model; however, the methanol conversion was not. The authors believe that the discrepancy between actual and predicted performance was due to methanol rate equation. As the methanol reacts, its partial pressure decreases. When greater than 90% conversion is achieved, the methanol partial pressure is 3 kPa or less, which is outside the range of the data used to derive the methanol rate equation. They hypothesize that at the lower partial pressures, the reaction order may be increased making 100% conversion difficult to achieve in their reactor design[29].

In 2010 Chein et al. [16] reported a one dimensional model for ammonia decomposition using a Ni-Pt/Al$_2$O$_3$ catalyst with a packed bed design. (Chiuta et al. (2014) proposed a three dimensional model of a single channel ammonia decomposition reactor, as part of a multi-
channel system, but since the system would likely result in a device larger than 5 W it is not reviewed here [31].) Ammonia was chosen by the authors due to its ease of gas clean up compared to hydrocarbon reforming (i.e. there is no need for carbon monoxide removal, and unreacted ammonia can be adsorbed). They used standard incompressible equations for an incompressible fluid for heat and mass, but the Brinkman-Darcy-Forchheimer theory for momentum. For the thermal conductivity, dynamic viscosity, and molecular diffusivity the Chapman-Enskog theory for multi-component gas mixtures at low density was used [16]. The Carman-Kozeny model was used to determine the permeability. Finally, they defined the catalyst bed’s effective thermal conductivity, $\lambda_e$, as:

$$\lambda_e = \epsilon \lambda + (1 - \epsilon) \lambda_s$$  \hspace{1cm} (2.3)

Where $\lambda_s$ is the thermal conductivity of the catalyst, $\lambda$ is the thermal conductivity of the gas and $\epsilon$ is the porosity. The ammonia decomposition reaction can be written as:

$$NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$$  \hspace{1cm} (2.4)

There is literature indicating that the decomposition reaction depends solely on ammonia concentration and at low pressure is first order [16]. This is similar to methanol steam...
reforming and therefore they used a methanol steam reforming equation with Cu/ZnO catalyst for the ammonia decomposition kinetics:

\[ \text{rate} = C_r(1 - \varepsilon)\rho_s A R \exp\left(\frac{-E}{RT}\right) C_{NH_3} \]  

(2.5)

Where \(C_r\) is a correction factor accounting for the effectiveness and activity of the catalyst pellet, \(R\) is the universal gas constant, \(A\) is the pre-exponential factor \((3.639 \times 10^9 \text{ mol g}_{\text{cat}}^{-1} \text{ hr}^{-1} \text{ kPa}^{-1})\), \(E\) is the activation energy \((196.2 \text{ kJ mol}^{-1})\), and \(\rho_s\) is the catalyst density \((\text{catalyst mass/bed volume})\). The numerical simulation was performed using Fluent v6.2 at temperatures of 813-893K and the results compared to data in the literature. They adjusted the correction factor in order to get good correlation between their model and the literature data and found 1.5 to be a good factor.

2.3.0 Two dimensional models. Most of the models found in the literature are two dimensional. Two dimensional models provide more accurate predictions and more complicated designs compared to one dimensional models, while not requiring the high computing power needed for three dimensional simulations. They assume that variables change predominantly in two directions (x and y). This is more realistic compared to one dimensional models. The literature can be divided into methanol and methane microreactor
models. We will first review the methanol microreactor and then the methane microreactor models.

One of the earliest two dimensional models was developed by Karim et al. (2005) and used to compare the performance between a packed bed and a wall coated microreactor. They used the model to study the temperature profiles, impact of reactor size on apparent activity and for the wall coated reactor, the effect of catalyst wall-coating thickness and reactor diameter on apparent activity. The study focused on the catalyst bed and ignored microreactor materials of construction and other unit operations. A mixture of 1:1 steam to methanol was the fuel and a commercially available Cu/ZnO catalyst from BASF was the catalyst[27]. Since the purpose of the study was to examine the impacts of heat transfer on the methanol conversion, they felt the type of reaction rate law used would not impact the results. Thus they assumed that the reaction rate was first order in methanol, zero order in water and assumed a simplified methanol reforming reaction of:

\[ A \rightarrow 3D \quad (2.6) \]

With a reaction rate equation of:

\[-r_A = k_1 \frac{C_A(1-X_A) T_0}{(1+eX_A)} \frac{T}{T} (1 - \phi) \quad (2.7)\]
Where $\varepsilon$ is the change in number of moles at complete conversion divided by total number of moles fed to the reactor, $k_1$ is the rate constant found using the Arrhenius equation with $A = 14.5 \times 10^9 \text{ s}^{-1}$ for the wall coated reactor and $22 \times 10^9 \text{ s}^{-1}$ for the packed bed, and the activation energy being $82 \text{ kJ mol}^{-1}$, and $\phi$ is the void fraction. Stefan-Maxwell equations were used to calculate the mean binary diffusivity. It was assumed this was weakly dependent on methanol conversion and taken to be a constant in the model. Gas properties were taken as an average over several methanol conversions between 0 and 1[27].

Packed bed reactors with 1 mm to 4 mm i.d. were found to be heat transfer limited with temperature gradients up to 40 K in the bed (Figure 2.1). At 300 $\mu$m i.d. the reactor temperature gradients were eliminated. This diameter for a packed-bed reactor may not be practical[27]. Alternatively, the wall coated reactor model predicted no mass or heat transfer limitations over the range of 0.2 mm to 4.1 mm i.d. (Figure 2.2). In addition, the modeling indicated that the volumetric efficiency increases with wall coating thickness for the same reactor diameter[27].
Figure 2.1. Isothermal packed bed performance compared to experimental data at 503 K [27]

\( W = \) catalyst weight in kg and \( F = \) methanol flow in mol s\(^{-1}\).

Figure 2.2. Modeling predictions for wall coated reactors at 503 K. Unlike the packed bed reactor, no heat transfer limitations were predicted[27]. \( W = \) catalyst weight in kg and \( F = \) methanol flow in mol s\(^{-1}\). The numbers in parenthesis represent the catalyst coating thickness.

---

\(^5\) Reprinted from Catalysis Today, 110, Ayman Karim, Jaime Bravo, David Gorm, Travis Conant, Abhaya Datye, Comparison of wall-coated and packed-bed reactors for steam reforming of methanol, 86-91, Copyright (2005), with permission from Elsevier
Fazeli and Behnam [32] built upon Karim et al’s work and examined reactor geometry for wall coated microchannel reactors. They used modeling to compare hydrogen production between a strait channel and a zigzag configuration (Figure 2.3 and Figure 2.4) constructed of steel. Thermal energy for the reforming reaction was provided by methanol combustion in a channel adjacent to the methanol reforming channel. For a true microreactor multiple channels would be used; however, due to symmetry, only two parallel channels were modeled. The length and dimensions of the straight channel are in Figure 2.4. The zigzag channel had similar width, and was composed of 21 bends with 22 segments.

Figure 2.3. Schematic figure of zigzag and straight catalytic wall microchannel reactor configurations. [32] (used with permission).

In Fazeli and Behnam’s work, a Cu/ZnO/Al₂O₃ catalyst was used for the methanol steam reforming, but the combustion catalyst type was not described. The following reactions and rate equations were used for the methanol steam reforming and methanol oxidation reactions.
Figure 2.4. Dimensions used in microreactor model. TOX is the total oxidation or combustion side[32] (used with permission).

Methanol oxidation:

\[
\text{CH}_3\text{OH} + 1.5\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}, \quad \Delta H = -676.47 \text{ kJ mol}^{-1}
\]  

(2.8)

\[
\tau_c = \frac{k_c P_{\text{CH}_3\text{OH}}^{0.18} P_{\text{O}_2}^{0.18}}{P_{\text{O}_2}^{0.14}}
\]  

(2.9)

Where \( k_c = A_o \exp(-E_a/RT) \) with \( E_a \) equal to 115 kJ mol\(^{-1}\) and \( A_o \) being \( 6.0 \times 10^8 \text{ mol min}^{-1} \text{ g}^{-1} \) \text{cat}\(^{-1}\) kPa\(^{-0.22}\) [33].

Three reaction equations were used for methanol reforming as follows:

Methanol steam reforming:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 3\text{H}_2, \quad \Delta H = +49.53 \text{ kJ mol}^{-1}
\]  

(2.10)
\[ r_{SR} = \frac{k_{SR}K(P_{CH_3OH} - P_{H_2}^2P_{CO_2})}{(P_{H_2} + K_{CH_3OH}P_{H_2} + K_{CO}P_{CO_2} + K_{H_2}^2P_{H_2}O)(1 + K_{H_2}^0)^{P_{H_2}^0})} \] (2.11)

Water-gas-shift:

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2, \quad \Delta H = -41.15 \text{ kJ mol}^{-1} \tag{2.12}
\]

\[
T_{WGS} = \frac{k_{WGS}K_P^{0.5}(P_{CO}P_{H_2}O - P_{H_2}^2P_{CO_2}/K_{WGS})C_{S1}S_{a}}{(P_{H_2} + K_{CH_3OH}P_{H_2} + K_{CO}P_{CO_2} + K_{H_2}^2P_{H_2}O)^2} \tag{2.13}
\]

Methanol decomposition (MD):

\[
\text{CH}_3\text{O} \leftrightarrow \text{CO} + 2\text{H}_2, \quad \Delta H = +90.68 \text{ kJ mol}^{-1} \tag{2.14}
\]

\[
T_{MD} = \frac{k_{MD}K(P_{CH_3OH} - P_{H_2}^2P_{CO})}{(P_{H_2} + K_{CH_3OH}P_{H_2} + K_{CO}P_{CO_2} + K_{H_2}^2P_{H_2}O)(1 + K_{H_2}^0)^{P_{H_2}^0})} \tag{2.15}
\]

Unfortunately the equilibrium constants were not provided [32], only a reference to how to calculate them was given[34]. The \( C_{S1}, C_{S1a}, C_{S2}, C_{S2a} \) and \( S_a \) were not defined nor values given. They used the continuity equations for heat, mass, and momentum. Binary diffusion
coefficients were calculated using Chapman-Enskog’s equation [32]. The model used momentum, continuity, mass balance, and heat balance equations.

The model results (Figure 2.5) indicated that the zigzag design promoted heat and mass transfer. These improvements increased the hydrogen production rate while lowering the carbon monoxide selectivity. Interestingly, the outlet temperature was lower and the temperature drop between the inlet and outlet was greater for the zigzag design than the straight design.

Figure 2.5. Zigzag configuration has a higher (a) hydrogen production (mole fraction) and a lower CO selectivity (b) than the straight configuration [32] (used with permission).

Chein et al.[35] studied the impact of heat supply mechanisms and materials on tubular reactor performance. The analysis was done on a cylinder reactor of 1mm diameter, 10mm in length, packed with CuO/ZnO/Al₂O₃ catalyst. The reactor wall was assumed to be infinitely thin
at a constant wall temperature. They looked at four different materials chromium alloy, silica, copper, and stainless steel (AISI4340). Ideal gas was assumed with gas flow that is weakly compressible, axisymmetric, steady state and laminar. They used Brinkman-Darcy-Forcheimer model for fluid flow through porous media. For the reformer wall they assumed only conduction heat flow, but conduction plus convection in the reactor. For the reactions, they used the reaction equations [10], [12], and [14]. The reaction rate equations for the reforming reaction [10] and decomposition reaction [14] were respectively:

\[ r_R = (1 - \varepsilon)\rho_s k_R C_{CH_3OH} \]  
\[ r_D = (1 - \varepsilon)\rho_s k_D \]  

Where \( \rho_s \) is the catalyst density, \( k_R \) and \( k_D \) were rate constants calculated as:

\[ k_R = C_R [A_1 + B_1 ln(\varphi)] \exp \left( -\frac{E_R}{RT} \right) \]  
\[ k_D = C_D A_2 \exp \left( -\frac{E_D}{RT} \right) \]
Where $A_1, A_2,$ and $B_1$ were $1.15 \times 10^6$ m$^3$ s$^{-1}$ kg$^{-1}$, $7.09 \times 10^7$ mol s$^{-1}$ kg$^{-1}$, $9.41 \times 10^5$ respectively, $C_R$ and $C,$ were correction factors to account for catalyst activity and effectiveness chosen as 5.5[35]. The water-gas-shift reaction rate equation used was:

$$r_{WGS} = C_{WGS} k_{WGS} \left( P_{CO} P_{H_2O} - P_{CO_2} P_{H_2} \right) / K_{eq}$$  \hspace{1cm} (2.20)

With

$$K_{WGS} = 1.78 \times 10^{22} (1 - 0.154\delta + 0.008\delta^2) T^{-\alpha} \exp \left(-\frac{E_{WGS}}{RT} \right)$$  \hspace{1cm} (2.21)

$$K_{eq} = \exp \left(\frac{4577.8}{T} - 4.33 \right)$$  \hspace{1cm} (2.22)

Where $P$ was the species partial pressure, $\alpha$ was -8 as determined by experiments, and $\delta$ was the molar ratio of water to CO. The activation energy $E_{WGS}$ was 70 kJ mol$^{-1}$. They verified their model by comparing their computational results with literature values and found they were in acceptable agreement[35].

Three heat supply mechanisms were examined in the study: constant heat flux, internal heat generation, and constant temperature all at the reformer outer wall[35]. For the first two mechanisms it was found that axial heat flux played had an impact on heat transfer and
therefore the methanol reforming performance. They developed an axial conduction parameter, dependent on the gas inlet rate ($\rho_{ave}Q_{in}$), wall conductivity, $\lambda_c$, wall cross sectional area, $A_c$, reformer length, $L_b$, and gas mixture specific heat, $c_{p,ave}$:

$$\Lambda = \frac{\lambda_c A_c}{\rho_{ave}Q_{in}c_{p,ave}L_b}$$

(2.23)

As the axial conduction parameter increased, the actual heat transferred to the methanol reforming reaction decreased. The decrease in heat transfer negatively impacted the reaction temperature and therefore the reactor performance. By examining the equation, it can be determined that several ways to mitigate this effect would be to 1) choose materials with low thermal conductivity, and/or 2) construct the device with thin walls[35]. Their analysis revealed that choosing a metal with a low thermal conductivity improved reformer performance since there was an excess heat flux supply due to the wall’s temperature distribution. This effect was determined to be more significant, i.e. reformer performance was greater, than an infinitely thin walled reformer. Finally, their analysis revealed that the impact of axial conduction decreased with rising temperature since at the higher temperatures the temperature distribution at the wall was negligible. They recommended that for lower temperature reformers, the materials of construction should have a low thermal conductivity and be thin. As operational temperatures increase, these considerations were less important[35].
In addition to studying the axial heat effects, Chein et al. did a numerical simulation of a miniature annulus methanol reformer[36]. They examined a tubular annular reactor where hot gas is in the outer shell with the inner tube being a packed bed reformer. They used the model to compare reactor performance with incline and fishbone shaped fins (Figure 2.6), and a baseline without any baffles. The distance between the fins was varied by modeling a system with baffles at a distance of L/5 and a second system with baffles spaced at L/9 (Figure 2.6)[36].

Figure 2.6. Annular reformer with hot gas in the outer tube and packed bed reformer with incline and fishbone-shaped baffle plates inside the reformer from reference [36] Reprinted with permission from Energy and Fuels reference 35. Copyright (2012) American Chemical Society.
Chen et al. modeled a stainless steel reactor using a CuO/ZnO/Al$_2$O$_3$ as the catalyst. They used the same reaction rate detailed in equations (16) through (22). The ideal gas law was assumed, with gas flow that was weakly compressible, axisymmetric, steady state and laminar. The Brinkman-Darcy-Forcheimer model for fluid flow through porous media and Chapman-Enskog theory for multicomponent gas mixtures at low pressure for the thermal conductivity, dynamic viscosity and molecular diffusivity was assumed. The model was validated by comparing it to experimental results of an annular reactor, without baffles, reported by Suh et al.[37]. The major findings included[36]:

- The baffles increased the flow disturbances increasing the mass transfer between the catalyst particle and reactant flow improving conversion.
- The baffles increased the heat transfer raising the temperature closer to the hot gas temperature.
- The pressure dropped through the catalyst bed, but not significantly.
- There was not a significant difference between the L/5 and L/9 baffle placements.
- They indicated that the performance improvements of including the baffles in the annular reactor could be done by using a plate type reactor system. The plate type system would be easier to build than the annular reactor with baffles.
In 2013 Chein et al. [38] published a third paper on an annulus methanol reformer. In this paper, they added a methanol air a catalytic combustor for methanol-air. They examined the impact of the combustor being in the shell side of the annulus or the inner tube (Figure 2.7).

Figure 2.7. Physical domain of the annulus design methanol reformer with methanol air combustor proposed by Chen et al. [38]. $Q_{in,R}$ is reformer inlet volumetric flow rate (m$^3$ s$^{-1}$), $T_{in}$ is inlet temperature (K), $R_b$ is reformer radius (m), $R_c$ is combustor radius (m), $t_c$ is combustion wall thickness (m), $t_r$ is reformer wall thickness (m), $L$ is the inlet and outlet length (m), and $L_b$ is the reformer length (m).

The model development presented was the same as they used in their previous studies [35, 36, 38], with the addition of a packed bed combustor. The physics for the

---

combustor were the same as used for the reformer, and the methanol combustion reaction rate equation was:

\[ r_c = k_c \exp \left( -\frac{E_c}{RT} \right) C_{CH_3OH}^{1.4} \]  

(2.24)

Where \( k_c \) and \( E_c \) are the reaction constant \((3.153 \times 10^6 \text{ m}^{1.2} \text{ mol}^{-0.4} \text{ s}^{-1})\) and the combustion reaction activation energy \((18.1 \text{ kJ mol}^{-1})\) [38]. The combustion catalyst is \( \text{Pt/Al}_2\text{O}_3 \). The combustor and reformer were set up in a co-flow configuration. Again the reformer model was validated by comparing the methanol conversion to the literature. Using the model, they were able to show that the methanol-air combustor can be lit off at room temperature without an external heating source. This was significant since it simplifies the design of the entire system. Similar to their other studies, they found that high temperatures resulted in higher CO production due to an increase in the reverse WGS reaction. They also studied the impact of insulation. As was mentioned previously, heat loss to the environment is significant issue for micro-scale reactors. The heat transfer coefficient was varied from 0 to 50 W m\(^{-2}\) K\(^{-1}\) and found that as heat loss increased the methanol conversion decreased with limited methanol conversion occurring when the heat transfer coefficient was 50W m\(^{-2}\) K\(^{-1}\). Finally, the shell side combustor configuration yielded better performance compared to when the combustor was located in the inner tube of the annulus. The simulations showed a larger bulk gas temperature.
drop occurred in the combustor entrance for the tube combustor configuration compared to the shell side configuration. This implies that methanol-water vaporization was more effective and efficient (i.e. less heat loss to the environment) for shell- combustor configuration compared to the tube-combustor configuration[38]. All of the simulations were done in the co-flow configuration. It would have been interesting to see a counter-flow configuration to see if there would be any significant changes.

In addition to the methanol reformers, several methane microscale reformers have been modeled. In 2008, Stefanidis and Vlachos[18] developed a model of a parallel plate microscale reactor where propane combustion and methane steam reforming occur on opposite sides of the wall. They used a Pt combustion catalyst and Rh steam reformer catalyst. In their prior work they determined that a co-current flow distribution would minimize hot spots and give better overlap of reaction zones, so this configuration was used[18]. The reactor length was 5 cm, with a wall thickness \((d_w)\) of 750 \(\mu\)m, CR gap \((d_1)\) was 300 \(\mu\)m, SR gap \((d_2)\) was 200 \(\mu\)m. The propane air equivalence ratio was 0.85. For the methane reformer the steam to carbon ratio used was only 2. This seems rather low, as typically S:C for methane reforming is 3-4 (usually closer to 4), in order to ensure conversion and prevent coking[2]. They should have used a higher S:C ratio and this may impact their findings.

For the heat and mass transfer, they used standard continuity equations, gas-phase and solid phase energy balance, and the gas and surface species mass balance. CHEMKIN was used to determine the thermophysical and transport properties for the model. The solving strategy
was as follows. The continuity equation was solved using a backward Euler scheme, and the rest were solved with central difference. The partial differential equations were solved with a DASPK solver. Global rate equations for propane combustion, methane reforming and WGS were used. Kaisare et al.’s[39] propane combustion on Pt was used to represent the combustor. They used a rather complex set of equations to represent the methane SR on Rh and WGS and the reader is referred to the paper for details. The major findings in this work include[18]:

- Methane can be reformed on a highly active catalyst such as Rh in a microscale reformer with millisecond contact times.
- The reaction rates can be increased by increasing the catalyst loading and decreasing mass transfer limitations.
- Operation at lower S:C increases the power output at lower reaction temperatures. This point is well known in the literature, but was not typically pursued in practice since the lower S:C decreases the catalyst life.
- Using microchannel architecture decreases transport limitations making the SR to be essentially reaction controlled. Interestingly, the combustion process was determined to be both reaction and transport controlled even with the small gap. Therefore, they recommend a low combustion channel gap size of 0.6 mm or less for complete fuel conversion in the combustor and reformer channels.

In a companion article Stefanidis et al.[19] continued the examination of steam methane reforming in their microchannel system by looking at operating regions, operating strategies,
and materials of construction. They used the same equations and approach reported[18]. From their analysis, they recommended the following operating strategies for methane reforming:

- First, derive an approximate ratio of reforming to combustible stream that is close to the breakthrough limit. This can be done using an energy balance and an outlet temperature. From their simulations, they recommended 1300 K for methane.
- Adjust the flow rates to the desired power output
- The maximum power output is limited by temperature and therefore materials. Similarly, the minimum operating conditions were dictated by heat losses to the environment that would cause combustion extension.
- In addition to adjusting the flow rates, the desired power output can be achieved by adding multiple reactors.
- For system design, the dimensions must be picked to minimize transfer limitations, achieve an acceptable pressure drop and avoid plugging.
- The construction materials will depend on the overall system optimization. In particular the most important was the thermal conductivity. They found that a highly conductive material was good for eliminating hot spots, while conversion increased with a decrease in conductivity. Thus, they recommended “medium” thermal conductivity materials as a suitable compromise.
While the two dimensional models are far superior to one dimensional models, they still have some limitations. They are able to show changes in the x and y direction for many situations. They must assume that changes in the z direction are not significant. This works well for modeling of cylindrical designs. Two dimensional models require less computational power than three dimensional designs, which can be an advantage. However, most small scale reformers are plate type systems which means that the physical phenomena changes in the z-direction are significant. Therefore, to achieve greater accuracy in predicting and understanding reactor performance, three dimensional models are needed.

### 2.3.0 Three dimensional models

With an increase in computing power, 3-D reactor modeling became more prevalent. One of the first 3-D models was proposed by Alfadhel and Kothare published in 2005[28]. They modeled a silicon based membrane water-gas-shift reactor using Navier-Stokes equation. They solved the equations analytically using Fourier Transforms. The modeled reactor was a rectangular microchannel (Figure 2.8). Three sides of the channel are made of silicon with the top of the channel being made of palladium, which hydrogen can permeate, but other gases cannot. The channel width (2Lₓ) was 1000 µm, depth (Lₜ) was 500 µm, and length (Lᵧ) was 1cm making the hydraulic diameter the same order of magnitude as Lₓ. This resulted in a low Reynolds number, but high Knudsen number. They simplified the Navier-Stokes equation in a
rectangular duct at steady state with assumed constant viscosity and density shown in equations 2.25 and 2.26. For flow in the Y direction:

\[
\frac{1}{\mu} \frac{dP}{dY} = \frac{d^2v_y}{dX^2} + \frac{d^2v_y}{dY^2} + \frac{d^2v_y}{dZ^2}
\]  

(2.25)

since there was no flow in the x direction. Note that in this case \( P \) is the dynamic pressure which was assumed to only be a function of flow direction \( y \).

![Figure 2.8. Microchannel cross section. This drawing shows the dimensions, location of coordinate axes and direction of flow][28]7.

The boundary conditions were slip conditions along the walls, symmetry along the x-axis and the dynamic pressure at the inlet being the set. For the Z velocity component, the Navier-Stokes equation

---

7 Reprinted from Chemical Engineering Science 60, Khaled AliAlfadhel, Mayuresh V. Kothare, Microfluidic modeling and simulation of flowing membrane microreactors, 2911-2926, Copyright (2005), with permission from Elsevier.
\[
\frac{1}{\mu} \frac{dP}{dZ} = \frac{d^2V_z}{dX^2} + \frac{d^2V_z}{dY^2} + \frac{d^2V_z}{dZ^2}
\]  \hspace{1cm} (2.26)

However, since the dynamic pressure was only a function of Y, eqn 26 simplified to:

\[
\frac{d^2V_y}{dX^2} + \frac{d^2V_y}{dY^2} + \frac{d^2V_y}{dZ^2} = 0
\]  \hspace{1cm} (2.27)

The boundary conditions for [27] were slip only occurs on surfaces where the velocity had a tangential component and symmetry on the x-axis. The last boundary condition takes into account permeation of the hydrogen through the permeable membrane with the assumption that the velocity of the gases through the membrane was only a function of temperature due to an Arrhenius type of diffusivity[28]. They then did a dimensionless analysis to simplify the equations and solve them analytically using Fourier transforms.

The dimensionless velocity \((\theta_y(x,y,z))\) in the Y direction was found to be:

\[
\theta_y(x,y,z) = I(x,z) - \left[ \frac{1}{\eta_x} + \sum_{n=1}^{\infty} \frac{(-1)^n \cos(\lambda_n z) \cosh \lambda_n x / \cosh \lambda_n \eta_x}{1 + \zeta \lambda_n \tanh \lambda_n \eta_x} \right] \times \int_0^y \theta_p(y)dy
\]  \hspace{1cm} (2.28)

Where \(I(x,y)\) was the dimensionless inlet velocity, \(\eta\) was dimensionless length, \(\lambda\) was the mean free path, and \(\zeta\) was the dimensionless slip length. And the dimensionless pressure \((\tau)\) was...
\[ \tau = \tau_0 + y \nabla^2 I(x, z). \]  

(2.29)

Finally, the dimensionless inlet velocity was determined to be:

\[
I(x, z) = (\frac{dx}{dy})_0 \left[ \frac{x^2 - (x+\zeta)\eta_x}{2} + 2 \sum_{m=1}^{\infty} \frac{[(\zeta \lambda_m^2 + 1)\cos(\eta_x \lambda_m + \epsilon_m) \sin(\eta_x \lambda_m + \lambda_m \epsilon_m)]}{\lambda_m^2(2\zeta + \eta_x [\zeta \lambda_m^2 + 1])[1 + \zeta \lambda_m \tanh(\eta_x \lambda_m)] \cosh(\eta_x \lambda_m)} \right].
\]

(2.30)

They validated their result against reported findings in the literature. The major findings of this paper were the analytical solution for the complex 3-D model for gas permeation through a membrane in microchannels. In addition, they compared their pressure drop equations found in the literature and were able to show that their correlation was superior in that it was not limited to a no slip condition (Knudsen number less than 0.001) and eliminated the need for use of correlated values[28].

In 2009, a group out of HuFan University and National Chiao Tung University published two papers on numerical studies on plate type microreformers[40, 41]. In the first paper (ref 34), they examined a multi-channel parallel plate reactor with diagonal inlets and outlets with the focus on the impact of the aspect ratio on methanol conversion, hydrogen and carbon monoxide generation rate. The stainless steel reactor had 10 channels, each channel with a
depth of 0.5 mm and configuration shown in Figure 2.9. It was presumed that the channel surfaces were coated with a 30 µm thick Cu/ZnO/Al₂O₃ catalyst. For the model, it was assumed the methanol water mixture entered the reactor as a gas, was an incompressible fluid, behaves as an ideal gas, and the reactions only occur within the catalyst layer[40].

They used standard continuity and momentum equations from the Fluent software programs. For the source term ($S_i$), they used flow through a porous media to simulate the catalyst layer.

$$S_i = -\frac{\rho u_i}{k_p} - \frac{\beta u_i}{2} |u_i|$$  \hspace{1cm} (2.31)

---

Where $k_p$ was the permeability, $\beta$ is the inertial loss coefficient which exists only in the catalyst layer and was zero in the flow channel. The energy balance equation was

$$\rho C_p u_j \frac{dT}{dx} = k_{\text{eff}} \frac{d^2T}{dx^2} + S_t$$

(2.32)

Where $S_t$ was the heat source term from the reactions and $k_{\text{eff}}$ was the effective thermal conductivity which was the volume average of the fluid conductivity and the solid conductivity essentially the same as eqn [2.3]. The reaction pathway assumed methanol decomposing to carbon monoxide followed by a water gas shift reaction. The rate equations were:

$$r_{SR} = k_1 C_{\text{CH}_3\text{OH}}^{0.6} C_{\text{H}_2\text{O}}^{0.4} \exp\left(-\frac{E_1}{RT}\right)$$

(2.33)

$$r_{WGS} = k_2 C_{\text{CO}} C_{\text{H}_2} \exp\left(-\frac{E_2}{RT}\right) - k_{-2} C_{\text{CO}} C_{\text{H}_2\text{O}} \exp\left(-\frac{E_2}{RT}\right)$$

(2.34)

Where $E_1$ was 76 kJ mol$^{-1}$ and $E_2$ was 108 kJ mol$^{-1}$. The pre-exponential factors were $8.8 \times 10^8$, $6.5 \times 10^9$, and $4.0 \times 10^7$ for $k_1$, $k_2$ and $k_{-2}$ respectively[42]. They examined the impact of temperature, flow rate, S:C, and channel dimensions. Unsurprisingly, they found that conversion and CO production increases with temperature when at a given feed rate and S:C. At a constant temperature and feed rate, the CO production decreased with increasing S:C.
The more interesting results were that, with this design, there are non-uniform reaction rates in each microchannel which impacts the reactor performance. The concentration non-uniformities were heavily dependent on temperature, S:C, and feed rate, an example of which is shown in Figure 2.10[40]. While they do not discuss this, the non-uniformities are likely caused by uneven flow distribution to the channels due to the inlet and outlet design. Ensuring even flow distribution in multi-channel designs is difficult, especially in designs with catalyst coating walls since, it is difficult to ensure even wall coating of the catalyst.

Figure 2.10. Methanol conversion at three different temperatures. Notice the differences in methanol conversion between the channels illustrating the non-uniform reaction rates [40].

The same group published a second paper in 2009[41] which varied the height and width ratio as well as Reynolds numbers to understand their impacts on methanol conversion and gas

---

transport. They used essentially the same equations, but a different geometry, Figure 2.11, compared to the paper just discussed. The simulation results predicted that lower $H/W$ ratio resulted in better overall performance (Figure 2.12). This was ascribed to the improved surface area to volume ratio. A smaller micro channel size would make the temperature distribution more even, thereby increasing the methanol conversion. And finally, methanol conversion would decrease with increased Reynolds number[41].

Figure 2.11. Schematic diagram used by Hseuh et al.[41]^10. $H$ is the microchannel height (m), $W$ is the microchannel width (m), $L$ is the microchannel length (m), $T_w$ is the wall temperature (°C), $x$, $y$, and $z$ are coordinates, $?_1$ is the open channel height (m), and $?_2$ is the catalyst thickness (m).

Figure 2.12. Effect of microchannel aspect ratio ($\gamma=H/W$) and wall temperature on methanol conversion ($\eta$) and CO concentration at channel outlet\[41]\textsuperscript{10}.

Finally, in 2010, this group published a third study on plate type micro reactors\[43\]. This study examined the performance of a serpentine flow field (Figure 2.13). Again, they used essentially the same equations as their previous studies\[40, 41, 43\]. Similar to their previous studies, a higher wall temperature increases the reaction rate and therefore the methanol conversion, increasing the S:C increases the conversion, as does lowering the Reynolds number. They examined the impact of heating the reactor from the bottom or the top and found that heating from the top improved performance. This was not surprising since the catalyst was on the top plate, so it would be directly heated. It would have been interesting to see if heating from the bottom would be superior if the catalyst was on the bottom. The most interesting point finding was that axial conduction through the wall had a non-trivial effect on the local temperature distribution (Figure F.14)and must therefore be included in the model\[43\].
Figure 2.13. Schematic of Hseuh et al. 2010 serpentine microreactor design[43]. $T_w$ is the wall temperature (°C), $H$ is the channel height (m), $W_x$ is the solids width in the channel (m), $x_w$ is the open portion of the channel (m), $\delta_1$ is the catalyst thickness (m), $\delta_2$ is the open channel height (m), and $x$, $y$, and $z$ are coordinates (m).

Apparently the first 3-D model of a plate type microreactor integrated with a combustor was presented in 2009 by Arzamendi et al[44]. The reformer plate converted methanol water mixture to hydrogen with the heat provided by a combustor plate, in physical contact, which oxidized methanol. They considered a 4-channel system and a reformer plate of 20 channels. For both systems half the number of channels was for fuel processing the other for combustion. Each channel was 20 mm long, 0.35 mm, 0.7 mm, or 1.4 mm of side. The 4-channel reactor was in co-flow configuration. However, the 20-channel reactor was in co-flow, counter flow, and cross-flow configurations. They used Ansys CFX package for their simulations with Navier-

---

Figure 2.14 Local temperature distribution ($\theta$) and methanol conversion predicted results with and without wall conduction. This shows that wall conduction must be considered\textsuperscript{[43]}\textsuperscript{[11].} $T_w$ is the wall temperature ($^\circ$C), $T_o$ is the inlet temperature ($^\circ$C), Re is the Reynolds number, S/C is the steam to carbon ration, X is the dimensionless distance from the flow channel inlet to outlet, $M_{\text{CH}_3\text{OH}}$ is the mole fraction of methanol.

Stokes as the governing equations. They used the Chapman-Enskog kinetic theory to estimate the diffusion coefficient ($7.8*10^{-5}$ m$^2$ s$^{-1}$). For the methanol decomposition to hydrogen and carbon monoxide they used:

$$r_{SR} = 5.3 \times 10^{12} \exp\left(\frac{-105kJ/mol}{RT}\right)P_{\text{CH}_3\text{OH}}^{0.26}P_{\text{H}_2\text{O}}^{0.03}$$ \hspace{1cm} (2.35)

With the rate in mmol methanol kg$^{-1}$ s$^{-1}$ and the pressure in kPa\textsuperscript{[44, 45].} The WGS reaction rate equation was\textsuperscript{[44, 46]}:
\[ r_{CO} = 2.96 \times 10^5 \exp \left( -\frac{47,400 \text{J/mol}}{RT} \right) \left( P_{CO}P_{H_2O} - \frac{P_{CO_2}P_{H_2}}{K_e} \right) \]  \hspace{1cm} (2.36)

With the rate in mol gcat\(^{-1}\) hr\(^{-1}\), pressures in atmospheres, and \(K_e\) given being:

\[ K_e = \exp \left( \frac{4577.8}{T} - 4.33 \right) \]  \hspace{1cm} (2.37)

The methanol combustion reaction was the same as equation (2.9). They assumed a wall coated Cu/ZnO catalyst for the methanol decomposition and WGS reactions, and found that high gas hourly space velocities (GHSV) of 50,000 hr\(^{-1}\) could be achieved on the methanol reforming side (Figure 2.15)[44]. The 20-channel arrangement allowed for examination of larger systems and predicting the impacts of different flow configurations. The results showed the channel width can be scaled from 0.35 mm to 1.4 mm with only some loss in conversion occurring at the highest GHSV for the largest (1.4 mm) channel width. The co-flow configuration had the smallest variation in temperature of approximately 4 K, while the counter flow had the highest difference in temperature of 17 K. The counter flow also had the coolest inlet and hottest outlet. The cross flow configuration had the widest relatively hot zone compared to the three designs. There was no significant difference in performance, so the cross-flow was recommended since it would allow for the easiest manifolding[44]. A weakness of this model was that no experimental validation was performed[44].
Figure 2.15. Methanol conversion (circles) and mean channel temperatures at the outlet (triangles) as a function of the GHSV in the 4 channel arrangement[44]12. The 1.40 mm, 0.70 mm and 0.35 mm refer to the channel size. SRM is the steam reforming of methanol to distinguish from combustion reactions.

Figure 2.16. Temperature distribution in the co flow, counter flow and cross flow configurations d=0.7mm, reforming 28,224 hr⁻¹, and combustion at 75,263 hr⁻¹ [44]12.

Tadbir and Akbari[1] performed a very similar analysis as Hseuh et al[41, 43]. They looked at an array of microchannels in a cluster for methanol reforming directly heated by combustion (Figure 2.17). For their model, they used two channels, a steam reforming channel on top of a combustion channel (Figure 2.17). The channels were 0.7 mm on a side and 1 cm long. The plate between the combustion and reforming channels was 0.3 mm thick. They assumed a catalyst coating of Cu/ZnO/Al₂O₃ (0.052 kg m⁻²) on walls for both the combustor and reformer. The proposed construction material was not reported. The methanol water mixture flow rate and steam to carbon ratio were varied to find the best combination for the proposed reactor. On the combustion side, methanol was oxidized. Co-flow configuration was assumed[1].

![Figure 2.17. An array of microchannels forming a complete reactor and the reactor specifications for the baseline case[1].](image-url)
Due to the low Knudsen number for their case, the flow regime was continuum and therefore the Navier-Stokes equations as well as no-slip conditions were used[1]. For the source terms in the Navier-Stokes equations, they used a three step mechanism proposed by Peppley et al. [47]

\[
\begin{align*}
\text{r1.} & \quad CH_3OH \rightarrow 3H_2 + CO_2, \ \Delta H_{298} = 49.5 \text{ kJ mol}^{-1} \\
\text{r2.} & \quad CH_3OH \leftrightarrow 2H_2 + CO, \ \Delta H_{298} = 90.7 \text{ kJ mol}^{-1} \\
\text{r3.} & \quad CO + H_2O \leftrightarrow CO_2 + H_2, \ \Delta H_{298} = -41.0 \text{ kJ mol}^{-1} \\
\text{r4.} & \quad CH_3OH + 1.5O_2 \leftrightarrow 2H_2O + CO_2, \ \Delta H_{298} = -676.0 \text{ kJ mol}^{-1}
\end{align*}
\]

The rate equations and constants are listed in reference [47]. They used the SIMPLE algorithm to solve the coupled velocity and pressure fields. A computer code was developed in the FORTRAN language to generate the meshing and solving the governing equations.

The baseline simulations (SR inlet temperature of 423 K with a 1:1 S:C feed and oxidation channel temperature of 473 K with 1% methanol in the feed) illustrated that the reaction rates started low as the reactants heated up on entering the channels. The maximum was in the middle of the channel length with the rates decreasing as the reactants are consumed. The methanol decomposition reaction had a higher rate than the WGS reaction. This
was not surprising since in the baseline only 40% of the methanol was reacted. By increasing the methanol in the combustion channels to 2% they were able to raise the temperature to 477 K and increased the S:C to 2. With these changes methanol conversion >90% was achieved. The S:C was kept low in order to decrease the amount of water in the exit. Finally, by increasing the length of the reactor from 10 mm to 20 mm and operating under the baseline conditions the conversion was increased from 40% to almost 80%. The outcome from all these simulations was recommendations for reactor operations being- 20 mm in length, 1.5% methanol in combustor inlet, S:C 1.5, catalyst thickness of 0.13 kg m\(^{-2}\) (twice the baseline), and a gas hourly space velocity of 4000 hr\(^{-1}\). Under these conditions, the projected conversion, % CO in the output and efficiency were >97%, 0.56% CO and 55% respectively. The reactor output was 0.039 W for this block[1].

In 2010 a group from the National Cheng-Kung University in Taiwan reported a 3-D model on a reactor system using a microchannel architecture. The reactor was built of stainless steel with 20 microchannels each 33 mm long, 0.5 mm wide and 0.6 mm deep (Figure 1.18). The catalyst layer, Cu/ZnO/Al\(_2\)O\(_3\) was 0.03 mm thick on the bottom of the channel[48].
Figure 2.18. Microchannel plate reactor by Jang et al.[48].

The model used standard continuity and momentum equations. The dynamic viscosity was based upon the Chapman-Enskog theory for multi-component gas mixtures at low density described by Bird et al. [49]. The energy equation was also detailed in Bird et al. [49] as

\[
\nabla (\varepsilon \rho v h_o) = -\nabla q + \varepsilon \tau \nabla v
\]

(2.42)

Where \( h_o \) is the total enthalpy and \( q \) accounts for thermal conduction and energy transport equations as developed in Bird et al[49]. Fick’s diffusion caused by concentration gradients and also thermal diffusion was assumed. Stefan-Maxwell equations for multi-component systems

---

were used. The following multi-step methanol reforming reaction with methanol decomposing to carbon dioxide and hydrogen and then the reverse water gas shift reaction causing some of the carbon dioxide to react with hydrogen to form water and carbon monoxide was used:

\[
\text{Step 1. } CH_3OH \rightarrow H_2 + CO_2 \tag{2.43}
\]

\[
\text{Step 2. } CO_2 + H_2 \rightarrow CO + H_2O \tag{2.44}
\]

The reaction rate equations for this mechanism were proposed by Coltrin et al.\[50\]

\[
r_1 = A_1 T^n \left( \frac{p}{p_{atm}} \right)^m \exp \left( -\frac{E_{a1}}{RT} \right) C^{a_{1a}}_{H_2O} C^{a_{1b}}_{H_2O} \tag{2.45}
\]

\[
r_2 = A_2 T^n \left( \frac{p}{p_{atm}} \right)^m \exp \left( -\frac{E_{a2}}{RT} \right) C^{a_{2a}}_{CO_2} C^{a_{2b}}_{H_2} \tag{2.46}
\]

Where \(m, A_1, A_2, n, E_{a1}, E_{a2}, \alpha_{1a}, \alpha_{1b}, \alpha_{2a}, \alpha_{2b}\) are found in Chemkin as reported in references\[48\].

The inlet flow rate was varied from 0.1 ml min\(^{-1}\) to 1 ml min\(^{-1}\) of a methanol water mixture (1:1.1 S:C). Vaporization was assumed to happen at the inlet and the inlet temperature was held constant at 393 K\[48\]. Ideal insulation, except for the top surface which was electrically heated, was used. The top surface temperature was assumed to be uniform and ranged from 473 to 533 K. They used a CFD-ACE+ commercial simulation package for the modeling.

85
package uses a finite volume method with SIMPLEC algorithm. To better understand the impact of the inlet and outlet manifolds, they used five different configurations: right inlet/left outlet, right inlet/right outlet, right inlet/central outlet, central inlet/central outlet, central inlet/two outlets (Figure 2.19).

They compared their simulation results using the right inlet/left outlet configuration with experimental data provided by Seo et al. [51] and found good agreement giving confidence in the model. The right inlet/right outlet had the lowest methanol conversion and CO concentration with the central inlet/two outlets having the best conversion over the range of flow rates (Figure 220).
Figure 2.20. Methanol conversion and mole fraction of CO with different configurations and over a range of flow rates. The Central inlet/two outlets had the best performance\[48\].

The velocity distributions (Figure 2.21) in the channels showed that there was uneven flow distribution between the channels. Based upon the model simulations they recommend that a central inlet/two outlet configuration be used\[48\].

Figure 2.21. Flow velocity in the channels\[48\].
Zeng et al. (2012) [52] used simulations to investigate the impact of manifold shape on methanol microchannel plate reactor performance. Specifically they examined a right-angle manifold (MPRM) and an oblique angle manifold (MPOM). Each plate contained 50 microchannels (35 mm long, 0.27 mm width, and 1 mm in depth) see Figure 2.22. The channels were made by micro-milling a 2 mm thick copper plate. Cu/Zn/Al/Zr catalyst was wash-coated in the microchannels. The same reactions as eqns [37]-[39] were used, but different reaction rate equations were assigned as follows:

\[ r_{SR} = 1.152 \times 10^{17} \exp \left( \frac{-149.700}{RT} \right) P_{CH_3OH}^{1.002} P_{H_2O}^{0.9105} \left[ 1 - \frac{P_{H_2O}^2 P_{CO_2}}{K_{p,SR} P_{CH_3OH} P_{H_2O}} \right] \]  

\[ r_{DE} = 4.58 \times 10^{14} \exp \left( \frac{-181.700}{RT} \right) P_{CH_3OH}^{-0.01496} \left[ 1 - \frac{P_{H_2O}^2 P_{CO}}{K_{p,DE} P_{CH_3OH}} \right] \]  

Figure 2.22. Microchannel plates with two different manifold structures[52].

\[ \text{Reprinted with permission from Renewable Energy, 39, Dehuai Zeng, Minqiang Pan, Yong Tang. Qualitative investigation on effects of manifold shape on methanol steam reforming for hydrogen production, 313-322. Copyright (2012), with permission from Elsevier} \]
\[ r_{CO} = 2.96 \times 10^5 \exp \left( \frac{-47400}{RT} \right) \left[ P_{CO}P_{H_2O} - \frac{P_{CO_2}P_{H_2}}{K_e} \right] \] (2.49)

Where \( K_e = \exp(4577.8/T-4.33) \) [46], and \( K_{p,SR} \) and \( K_{p,DE} \) are given by Dong et al [53]. The methanol water mixture feed (1.3 S:C) was assumed to be in the gas phase. Navier-Stokes equation with non-slip boundary conditions, laminar flow, gravity impact was negligible, and an outlet pressure of zero were used. The simulations were run with Fluent software. Of particular interest was that they defined an estimating parameter \( \sigma_u\% \) where the smaller the number the more uniform the distribution. \( \sigma_u\% \) is defined as:

\[ \sigma_u\% = \frac{1}{\sqrt{N} \sum_{i=1}^{N} \left( \frac{U_c(i)}{U_m} - 1 \right)^2} \times 100 \quad (i = 1,2, ..., N) \] (2.50)

Where \( U_c(i) \) was the velocity in the center of each microchannel and \( U_m \) was the microchannel velocity mean value defined as:

\[ U_m = \frac{1}{N} \sum_{i=1}^{N} U_c(i) \quad (i = 1,2, ..., N) \] (2.51)

The simulations compared the velocity distribution with and without reaction occurring for both manifold designs. The mixture flow rate was 0.5 to 12 ml hr\(^{-1}\) and heating temperature of 673-723K [52].
When no reaction was used, the temperature did not seem to impact the flow distribution. Under low inlet velocities the distribution seemed symmetrical. However, as inlet velocity increased, the flow became asymmetrical with larger velocities found to be in the channels further away from the inlet. Finally, the MPRM had a lower $\sigma_u\%$ than the MPORM indicating that it had a more uniform distribution[52].

When reaction was included the flow distribution changed from a “U” shape when no reaction was flowing to a “wave” shape (Figure 2.23). Figure 2.24a shows the $\sigma_u\%$ plotted against the inlet velocity which clearly indicates that the right angle manifold has better flow distribution compared to the oblique. This resulted in improved methanol conversion (Figure 2.24b). Thus they recommend the right angle manifold[52].

![Figure 2.23. Velocity Distribution (a) without reaction and (b) with reaction. MPOM is oblique manifold and MPRM is the right angle manifold[52].](image)
The next 3-D microscale methanol reformer reviewed here is a microreformer with a micro-pin-fin array (Figure 2.25) designed and modeled by Mei et al. [7] and Qian et al. [54]. The objective of this work was to increase the surface area to volume ratio using the micro-pin-fin design thus “enhancing the compactness” of the reactor [7]. They used the semi-solid micro thixo-forming process. In this process the desired material, aluminum alloy A356 in this case, was hot stamped to form the micro-pins. The thixo-forming process is capable of making the desired 3-D microstructures required and was developed to be able to do large volume, low cost manufacturing [7]. Both the experimental and modeled results indicated that the micro-pin design reactor performed better than a flat plate microchannel reactor under the same operating conditions. However, the authors indicated that the 87.5% methanol conversion and
CO amount of <1% was acceptable for fuel cell applications. This may not be true for some types of PEM fuel cells which require extremely high purity hydrogen (CO lower than 10 ppm) and the unreacted methanol may substantially decrease the fuel cell performance. In a subsequent paper, the same group used their model to improve the velocity distribution in their reactor by modifying the manifold [54]. An equivalent electrical resistance network model validated via simulation was used. The results showed that by increasing the y-direction coordinate of the flow manifold inlet tube, improved velocity distribution could be obtained[54].

Figure 2.25. Micro-pin-fin methanol reformer design. a) is the 2-D diagram, b) fabricated catalyst support, and c) completed microreactor[7]15.

---

15 Reprinted with permission from Journal of Power Sources, 205, Deqing Mei, Miao Qian, Binhong Liu, Biao Jin, Zhehe Yao, Zichen Chen. A micro-reactor with micro-pin-fin arrays for hydrogen production via methanol steam reforming, 367-376. Copyright (2012), with permission from Elsevier
Finally, Yao et al. proposed an interesting disc microreactor with tree-shaped flow architectures[55]. Their objective was to improve the flow distribution in the microreactor compared to single or parallel channel designs. The design consisted of three branches connected to one central flow point (Figure 2.26). The radius of the disc was 15 mm and the microchannels had a depth of 2 mm. Four different scenarios of channel width were examined to identify the optimal width. In the model, the total channel volume was the same. They compared the performance of their disc reactor with that of a more conventional parallel channel reactor with the same reactor volume. The reactors were assumed to be made out of silicon with CuO/ZnO catalyst on an Al₂O₃ support. For the reaction equations and kinetics they used equations (38)-(40) and with kinetics described by Peppley et al and Amphlett et al [47, 56].

Figure 2.26. Schematic of disc reactor with tree shaped network (a) compared to microreactor with parallel flow pattern (b)\textsuperscript{16} [55].

\textsuperscript{16} Reprinted with permission from International Journal of Heat and Mass Transfer, 64, Feng Yao, Yongping Chen, G.P. Peterson. Hydrogen production by methanol steam reforming in a disc microreactor with tree-shaped flow architectures, 418-425. Copyright (2013), with permission from Elsevier
The governing equations for the microreactors were the Continuity equation, Momentum and Energy conservation, and chemical species conservation with Maxwell-Stefan for diffusion and mixing. These equations were solved using a finite volume approach and the SIMPLE algorithm for the pressure velocity coupling. The model was validated against a wall-coated tubular microreactor reported in the literature[55].

The model results predicted that the bifurcation effect of the tree-shaped branches caused the reactant gas mixture to come in better contact with the catalyst layer compared to the parallel channel design (Figure 2.27 and Figure 2.28). This resulted in improved conversion and increased hydrogen production.

Figure 2.27. Hydrogen mole fraction distribution at T=503 K, $V_{in}=0.3 \text{ m s}^{-1}$, and steam to carbon ratio of 1.3 for the (a) tree shaped network and (b) parallel flow channel$^{16}$[55].
The major findings of the model were the methanol conversion was 10% higher in the tree-shaped network compared to the parallel channel and the branching increases the surface to volume ratio resulting in an improved conversion for the same reactor volume[55]. This paper proposed a novel design. It would be interesting to see the results of a manufactured device.

2.4.0 Conclusion.

Considerable progress has been made on the development of microscale low power fuel processors for hydrogen production. These systems utilize many of the manufacturing technologies developed for microelectronics. In these miniature systems, it is extremely
difficult to be able to determine the heat and mass transfer characteristics (i.e. flow distribution, temperature distribution, etc.) internal to the reactors and other unit operations. Numerical simulations are critical to understand what is occurring internal to the reformers and be able to improve the designs to achieve the desired performance. Numerous simulation models have been developed ranging from one to three dimensions. As computational power has increased and cost has decreased, the models have increased in complexity and accuracy. The new three dimensional models are very powerful and allow faster, less expensive, and more accurate design. The primary fuel used has been methanol due to its lower reforming temperature. However, several interesting designs have been reviewed which use methane. Initial simulations were simple and focused on wash coated plates and packed bed designs. The recent simulations increased in complexity and included multiple unit operations beyond just the reactor to include vaporization and heat recovery. The majority of designs analyzed were flat plate or annulus designs with the micropin and disc designs as variations from the conventional parallel channels. The numerical simulation tools have proven to be extremely useful in evaluating new designs, understanding the manifold impact on flow distribution, projecting thermal distribution and efficiency.
2.5 References


CHAPTER 3 3-D MODEL OF A RADIAL FLOW SUB-WATT METHANOL FUEL PROCESSOR\textsuperscript{1}

J.D. Holladay\textsuperscript{a,2} and Y. Wang\textsuperscript{a,b}

\textsuperscript{a}Pacific Northwest National Laboratory, 902 Battelle Blvd. Richland WA. 99352 USA

\textsuperscript{b} The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman WA. 99164-6515.

Abstract

A 3-D model is presented for a novel sub-watt packed bed reactor. The reactor uses an annular inlet flow combined with a radial flow packed bed reactor. The baseline reactor is compared to a reactor with multiple outlets and a reactor with 3 internal fins. Increasing the outlets from 1 to 4 may have improved flow distribution, but did not increase the performance. However, inserting fins allowed >99% methanol conversion with approximately 30K decrease in temperature with same inlet flow.

Keywords: microreactor, hydrogen production, methanol reforming, modeling

\textsuperscript{1} Accepted by Chemical Engineering Science 2015.
\textsuperscript{2} Corresponding author. Tel/fax 509-371-6692/509-375-2323. email: jamie.holladay@pnnl.gov

106
3.1. Introduction

Driven by Mohr’s law and exceptional ingenuity of modern engineers and scientists, electronic devices continue to shrink in mass and volume while increasing in capabilities. Despite great improvements in the efficiency of the device electronics, the power and energy demand for these devices has also increased. While Mohr’s law applies to semi-conductor devices, similar improvements in batteries have not been realized. Miniature proton exchange membrane fuel cells (PEMFC) have been proposed to fill this gap, but these fuel cells typically utilize gaseous hydrogen which is difficult to store (1-12). However, the advances in semi-conductor processing can be applied to the development of chemical processing systems resulting in miniature fuel processors which can produce hydrogen from chemicals (1-13).

Methanol is a good fuel for such miniature devices since it: (i) has a high gravimetric density of hydrogen (12.5 wt%), (ii) is a liquid at ambient temperatures, (iii) is miscible in water enabling premixing of the fuel required for steam reforming, (iv) is biodegradable, (v) is sulfur and other contaminant free, (vi) reforms at low temperatures (typically 200-350°C) making thermal integration much easier than paraffinic hydrocarbons such as butane, propane, or methane which reform at temperatures greater than 600°C, (vii) the low temperature reforming favors water-gas-shift and, consequently, produces a low CO content stream which can be utilized directly by Polybenzimidazole fuel cells (14,15), or can be readily cleaned-up via the selective oxidation (16-18) or methanation (10,11,19) to levels suitable for PEMFC and (viii) the low steam to carbon (S:C) ratio required for methanol reforming (1.2:1) compared to the >3:1
typically required for paraffinic hydrocarbons to minimize coke formation \(^{(19,20)}\). The major
disadvantage of methanol is its relatively high toxicity, which can be handled by engineering
solutions to minimize exposure.

### 3.2 Background

Some of the first micro-scale reactors for hydrogen production at 5W hydrogen
equivalent or less were developed in the late 1990’s and shortly thereafter numerical models of
the reactors were reported \(^{(21)}\). The initial models were relatively simple one-dimensional \(^{(1,3,21)}\).
One of the first 3-D models was proposed by Alfadhel and Kothare published in 2005\(^{(22)}\). They
modeled a silicon based membrane water-gas-shift reactor using Navier-Stokes equation and
solved the equations analytically using Fourier Transforms. As computational power increased
new modeling tools, such as COMSOL, were developed and the complexity increased and at
first 2-dimensional \(^{(4,23-27)}\) models were developed and now many 3-dimensional models \(^{(22,28-36)}\).
The fuel of choice was primarily methanol, although there are several methane\(^{(4,27,37)}\) and
ammonia \(^{(1,38)}\) micro-scale reactor models were reported in the literature also. For the
methanol reformers only Cu/ZnO catalysts were considered. The fuel processors modeled
consisted or micro-scale fuel reformers typically wall coated microchannels as the reactors
\(^{(3,26,29,30,33,36)}\) and reformers integrated with combustors \(^{(4,25,27,28,37,39)}\). When integrated with the
combustors the annulus design with the hot gas in the outer shell performed the best\(^{(40,41)}\) with
a cross flow design also showing promise\(^{(28)}\). The most novel micro-scale reactors presented
were a micro-pin based reactor \(^{(34)}\) and disc microreactor with tree-shaped flow
architectures\(^{(42)}\). In the micro-pin reactor, needles were used in place of microchannels with the objective of increasing the surface area to volume ratio thus “enhancing the compactness” of the reactor\(^{(34)}\). Both the experimental and modeled results indicated that the micro-pin design reactor performed better than a flat plate microchannel reactor under the same operating conditions. Yao et al. proposed an interesting disc microreactor with tree-shaped flow architectures\(^{(42)}\). Their objective was to improve the flow distribution in the microreactor compared to single or parallel channel designs. The design consisted of three branches connected to one central flow point. The model results predicted that the bifurcation effect of the tree-shaped branches caused the reactant gas mixture to come in better contact with the catalyst layer compared to the parallel channel design. The heat for both the micro-pin reactor and the tree-shaped flow reactor was to be provided by a microchannel combustor, though it was modeled as a heat source (i.e. the combustion equations were not included).

The literature work was very well done. However, all of the models assumed the reactants entered as a vapor, so vaporization was not included in their models. In addition, other than the micro-pin and the tree-shaped flow reactor, alternative geometries that are available at the micro-scale compared to conventional scale were not examined. In this work, the methanol fuel is being fed as a liquid so the impact of vaporization is considered. In addition, an alternative design with radial flow and the combustor and methanol reformer impinging on each other is examined. This design was selected in order to locate the area of the highest need for heat (methanol reformer reactor entrance) with the area of highest
temperature from the combustor. Finally, a more robust catalyst, Pd/ZnO was used rather than the more common Cu/ZnO.

3.3 Reactor design

Numerous miniature fuel processors have been proposed, designed, and built for this application. The most common designs are variations of a coated wall plate reactor with zig-zag’s internal fluid flow, coated wall Swiss-roll reactors, and packed bed reactors\(^{(29,43-49)}\). For this work a radial flow packed bed fuel processor first proposed by Holladay et al. is considered\(^{(15,19,50-52)}\). This fuel processor was scaled to produce less than 1W hydrogen equivalent from a compact source and was composed of a radial flow methanol steam reforming reactor in intimate contact with a catalytic combustor (Figure 3.1). The direct contact of the endothermic methanol steam reforming reactor with the exothermic combustor focused the thermal energy where it was most needed with the intention of maximizing efficiency. Unlike many of the other proposed designs, this design included an internal vaporizer coupled with the methanol reformer, catalytic combustor and a unique design which enables some heat recuperation via preheating the inlet streams. The methanol-water mix was vaporized and preheated by entering the reactor through a central tube in an annulus configuration, thus capturing waste heat further improving efficiency. On the combustor side, the fuel air mixture was also fed through a central tube in annulus configuration which would pre-heat the incoming fuel/air mix also, with the intention of improving efficiency\(^{(15,19,51,52)}\). The design had a single exit point and no internal mixing other than that which occurred in the packed bed (i.e.
no internal baffles or fins). In this paper we use a 3-D model to explore two proposed design changes with the intention of improving the reactor performance. The first is to increase the single outlet to four exit points with the intention of equalizing flow throughout the reactor. The second is the inclusion of several baffles or fins to control the flow to better utilize the reactor bed the flow. The inclusion of fins in reactors is well known to improve performance \cite{40,53,54}.

![Schematic of baseline reactor design](image)

**Figure 3.1. Schematic of baseline reactor design**

The fuel processor was constructed of stainless steel as previously described \cite{15,19,51,52}. The outer wall thickness was approximately 0.25mm. The inlet and outlet tubes OD and ID of 0.46mm and 0.25mm respectively. The fuel processor’s diameter was 6.35mm OD, and approximately 5.8mm ID. The entire fuel processor had a length of approximately 10mm which included the combustor, methanol steam reforming reactor, and end-caps. The steam reformer and combustor sections were each 4.4mm in length. The plungers had a diameter of 5mm and there was approximately 0.25mm of catalyst bed between the plunger and shim separating the methanol steam reformer reactor and the catalytic combustor. The fluid enters the middle
tube, where it is vaporized and preheated. It exits the tube into the catalyst bed where it moves radially to get to the edge of the reactor and go around the plunger. For the reformer section, the gases then flow through the packed bed reactor and exit. On the combustor side, there is no additional catalyst between the plunger and outlet tube, so the gases flow through the empty section and then exit the reactor. A thermocouple was inserted into the exit tube of the combustion section to monitor and control the reactor temperature. Since the reactor is not isothermal, it is difficult to identify a single condition for comparison purposes especially for conversion. Therefore, all temperatures in the figures for conversion reported are from the combustion side as measured by this thermocouple and are referenced as Tcr. Kao-wool, approximately 3mm thick was used as the insulation. The fuel processor operation was described previously. The methanol steam reformer used a Pd/ZnO catalyst. Details on the Pd/ZnO methanol reforming catalyst used was described previously\(^7\). The combustion catalyst was 10 wt% Pd on \(\gamma\)-alumina prepared by incipient wetness technique (Appendix D).

### 3.4 Model development

COMSOL 4.3 was used to develop a 3-D model the fuel processor. A line of symmetry through the length of the reactor was used to decrease computational time. Continuity, momentum balance, mass conservation and energy conservation equations were used to model the fuel processor. The methanol water mixture entered the system as a liquid and was
vaporized in the inlet tube. For the momentum balance, the fluids in the packed bed reactors were assumed to follow Darcy’s law in the packed bed reactor.

\[ U = -\frac{\kappa}{\mu} \nabla P \]  \[ 3.1 \]

Where \( \mu \) is the fluid viscosity (Pa*s), \( P \) is the pressure (Pa), \( \kappa \) is the permeability (m²) and \( U \) is the flow rate (m s⁻¹).

The Reynolds number (equation 3.2) for the flow in the inlet and exit tubes was between approximately 6 to 1 for the methanol reformer portion and 600 and 32 for the combustor portion. Since this is laminar flow in a tube, equation 3.3, was used in the inlet and exit tubes\(^{(55)}\).

\[ Re = \frac{\rho Ud_h}{\mu} \]  \[ 3.2 \]

Where \( \rho \) is the fluid density (kg m⁻³), and \( d_h \) is the hydraulic diameter with \( d_h = 4 \times \text{area/ perimeter (m)} \) which for a tube is twice the radius (2r).

\[ U = -\frac{r^2 \nabla P}{8 \mu} \]  \[ 3.3 \]

We used COMSOL’s transport of concentrated species equations for the conservation of mass:

\[ \nabla \left( -\rho D_{i,l}^{m} \nabla w_l - \rho w_l D_{i,l}^{m} \frac{\nu M_i}{M_l} \right) + \rho (U \cdot \nabla) w_l = R_l \]  \[ 3.4 \]
Where $D_{i,i}^m$ is the diffusivity (m$^2$ s$^{-1}$) which included the dispersion effects, $w_i$ is the mass fraction of component $i$, and $R_i$ is the change in mass of component $i$ from reactions.

$$M_n = \left( \sum_i \frac{w_i}{M_i} \right)^{-1}$$  \[3.5\]

We used the Stefan-Maxwell diffusivity

$$D_i^m = \frac{1-w_i}{\sum_{k \neq i} x_k D_{ik}}$$  \[3.6\]

The Stefan-Maxwell equations were used to estimate the mean effective binary diffusivity and the dispersion effects were accounted for by using $D_{i,i}^m = D_i^m \left( 0.7 + 0.5 \frac{d_p \mu}{\rho D_i^m} \right)$ with units of m$^2$ s$^{-1}$ (56). In these equations $x_k$ is the mole fraction of component $k$, $D_{ik}$ (m$^2$ s$^{-1}$) is the mutual diffusivity of components $i$ and $k$, $D_i^m$ is the Stefan-Maxwell diffusivity (m$^2$ s$^{-1}$) and $D_{i,i}^m$ is the effective diffusivity taking into account dispersion due to the packed bed.

The methanol reforming reaction was simplified to:

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$$  \[3.7\]

We used the reaction rate equation developed by Cao et al.\(^7\):

$$-r_{\text{meoh}} = 2.9047 \times 10^{10} e^{\frac{-E_a}{RT}} P_{\text{meoh}}^{0.715} P_{\text{H}_2\text{O}}^{0.088}$$  \[3.8\]
Where \(-r_{\text{meoh}}\) is the reaction rate of methanol in \(\text{mmol kg cat}^{-1} \text{ s}^{-1}\), and \(P_{\text{meoh}}\) and \(P_{\text{H2O}}\) are the partial pressures of methanol and water in kPa, respectively and \(E_a\) is the activation energy 94,800 J mol\(^{-1}\) K\(^{-1}\). Standard energy conservation equations were used in the model:

\[
\rho C_p V \cdot \nabla T = \nabla \cdot (\lambda \nabla T) + Q
\]  

[3.9]

Where \(C_p\) is the heat capacity, \(\lambda\) is the thermal conductivity (W m\(^{-1}\) K\(^{-1}\)), and \(Q\) is heat (W m\(^{-3}\)) into or out of the model. This is from the endothermic methanol reforming reaction or the exothermic combustion reaction plus loses to the environment. For the heat input from the combustor, a thermal heat source was used in place of the combustion reaction. In the model, this heat source was located in the combustor catalyst section. The heat losses due to the endothermic methanol reforming reaction were calculated as the heat of reaction, found in Table 3.1, times the moles methanol reacted.

As mentioned previously, the methanol-water mix entered the reactor as a liquid and was vaporized. Vaporization can be difficult to simulate. So for only the methanol water mixture inlet tube on the methanol reformer portion of the fuel processor, the \(C_p\) and density were estimated as follows. \(C_p\) was estimated by taking into account the heat of vaporization. Recognizing that \(C_p = dH/dT\), we used ChemCad\(^\circledR\) to determine the \(\Delta H\) of the mixture over a temperature range from room temperature 293K – 475K (Figure 3.2). The thermodynamic settings were as follows: NRTL was used for the vapor liquid equilibrium and the global K-value.
The SRK equation of state was used to determine the vapor fugacity. Finally the global enthalpy model (latent heat) was used with ideal heat capacity and data from the DIPPR data set. Using these numbers we were able to calculate an average Cp over the vaporization range (346K-359K) calculated to be 122.1 J g\(^{-1}\) K\(^{-1}\). The data was entered into a table format into the COMSOL model and used the interpolation function. Similar, for the density, ChemCad\(^\circ\) software with the same settings was utilized to determine the vapor and liquid mole fraction over the same range (Figure 3.3). This approximated the density during vaporization. The methanol-water mixture liquid phase density was 898 kg m\(^{-3}\) and the ideal gas law was employed to calculate the density in the vapor phase. It was assumed that the vaporization would occur quickly so two phase flow could be neglected. In the methanol reactor portion and exit tubes where the reactants and products are gases, the ideal gas law was used for the density. The heat capacity of a gas mixture of methanol, water, H\(_2\) and CO\(_2\) at 50% methanol conversion and 575K was used as the Cp (Table 3.1). For the combustion sections, the density and Cp of air as found in Table 3.1 was used.

For the bed thermal conductivity an effective thermal conductivity was found using, Yagi and Kunii’s\(^{(57)}\) formulas as proposed by Karim et al\(^{(58)}\):

\[
\frac{\lambda_{eff}}{\lambda_{gas}} = \frac{\lambda_{eff}^0}{\lambda_{gas}} + (\alpha\beta)(PrRe) \tag{3.10}
\]
Figure 3.2. Enthalpy change of the water-methanol mixture (1.2:1 molar). This was used to calculate a Cp over the vaporization range to simulate vaporization in the reformer.

Figure 3.3. Density change of the water-methanol mixture (1.2:1 molar).

Where $\lambda_{eff}$ is the effective conductivity with a stagnant gas (Re=0); $\lambda_{gas}$ is the gas thermal conductivity, $\alpha$ is the mass velocity in the direction of heat transfer/mass velocity based on area of the empty tube in the direction of fluid flow , and $\beta$ is the effective length between the centers of two particles/mean particle diameter. It was reported\(^{(58)}\) that $\alpha\beta = 0.05$ for a
diameter of the reactor/particle diameter ratio of ~29 similar to this reactor. Yagi and Kunii\textsuperscript{(57)} gave equation [3.13] for calculating \( \frac{\lambda_{\text{eff}}}{\lambda_{\text{gas}}} \):

\[
\frac{\lambda_{\text{eff}}}{\lambda_{\text{gas}}} = \beta \left( \frac{1 - \phi}{\lambda_{\text{gas}} / \lambda_p + \psi} \right)
\]

[3.11]

Where, for spherical particles \( \beta = 1 \); \( \phi \) is the void fraction which was 0.4 and \( \psi \) was the effective thickness of fluid film adjacent to contact surface between two solid articles/mean particle diameter. From the literature 0.04 was a good number for round particles in a packed bed for methanol steam reforming\textsuperscript{(58)}. The thermal conductivity of the catalyst particles (\( \lambda_p \)) was 1.3 W m\(^{-1}\) K\(^{-1}\)\textsuperscript{(59)}. Other parameters used in the model are in Table 3.1.

The boundary conditions were as follows. The incoming liquids and gases were at room temperature (298K). The methanol water mixture was at 1.2:1 steam to carbon ratio and had a flow rate as indicated in the text. Exit was at convective flux for heat and mass. For the insulation convective flux the heat transfer convection coefficient of 12 W m\(^{-2}\) K\(^{-1}\) which was estimated using the procedure described by Raithby and Hollands\textsuperscript{(60)} for small horizontal cylinders. The exit pressure was 1 atmosphere.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Insulation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>128 kg m(^{-3})</td>
<td>[61]</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>835 W m(^{-1}) K(^{-1})</td>
<td>[61]</td>
</tr>
<tr>
<td><strong>Methanol reformer</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat of Reaction</td>
<td>201.2 kJ mol(^{-1})</td>
<td>[20]</td>
</tr>
<tr>
<td>Heat Capacity</td>
<td>0.0794 W m(^{-1}) K(^{-1})</td>
<td>[61]</td>
</tr>
<tr>
<td>Viscosity (at 50% methanol conversion at 575K)</td>
<td>196.7e-7 <em>Pa</em>s</td>
<td>[61]</td>
</tr>
<tr>
<td>Permeability (packed bed)</td>
<td>4.76e-11 m(^{2})</td>
<td></td>
</tr>
<tr>
<td>Porosity</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>Catalyst thermal conductivity</td>
<td>1.3 W m(^{-1}) K(^{-1})</td>
<td>[59]</td>
</tr>
<tr>
<td><strong>Combustor</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst thermal conductivity</td>
<td>1.3 W m(^{-1}) K(^{-1})</td>
<td>[59]</td>
</tr>
<tr>
<td>Volume fraction</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td><strong>Air</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>(-2.664e-8<em>T(^3)+9.149e-5</em>T+1.415e-3) W m(^{-1}) K(^{-1})</td>
<td>Data from [61]</td>
</tr>
<tr>
<td>Density</td>
<td>(-2.954e-9<em>T(^3)+7.523e-6</em>T(^2)-6.827e-3*T+2.6) kg m(^{-3})</td>
<td>Data from [61]</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>(-3.8172e-7<em>T(^3)+8.3379e-4</em>T(^2)-0.36177*T+1050) W m(^{-1}) K(^{-1})</td>
<td>Data from [61]</td>
</tr>
<tr>
<td>Viscosity</td>
<td>(7.076e-11<em>T(^2)+6.046e-8</em>T-8.945e-6) Pa*s</td>
<td>Data from [61]</td>
</tr>
<tr>
<td><strong>Steel</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>19.8 W m(^{-1}) K(^{-1})</td>
<td>[61]</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>557 W m(^{-1}) K(^{-1})</td>
<td>[61]</td>
</tr>
<tr>
<td>Density</td>
<td>7900 kg m(^{-3})</td>
<td>[61]</td>
</tr>
</tbody>
</table>
3.5 Results

3.5.1 Baseline model results

The baseline model was exercised at a methanol water mix feed rates of 0.15 ml hr\(^{-1}\) and 0.2 ml hr\(^{-1}\). On the combustion side, the inlet air flow was held constant at 25 sccm while the thermal energy input was adjusted until the desired temperatures were reached. It was assumed that increasing the methanol for the combustor did not significantly increase the gas flow. The methanol conversion model results were compared to experimental data from Holladay et al. in reference\(^{(51)}\). The model predicts a large temperature gradient in the reactor, which was consistent with the microreactor design intentions\(^{(15,19,51,52)}\). In fact, the design theory was to have the hottest portion of the system be in the middle where the thermal energy is needed for the reaction, and then to have the system cool from the middle to the outer edges in order to make thermal insulation easier. The design accomplishes that goal as can be seen in an example temperature profile shown in Figure 3.4. The reactor had a temperature differential of approximately 75-100K with the middle of the combustor projected to be around \(~655K\) and the temperature at the exit of the steam reformer reactor bed at the exit tube being projected to be approximately 550 - 575K during the hottest conditions. The model was able to capture the liquid vaporization as can be seen in Figure 3.7 where the flow rate suddenly increases in the velocity contours. As anticipated, the vaporization occurs quickly which supports the assumption that two phase flow could be ignored. The temperature profiles also show the vaporization (see Figure 3.4). As discussed previously, for the experiments as
reported in reference \(^{(51)}\), a thermocouple was inserted through the combustor exit tube and connected to the plunger on the combustor side. This thermocouple position was outside the hottest point in the combustor and measured \(~618K\) when the reactor achieved 100\% conversion. The approximate position of the thermocouple was located in the model and the temperature at this point was designated as \(T_{cr}\) which would correspond to the thermocouple temperature in the experimental data. The conversion data are presented using this temperature \((T_{cr})\). Figure 3.5 shows the reaction rate in kg m\(^{3}\) s\(^{-1}\) which clearly shows the majority of the reaction occurs at the reactor inlet where it is hottest and the rest of the bed.

![Figure 3.4. Reformer system projected temperature isotherm (temperature in K) contours with 0.2 ml hr\(^{-1}\) methanol water mix flow and a >99.5\% methanol conversion. The steam reformer is the upper reactor and the combustor is in the lower section.](image)
serves to achieve the high conversion desired. The heat input to the reactor from the experimental side was 1.27W while the model predicted a 1.14W input. This is within 15% showing acceptable agreement. Finally, as shown in Figure 3.6, there is fairly good agreement between the predicted methanol conversion results and the limited available experimental data. All of these results gave us confidence that simulation can be used to explore variations in the methanol reformer design.

The baseline reactor worked well; however, it was believed that the performance could be improved. The baseline model showed that there was poor utilization of the reactor bed since the gases would preferentially flow towards the exit leaving large portions of the bed
stagnant as illustrated by the velocity contour plot shown in Figure 3.7. These conditions would be caused by the tendency of the gas to flow through the path of least resistance. Therefore, with only one exit and nothing blocking the gas’s path, the gases will preferentially flow to the side of the reactor with the exit and large portions of the catalyst bed will be by-passed.

Figure 3.6. Predicted methanol conversion (solid line) compared to experimental results at 0.15 ml hr$^{-1}$ and 0.2 ml hr$^{-1}$ methanol-water mixture flow rates. Temperature corresponds to the thermocouple temperature in the experiments and the temperature at approximate location of the thermocouple in the model (Tcr).

Two simple design variations were proposed and explored to address these issues. The first was to increase the number of exits. It was hypothesized that with exits equidistant from each other, the flow distribution should become more uniform and more of the catalyst bed
would be accessed. The second permutation was the inclusion of fins. The fins would force the gases to take a longer pathway to the exit. More details on how these permutations were implemented and the study results are presented next.

![Figure 3.7](image.png)

Figure 3.7. Predicted velocity profiles (velocity in m s\(^{-1}\)) at inlet fluid flow for 0.2 ml hr\(^{-1}\) methanol water mixture feed and >99.5% methanol conversion. A) shows the cross-cross section and B) shows the outside. The methanol reformer is the top reactor and the combustor is the bottom reactor. The circular insert shows the velocity contours where vaporization is occurring. The maximum velocity of the methanol section was \(~3.1\) m s\(^{-1}\), but a finer scale was used in order to see the velocity profile in the reactor sections more clearly.

### 3.5.2 Multiple outlets results

The first modification was to increase the number of reformer outlets from 1 to 4. It was believed that by increasing the number of outlets the flow distribution would be improved.
through the catalyst bed which would increase the amount of catalyst utilized resulting in
improved reactor performance. As shown in velocity contour plot in Figure 3.8, the fluid flow
uniformity was somewhat improved. Increasing the number of exits may have improved the
flow distribution, but the reactor performance did not increase as shown in Figure 3.9. It is
believed that the improve flow distribution minimized gas channeling, but did not change the
residence time. While some additional catalyst may have been accessed, the amount was not
increased enough to improve performance. In addition, the portion of the reactor where the

![Figure 3.8. Predicted velocity profiles (velocity in m s⁻¹) for the reactor design with 4 outlets at inlet fluid flow for 0.2 ml hr⁻¹ methanol water mixture feed and >99.5% methanol conversion. A) shows the cross-cross section and B) shows the outside. The methanol reformer is the top reactor and the combustor is the bottom reactor. The maximum velocity of the methanol](image)
section was \( \sim 3.1 \text{ m}^{-1} \), but a finer scale was used in order to see the velocity profile in the reactor sections more clearly.

Figure 3.9. Predicted baseline methanol conversion and predicted methanol conversion with multiple outlets. No significant improvement was predicted in the numerical simulation. Temperature corresponds to the thermocouple temperature in the experiments and the temperature at approximate location of the thermocouple in the model (Tcr).

Flow was increased was located in the sector of the methanol reformer that had the lowest temperature and reaction rate (see Figures 3.4 and 3.5). Therefore, it is necessary to improve the gas flow in the areas where the reaction rate is higher in order to improve performance.
3.5.3 Fined reactor design results

The final design permutation was to add a series of three fins to the baseline model to force the gases to flow through more of the reactor effectively increasing the amount of time the gases would need to be in the reactor as well as increasing the catalyst amount actively participating in the reaction and improve mixing. The hypothesis was that a design which uses fins or baffles would better be able to distribute the flow. The fins were 10\(\mu\)m thick with a diameter of 5.4mm and spaced evenly apart in the bed. Using the reactor geometry and ignoring tortuosity caused by the packed bed, a minimum distance for the gases to travel from exiting the plunger to the exit tube can be estimated. The minimum distance in the baseline reactor was approximately 6.5mm, whereas by adding the fins the minimum length increased >95% to approximately 12.8mm. Figure 3.10 shows the velocity contour plot which indicates better flow distribution until the section closest to the outlet. Another useful plot is a streamline velocity plot, which visualizes the path a particle would take as carried in the fluid and shows the highest probability of flow and the flow at the highest magnitude for the fluids. A streamline plot of all three reactors is shown in Figure 3.11 which reveals that there is improved catalyst bed utilization in the finned reactor compared to the other designs. In addition, it was anticipated that the fins would also increase or change the temperature distribution. However, by comparing Figure 3.4 and 3.12, it can be seen that no significant changes in the temperature distribution were observed.
Figure 3.10. Predicted velocity profiles (velocity in m s\(^{-1}\)) for the finned reactor design at inlet fluid flow for 0.2 ml hr\(^{-1}\) methanol water mixture feed and >99.5% methanol conversion. A) shows the cross-cross section view and B) shows the outside view. The methanol reformer is the top reactor and the combustor is the bottom reactor. The maximum velocity of the methanol section was \(~3\) m s\(^{-1}\), but a finer scale was used in order to see the velocity profile in the reactor sections more clearly.

Figure 3.11. Velocity streamlines (velocity in m s\(^{-1}\)) in the methanol reformer section only of the A) baseline reactor, B) multi-exit reactor design and C) finned reactor design. Inlet flow was 0.2 ml hr\(^{-1}\) and >99.5% methanol conversion. The maximum flow was \(~3.1\) m s\(^{-1}\).
As shown in Figure 3.13 the reactor with added fins improved the reactor performance as evidenced by the fact that >99.5% methanol conversion was attained at 29K lower temperature (~589K) compared to the original design which required ~618K to achieve the same methanol. The predicted thermal efficiency improved from 33% to 40%. The improved performance was attributed two primary reasons. First, the finned reactor design had a longer residence time forced by the longer distance the gases traveled from entrance to exit compared to the baseline reactor. This increased the amount of catalyst participating in the reaction and gave more time for the reactions to occur. It is believed that this is the primary reason for the improved performance. The second reason for improved performance was the finned design.

![Figure 3.12. Predicted temperature distribution (temperature in K) in finned reformer at 0.2 ml hr⁻¹ inlet rate and >99.5% methanol conversion. The top portion is the steam reformer reactor and the bottom section is the combustor.](image)
increased the mixing of the gases improving mass transfer. The achievement of >99% conversion at lower temperatures and the increased residence time suggested that higher feed rates at the same reactor temperature could be achieved with a 2x increase expected. Using the finned steam reformer reactor model, we tested this expectation and predicted that at ~618K the inlet flow could be increased 2.7x from 0.2ml hr$^{-1}$ (baseline reactor inlet flow at this temperature) to 0.54ml hr$^{-1}$ while still achieving >99.5% conversion. This would increase the potential hydrogen power from ~640mWt to ~1720mWt and the thermal efficiency was predicted to be ~60%. This improved production was more than the expected 2x increase could be explained by improved mixing mentioned previously and perhaps some improved heat transfer. The mass fraction of methanol in the reactor can also be helpful in understanding the reactor performance. Figures 3.14 and 3.15 show the mass fraction of the baseline and the finned reactor system at 0.2 ml hr$^{-1}$ and 0.54 ml hr$^{-1}$ at methanol conversion >99.5%. Figure 3.14 has the full range (0.6 to ~0 wt%) while Figure 3.15 has a more refined scale of 0.05 to ~0wt% which enables tracking of the methanol with better precision. In the baseline reactor, the majority of the methanol is reacted as it enters the reactor with the portion of the packed bed after the plunger reacting the remaining methanol. Whereas in the finned reactor, the concentration remains higher over half-way through the reactor which indicates the catalyst bed is better utilized and illustrates the improved reactor performance.
Figure 3.13. Predicted methanol conversion for 0.2 ml hr\(^{-1}\) methanol water mix inlet flow for the original reactor design (blue line) and the finned reactor (dotted red line). Temperature corresponds to the thermocouple temperature in the experiments and the temperature at approximate location of the thermocouple in the model (Tcr).

This design could possibly be implemented by creating metal inserts with the fins going from the outer wall towards the middle for the 1\(^{\text{st}}\) and 3\(^{\text{rd}}\) fins. The middle fin could have a hole close to the inlet tube diameter and slide into place after the first fin and associated catalyst layer is inserted. This would necessarily need to be a tight fit in order to prevent gases from flowing to the next layer through a gap between the middle fin and tube. It could be assembled by adding a catalyst felt followed by the plunger as is currently done. Next the insert with the 1\(^{\text{st}}\) fin would be positioned. The catalyst powder would be added. Next the middle fin would be inserted followed by a catalyst layer. Subsequently, the 3\(^{\text{rd}}\) fin would be put in place. Finally, the
Figure 3.14 Methanol mass fraction (wt% methanol) in (A) the baseline reactor, 0.2 ml hr\(^{-1}\) inlet feed and >99.5% methanol conversion, (B) finned reactor, 0.2 ml hr\(^{-1}\) inlet feed, and >99.5% methanol conversion, and (C) finned reactor, 0.54 ml hr\(^{-1}\) inlet feed, and >99.5% methanol conversion.

Figure 3.15 Methanol mass fraction (wt% methanol) in the reactors with finer scale. (A) the baseline reactor, 0.2 ml hr\(^{-1}\) inlet feed and >99.5% methanol conversion, (B) finned reactor, 0.2 ml hr\(^{-1}\) inlet feed, and >99.5% methanol conversion, and (C) finned reactor, 0.54 ml hr\(^{-1}\) inlet feed, and >99.5% methanol conversion.
rest of the catalyst powder would be added. It may be a challenge to ensure that the catalyst
beds between fins is completely filled with catalyst to prevent bypass.

There are a couple of alternative designs that could also be considered. The first would
be rather than using a loose powder, the catalysts could be coated onto the reactor walls and
the fins with an open channel or the catalyst could be coated onto a porous metal felt. Both of
these options would decrease the manufacturing complexity. Wall coating for methanol
reformers in micoreactors has been demonstrated with Cu/ZnO catalysts and there are several
models of such reactors reported in the literature \(^{(39,42,62)}\). Similarly, Pd/ZnO coated porous felts
for methanol reforming has also been reported \(^{(11,52)}\). Although the advanced finned reactor
design requires more complicated assembly compared to the baseline system, the finned
reactor’s improved performance makes this an attractive option.

An examination of the concentration profile in Figure 3.15 revealed that the majority of
the reaction occurred in the first half of the methanol reformer with most at the entry point
while very little occurred in the last section prior to the exit. Since the entry point was the
location with the highest reactant concentration, the highest temperature (see Figure 3.12 and
3.15), and the reaction is not zero order (equation 3.8 and reference 7) this seemed reasonable.
The low temperatures near the exit indicate that the reactor might be heat transfer limited.
This suggested that the reactor performance and catalyst utilization could be improved by
improving the heat transfer in the system. There are several ways this could be achieved such
as, i) increasing the thickness of the metal walls, ii) connecting the fins to the plunger directly,
iii) increasing the reactor diameter and decreasing the length, iv) increasing the distance of the plunger to the separating wall effectively increasing the size of the first and hottest reaction zone, or v) by changing the combustor exhaust flow such that it wraps around the reformer. Proposed improvements i and ii would likely result in only a minimal increase in heat transfer since the reactor bed is already full of catalyst and the distances are relatively short. In addition, building this into the small device may be difficult. Increasing the reactor diameter (improvement iii) could have a significant effect while being simple to implement. For example, if the diameter was increased by 41% the length could be decreased by 50% while keeping the same reactor volume. This design would increase the percentage of the reactor at high temperatures which would also improve the reactor rates and better utilize the catalyst. Benefits could include operating the reactor at a lower temperature for improved efficiencies or increasing the hydrogen productivity by increasing the inlet flow rates while operating at the same temperatures. The number of fins may need to be decreased from three to two since the shortened reactor length may make inclusion of all three fins difficult. Increasing the size of the first reaction zone by increasing the distance of the plunger from the combustor/steam reformer separating wall (iv) would be easy and effective. Similar to (iii) it may make adding the additional fins a more difficult. The final design suggestion (v) to improve heat transfer could be included in the finned reactor design or combined with improvement iii. In the current designs, the combustor exhaust gases are vented with relatively little heat recovery. However, by wrapping the exhaust gas around the methanol reformer portion as shown in Figure 3.16 the thermal energy in the exhaust gas could be better utilized. This design would heat the methanol
reformer walls thereby increasing the temperature of the reactor, particularly near the exit. In addition, it would be an insulating layer decreasing heat loss. The design is more complicated and may create a manifold challenge, but the potential improved performance may be worth the increased complexity.

While significant improvements in the methanol reformer design have been explored using numerical simulation, there are still development opportunities for the system. The next steps would include building and testing the proposed reactor, optimization of the finned reactor design in terms of number of fins and operating conditions. In addition, the combustion side needs to be addressed. Currently, the combustor requires a blower to provide the air. A new design that would siphon air into the combustor would be of interest. Finally, this design approach has been shown to be effective for micro-scale reactors. Obviously the design can be scaled-up for larger systems. The model can be used to predict what the limits for scaling up the device may be.

Figure 3.16 Fuel processor with the combustor exhaust flowing around the methanol reformer.
3.6 Conclusions

A model for a methanol fuel process was developed for an annular system. The model was validated against data we previously published and then used to propose improvements to the reactor design. The predicted internal gas flow path in the original design showed significant portion of the catalyst bed was being underutilized. Two design changes were proposed to improve the bed utilization. The first design change was to increase the number of outlet tubes from one to four. This had minimum impact on the predicted performance. The second design change was to insert several fins into the reactor. This substantially improved the predicted performance. The model predicted a 29K lowering of the reactor temperature to achieve >99.5% methanol conversion at an inlet flow of 0.2 ml hr\(^{-1}\). In addition, at the original reactor temperature of \(T_{cr} \sim 618K\) an increase in inlet flow of 2.7x was predicted. This would increase the reactor power from \(\sim 640\text{mW}_t\) to \(\sim 1720\text{mW}_t\). A manufacturing method was proposed for the new design. The reactor does have some thermal transport limitations. Several design modifications were proposed to minimize the limitations with the most likely to succeed being increasing the diameter and decreasing the thickness and/or wrapping the combustor exhaust around the steam reformer to heat and insulate the reformer section.
3.7 **Nomenclature**

Cp: heat capacity (J g\(^{-1}\) K\(^{-1}\))

d: diameter (m)

d\(_h\): hydraulic diameter (m)

D: diffusivity (m\(^2\) s\(^{-1}\))

\(D_{ik}\): mutual diffusivity of components \(i\) and \(k\) (m\(^2\) s\(^{-1}\))

\(D_{i}^{m}\): Stefan-Maxwell diffusivity (m\(^2\) s\(^{-1}\))

\(D_{i,k}^{m}\): diffusivity taking into account dispersion effects (m\(^2\) s\(^{-1}\))

DOE: Department of Energy

\(E_a\): activation energy (94,800 J mol\(^{-1}\) K\(^{-1}\))

H: Enthalpy (J g\(^{-1}\))

i: component

ID: inner diameter

k: component

M: mass (kg)

OD: outer diameter

P: Pressure (Pa)

p: particle

PEMFC: Proton exchange membrane fuel cell

PNNL: Pacific Northwest National Laboratory
Pr: Prandtl = momentum diffusivity / thermal diffusivity = $\frac{\mu C_p}{\lambda}$

Q: heat $W \ m^{-3}$

R: change in mass

r: radius (m)

$r_{\text{meoh}}$: methanol reaction rate (mmol kg$_{\text{cat}}^{-1}$ s$^{-1}$)

Re: Reynolds number = convective momentum transport / viscous momentum transport = $\frac{\rho U D_h}{\mu}$

S:C: steam to carbon ratio

T: Temperature (K)

$T_{\text{cr}}$: Temperature (K) at the approximate location of the thermocouple in the experimental data.

U: velocity

W: Watt

$w_i$ or $w_k$: mass fraction

$x_k$: mole fraction

Greek

$\alpha$: mass velocity in the direction of heat transfer/mass velocity based on area of the empty tube in the direction of fluid flow

$\beta$: effective length between the centers of two particles/mean particle diameter

$\lambda$: thermal conductivity ($W \ m^{-1} K^{-1}$)
\( \lambda_{\text{eff}} \): effective thermal conductivity of the bed for both gas and solids (W m\(^{-1}\) K\(^{-1}\))

\( \lambda_{\text{eff}}^0 \): effective conductivity with a stagnant gas (Re=0) (W m\(^{-1}\) K\(^{-1}\))

\( \lambda_{\text{gas}} \): gas thermal conductivity (W m\(^{-1}\) K\(^{-1}\))

\( \lambda_{\text{p}} \): thermal conductivity of the solid particle (W m\(^{-1}\) K\(^{-1}\))

\( \phi \): void fraction

\( \kappa \): permeability (m\(^2\))

\( \mu \): viscosity (Pa*s)

\( \rho \): density (kg m\(^{-3}\))

\( \psi \): effective thickness of fluid film adjacent to contact surface between two solid particles/mean particle diameter

Acknowledgements

We express our sincere appreciation to the Voiland School of Chemical Engineering and Bioengineering and the Agricultural Research Center at the Washington State University for their support. The authors would like to thank the U.S. DOE Energy Efficiency and Renewable Energy Office and Defense Advanced Research Projects Agency for their support. A special thanks is given to Dr. Paul Humble for many useful conversations.
3.8. References


CHAPTER 4 CONCLUSIONS AND FUTURE DIRECTIONS

4.1 General conclusions

Micro-scale fuel processors coupled with a fuel cell are an attractive power supply option for the next generation of personal power electronics and micro-scale sensors. This technology takes advantage of the high energy density of hydrocarbon fuels and the high efficiency of fuel cells. The hydrocarbon fuels have 1-2 orders of magnitude greater energy density than the current lithium-ion and lithium-polymer batteries. A micro-scale fuel processor coupled with a fuel cell can be scaled to lower power than the rotary engines. In addition, it can have a higher efficiency than thermoelectric generators since the efficiency is not limited to the Carnot cycle. Currently most micro-scale fuel processors are flat plates or annular designs with catalysts coating the walls. Steam reforming technology was selected over preferential oxidation and autothermal reforming since it does not require addition of oxygen, either pure or as a component in air, injection for the reactions to proceed. This simplified the design and created a purer product stream.

In the literature, the fuel of choice for micro-scale fuel processors is methanol, although there are some groups examining ammonia and methane. We have shown that unless the water is recycled from the fuel cell, methanol is the preferred fuel since:

- It has the lowest steam to carbon ratio, 1.2:1 compared to 3:1 for paraffinic hydrocarbons;
• Equal to or great energy density when water is included in the fuel;
• Reforms at the lowest temperature (<400°C);
• Produces the lowest level of CO, a fuel cell poison;
• Doesn’t require additional WGS reactors to maximize hydrogen and minimize CO;
• Is not a fuel cell poison like ammonia;
• And does not require sulfur or other contaminant removal like most paraffinic fuels.

Pd/ZnO is an excellent catalyst for methanol reforming in micro-scale reactors. In the literature, Cu/ZnO was the most common catalyst for methanol steam reforming. Cu/ZnO is an extremely active commercially available, non-PGM catalyst which in addition to methanol reforming is commercially used WGS, methanol and/or DME synthesis and other reactions. Pd/ZnO is a precious metal catalyst which can be used for the same type of reactions \(^{(1-3)}\). Advantages and disadvantages Pd/ZnO are in Table 4.1.

The rate equation and activation energy were fitted to the power law expression:

\[
(-r_A)(\text{mmol} / \text{kgcat} \cdot \text{s}) = 2.9047 \times 10^{10} e^{\frac{94800}{RT}} \left(\frac{P_{\text{MeOH}}}{P_{\text{H}_2 \text{O}}^{0.715}} \right)^{0.088}
\]

Which showed excellent correlation with experimental data.
<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Approximately the same activity for methanol steam reforming as Cu/ZnO (Chapter 2 and (1,4,5))</td>
<td>Precious metal</td>
</tr>
<tr>
<td>Water-gas-shift activity (2)</td>
<td>Methanation at temperatures &gt;450°C</td>
</tr>
<tr>
<td>Stable to temperatures &gt;450°C</td>
<td>Higher CO production than CuZnO</td>
</tr>
<tr>
<td>Non-pyrophoric</td>
<td></td>
</tr>
<tr>
<td>Stable with water at room temperature</td>
<td></td>
</tr>
</tbody>
</table>

A micro-scale radial flow reformer system with impinging methanol reforming and catalytic combustion reactors was shown to be a highly efficient design even for the low production levels (<1Wt hydrogen). The micro-scale reformer system integrated the catalytic methanol steam reforming reactor, catalytic combustor, fuel vaporizers and preheaters in a single design. The radial flow with the reactant inlet coming through the middle of the reactor allowed the product gases to vaporize and preheat the incoming methanol-water mixture on the methanol steam reformer side and the fuel-air mixture on the combustion side. This design allowed for heat recovery from the products without an external heat exchanger resulting in an effective and efficient integration of these unit operations into the system. Designing the methanol steam reformer and the catalytic combustor to be closely coupled and to have the
inlet flows essentially impinge on each other connected the highest temperature from the combustor to the area in the methanol reformer which had the highest temperature and energy need. The steam reformer design allowed a large temperature differential of almost 100°C from the hottest point to the coolest point at the exit. This was intentional to maximize the heat utilization in the reaction and to allow some water-gas-shift (WGS) reactions to occur. Lower temperatures in WGS reactions favor hydrogen production so they are desirable.

Three fuel processor system designs were made and tested. The initial baseline design had the smallest catalyst bed and successfully demonstrated the effectiveness of the design and was able to produce 200 mWt of hydrogen with 1.5% CO, achieve 9% thermal efficiency and operated at approximately 400°C. The total volume was approximately 0.1 cm³. Higher efficiencies were achieved by increasing the size, adding a packed bed catalyst section to the engineered catalyst area, and lowering the steam to carbon ration from 1.8:1 to 1.2:1. These changes increased the thermal efficiency from 9% to 15% and lowered the CO to 0.4-0.5% and the temperature to ~255°C with the same reactant feed flowrate. The flow rate could be increased by a factor of 4 resulting in 800 mWt hydrogen with 1% CO while still operating at lower temperatures (320°C) than the baseline. This improved performance translated to 33% thermal efficiency. The CO levels from these reactors were suitable for a medium temperature fuel cell such as PBI; however, lower CO levels would be needed for conventional PEM fuel cells. Thus a selective CO methanation reactor was added to the methanol reformer outlet. For PEM fuel cells, methane is inert and does not impact the performance. This approach would
consume some of the hydrogen produced, but in theory, heating value of the hydrogen could be re-captured by feeding the anode exhaust gas, which would contain the methane and any unreacted hydrogen to the combustor. CO methanation was selected since it was a passive solution to reducing CO compared to the more conventional preferential oxidation (PROX) approach. PROX reactors require a small amount of oxygen or air to be bled into the PROX reactor to preferentially oxidize CO to CO$_2$. The added complexity and parasitic power losses of the air supply were not desirable. The small selective methanation reactor was able to lower the CO to less than 100ppm with a slight increase in reactor temperature and decrease in thermal efficiency to 19%, while not substantially increasing the size of the entire fuel processor (<0.5cm$^3$) and did not require air addition. These results support the hypothesis that we could make a reactor <0.5cm$^3$ that produces <1 W equivalent of hydrogen at a thermal efficiency >10%.

The ultimate purpose of this reactor is for it to be combined with a fuel cell. A demonstration of this was done with a PBI based fuel cell provided by Case Western Reserve University. The baseline reformer output was sent to the fuel cell and successfully produced >20 mW$_e$ power (6). While not as much power as was anticipated, the test did show proof of concept. More details are available in Appendix E.

To better understand the methanol steam reformer reactor performance and to explore design variations a 3D model using COMSOL of the reactor was developed. The model used a novel way to include the effects of the methanol-water vaporization and phase change that was
hot previously reported in the literature. ChemCad® was used to determine the enthalpy and densities of the fluid from room temperature to temperatures in excess of the combustion temperatures. The enthalpy was used to calculate an effective Cp of the methanol-water mixture. Both the Cp and densities were used in the COMSOL model. Although not unexpected, the model was able to show that significant portions of the catalyst bed were not being fully utilized. Two reactor design variations were then explored using the model. The first was inclusion of multiple exit tubes. While some slight improvement of flow was determined, significant improvement in reactor performance was not achieved. The second variation was the inclusion of fins or baffles in the reactor. This significantly improved reactor performance at the same methanol-water feed rate by lowering the temperature required for complete conversion by 35°C. In addition, it also increased the reactor production capacity by 2.8x. The fins forced the reactants to take a longer path from the reactor entrance to the exit thus increasing the residence time and catalyst utilization. In addition, it was believed the fins increased mixing.

4.2 Future work

There are several areas of future work that should be further explored:

- Fuel processor scale up
- Jacketed reactor and combustion air siphon design
- Fuel cell integration and system development
Fuel processor scale up

The fuel processor currently is optimized for sub-watt scale power. The logical question would be how much can it be scaled-up? There are several limitations for methanol reforming. The heat in the reformer is primarily transferred by conduction between the combustor and the reformer and then by conduction and convection in the methanol reformer with conduction assumed to dominate. Therefore the thermal energy will be driven by the temperature differential between the reformer surface in contact with the combustor and the exit temperature. From the numerical model, it was determined that the reactor performance was hindered by heat transfer and that a larger diameter with a smaller $\Delta T$ between the reactor catalyst bed entrance and exit (therefore a thinner reactor) may perform better. The diameter of the reactor has less restrictions. Here the trick will be to avoid “hot spots” in the combustor which would be transmitted to the steam reformer. The hot spots for a catalytic combustor will occur where the concentration of the fuel and oxidant are highest and in contact with the catalyst (typically where the reactants enter the catalytic reactor). The “hot spots” can be mitigated in several ways. First would be to use staged catalyst design where multiple catalyst beds are used for the combustion. Each bed would be sized to burn only a fraction of the incoming fuel given the designed flow rates. This would spread out where the heat is released. The second mitigation strategy would be to increase the thickness of the plate between the combustor and the steam reformer. A thicker plate will spread the heat out more than a
thinner plate. With these approaches, in theory the steam reformer diameter will not be as limited as the steam reformer catalyst chamber thickness.

An excellent example of this was done by Wegeng et al. at PNNL\(^7,8\). They built a radial flow reactor (~5kW\(_t\)) that uses solar thermal energy to drive a methane steam reformer reactor operating at a target temperature of 700°C. The reactor is designed so the solar energy was focused directly onto the reactor. It was 27.3mm in diameter, 1.9 cm thick, with 6 mm deep reactor channels\(^7,8\). It has a very thick plate to distribute the heat and minimize hot spots. In addition, even though the channel is only 6mm deep, it still experiences a ΔT of 50-100°C. This is very consistent with the performance of the radial reactor discussed in this work. It illustrates that the reactor can be scaled by increasing the diameter and making the plate thicker to spread the heat out avoiding hot spots.

Figure 4.1. A) Radial methane steam reformer reactor with recuperative heat exchanger. B) Plate with catalyst inserts.
Jacketed reactor design

Heat loss is a major issue with micro-scale methanol reformers. In the current design there is still considerable heat in the combustor exhaust gases. One way to better utilize this heat is to have the exhaust gas wrap around the steam reformer. This would not only insulate the system, it would provide heat to the system. Figure 4.2 has a schematic of the proposed jacketed reactor design.

Figure 4.2 Jacketed reactor design. Notice the combustion exhaust gas wraps around the steam reformer providing heat and insulation

Models should be developed to determine if this design would improve the efficiency and to optimize it. In addition, there should be some modeling to determine the size of the methanation reactor and it should include fins in the methanation reactor similar to the steam reformer.
Another challenge for the micro-scale reformer system is how to provide the air to the combustor. One option that could be explored would be to create a siphon from the fuel feed to the combustor. Modeling could be used to determine if a strong enough siphon could be created. It is likely that in addition to modifying the inlet tube, modifications to the catalytic combustor design may be required. Finally, alternative fuels to methanol could be examined. Propane, butane, methane and other gaseous hydrocarbons have higher heating values and may make the system smaller. However, methanol has the advantage of being able to light off at room temperature whereas the other fuels require higher temperatures even with a catalyst. Some sort of ignition system could be employed, or a small amount of hydrogen could be mixed in with the gaseous fuel. The hydrogen would ignite and heat the catalyst so the other fuels could light off. Finally, fuel cells operating on reformate are typically design as a flow through system to prevent build-up of water and diluents. In these systems typically 80% of the hydrogen is consumed. For the low CO system, in addition to the hydrogen there will be a small amount of methane. In larger systems the methane and unused hydrogen is burned to provide heat for the fuel processor. This could also be explored via modeling.

Fuel cell integration and system development

While some proof-of-concept tests of integrating the fuel processor with the fuel cell have been done, further integration and testing is required. The PBI fuel cells are an attractive option in terms of not requiring CO clean-up; however, their high temperature operation could
be a problem. The exhaust gas from the combustor could be used to partially heat the fuel cell, but unless the fuel cell surface area and mass can be decreased, it is likely that additional thermal energy would be required. PEM fuel cells that operate at room temperature should also be explored.

In addition to the fuel cell, there are other balance-of-plant (BOP) components that need to be integrated. There will be a need for micro-valves, fuel tanks, controls, control electronics, a battery for start-up and perhaps peaking power, and, should the siphon not be effective, a blower. Fuel pumps can be avoided with a clever tank design. The tanks can be designed with a spring to provide pressure for liquid fuels and fuels with low condensation points such as butane. The pressurized tanks would be able to deliver the fuel without the need of a pump. The micro-valves will likely be on-off so the parasitic power draw will be minimal. Batteries will be required for start-up and peaking power. The control electronics can be integrated with the sensor electronics or other electronics for the device to be powered. This would minimize the size and power consumption. However, all of the control algorithms need to be developed. The control algorithms will need to be flexible since the power demands and power duty cycles of the electronics to be powered may vary widely.

While a great deal of progress has been accomplished in the development of the micro-scale fuel processor, there is still opportunity for further improvements. Given the rapid rate that personal electronics and micro-sensors continue to develop, as well as the lack of progress in battery improvements, there is a need for this type of small scale power.
Alternative use of micro channel architecture

For small scale power generation the designs need to be compact, have high mass and heat transfer rates, in order to meet the expectations of minimal volume, mass, and high efficiency. In this work, the characteristics of micro-channel based architectures were used to achieve these requirements and numerical modeling was used to propose improved designs. Low temperature waste heat recovery, particularly for mobile or transportable applications is another topic area that has similar requirements and could benefit from the work. A new waste heat recovery device is a multiferroic power. A multiferroic device (MFD) consists of a specialized magnetic material wrapped in a copper coil\(^9\). A change in temperature causes this material to change its magnetic field. Thus, following Faraday’s law, rapid temperature swings can cause the magnetic material to oscillate its magnetic field creating an electric current. This remarkable device can operate with a temperature swing as low as 20°C and temperatures <150°C making it perfect for low temperature waste heat recovery\(^9\). Microchannel architecture with its rapid heat transfer would be an ideal technology to provide the oscillating temperatures required for the MFD. One such microchannel based device is a pulsating heat pipe, which if designed correctly can have temperature oscillations as high as 20°C or more\(^{10}\). Current research in pulsating heat pipes is to minimize oscillations, so creating a pulsating heat pipe designed to maximize the oscillations would be a new area of research\(^{11-13}\). Numerical modeling should be used to develop a pulsating heat pipe with a temperature swing of 20°C or
more. In addition, the model can be used to identify where in the pulsating heat pipe the MFD should be integrated. Finally, a proof of concept integrated device could be built and tested based.
6.3 References


APPENDIX A. MICROFUEL PROCESSOR FOR USE IN A MINIATURE POWER SUPPLY

Jamelyn D. Holladay*, Evan O. Jones, Max Phelps, Jianli Hu
Battelle, Pacific Northwest National Laboratory, Richland, WA, USA

Abstract: A microscale fuel reformer for use with a miniature fuel cell has been built and operated at efficiencies that make them attractive for use as a miniature power supply for microelectronics. The fuel reformer and the results of initial tests are discussed. The fuel processor assembly consists of two vaporizer/preheaters, a heat exchanger, a combustor, and a steam reformer. Methanol was identified as a good candidate for use in the microscale reformer. A Pd/ZnO proprietary catalyst was developed to reform methanol. The catalyst was able to process a methanol water mixture (1:1 by weight) into a hydrogen-rich stream composed of 73–74 vol% H2, 25–26 vol% CO2, and 0.6–1.2 vol% CO on a dry basis. Almost 3 mols of hydrogen per mole of methanol reacted, which approached the theoretical maximum. An integrated fuel processor that used proprietary catalyst in the reformer and catalytic combustion to provide the heat was designed and built. The reformer and combustor were each less than 5 mm³ in volume and the entire fuel processor had a volume less than 0.4 cm³.

* Corresponding author. Present address: P.O. Box 999 MS K2-12, Richland, WA, USA 99352. Fax: +1-509-372-4732. E-mail address: jamelyn.holladay@pnl.gov (J.D. Holladay).

When 100 mW of hydrogen was produced, a thermal efficiency of 9%, or an estimated 4.5% net efficiency (including a hypothetical fuel cell), was achieved.

**Keywords:** Fuel reformer; Microscale power; Microdevice; MEMS; Fuel cell; Hydrogen generation

### A.1. Introduction

Supplying power to microelectronic devices for remote and autonomous operation has proven to be a formidable challenge [1,2], as current battery technology does not provide the energy densities needed to sustain power for extended periods. Even lithium-ion battery technology can only produce an energy density of 0.15 kW\textsubscript{e}-hr/kg, and, while expected to achieve 0.2 kW\textsubscript{e}-hr/kg in the next few years [3], Li-ion still will not come close to the potential energy densities that can be reached through thermal conversion of hydrocarbon fuels. Table A.1 shows a comparison of current practical battery technology and expected future energy densities.

In this paper, a miniature power supply technology is described that is based on hydrocarbon fuel sources. This technology, being developed by Battelle Pacific Northwest Division (Battelle) and Case Western Reserve University (CWRU), combines a miniature fuel cell (1–2 cm\textsuperscript{2}) with a micro hydrocarbon fuel reformer. Since hydrocarbons have much higher energy densities than batteries (e.g. 5.6 kW\textsubscript{t}-hr/ kg for methanol and 12.6 kW\textsubscript{t}-hr/kg for...
butane), converting the thermal energy in hydrocarbons to electricity with efficiencies even as low as 5% would result in devices with energy densities equivalent to current Li-ion batteries.

Table A.1. Current practical battery technology [4] and hydrocarbon energy densities.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Energy Density (kWe-hr/l)</th>
<th>Specific Energy (kWe-hr/kg)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Cells</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkaline</td>
<td>0.330</td>
<td>0.125</td>
<td>-</td>
</tr>
<tr>
<td>Zn-Air</td>
<td>1.050</td>
<td>0.340</td>
<td>-</td>
</tr>
<tr>
<td>Li/SOCl₂</td>
<td>0.700</td>
<td>0.320</td>
<td>-</td>
</tr>
<tr>
<td>Secondary Cells</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead Acid</td>
<td>0.070</td>
<td>0.035</td>
<td>Rechargeable</td>
</tr>
<tr>
<td>Ni-Cad</td>
<td>0.055</td>
<td>0.035</td>
<td></td>
</tr>
<tr>
<td>Ni-Metal Hydride</td>
<td>0.175</td>
<td>0.050</td>
<td></td>
</tr>
<tr>
<td>Li-ion</td>
<td>0.200</td>
<td>0.120</td>
<td></td>
</tr>
<tr>
<td>Li-polymer</td>
<td>0.350</td>
<td>0.200</td>
<td>Anticipated</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>4.384</td>
<td>5.6</td>
<td>Thermal energy</td>
</tr>
<tr>
<td>Butane</td>
<td>7.290</td>
<td>12.60</td>
<td>Thermal energy</td>
</tr>
<tr>
<td>Iso-Octane</td>
<td>8.680</td>
<td>12.34</td>
<td>Thermal energy</td>
</tr>
</tbody>
</table>
The technology discussed here is targeting efficiencies of 5% or greater using hydrocarbon fuel sources. This paper concentrates on the fuel reformer, which incorporates Battelle’s technology advancements in microchemical and thermal systems [5–12]. Tests were conducted with various catalysts, and the best suited catalyst was selected for testing in an engineered system with methanol as the hydrocarbon fuel.

A.2. Fuel processor overview

A typical fuel processor is composed of five unit operations: fuel vaporizers/preheaters, fuel reformers, clean-up (carbon monoxide) unit(s), heat exchangers (recuperators), and combustor. Pumps, blowers, valves, insulation and other miscellaneous peripheral devices are needed to feed the fuel, water, air, and to ensure the device operates properly. Fig. 2.1 is a schematic of a representative system.

![Fuel processor schematic](image)

Figure A.3. Fuel processor schematic.
A.2.1. Fuel reformer

The heart of a fuel processor system is the fuel reformer, which is a catalytic reactor where the hydrogen is stripped from a hydrocarbon fuel. A general fuel processing equation is:

\[ \text{C}_a\text{H}_b\text{O}_c + y(\text{O}_2 + 3.76 \text{ N}_2) + (2a - x - 2y - c) \text{ H}_2\text{O} = x\text{CO} + (a - x) \text{ CO}_2 + (2a - x - 2y - c + (b/2))\text{H}_2 + 3.76y\text{N}_2 \]  
(A.1)

Where the specific equation is dependent on the fuel type and the reforming technology. Typical reforming technologies for processing hydrocarbon fuels include partial or preferential oxidation, autothermal reformation, and steam reforming [13]. Both preferential oxidation and autothermal reformation introduce oxygen (air) into the system and burn with the reforming fuel to produce the heat required for the reforming reaction(s) to occur. In steam reforming, an external combustor is used to provide the heat. While each technology has advantages and disadvantages [13], steam reforming was applied in this work because it offers the highest theoretical efficiency and provides the highest hydrogen composition. These conditions may improve fuel cell performance in the product gas stream (reformate) compared with preferential oxidation and autothermal reforming [13,14]. With the reforming technology selected, we can simplify Eq. (A.1) so it is only dependent on the fuel type:

\[ \text{C}_a\text{H}_b\text{O}_c + (2a - x - c)\text{H}_2\text{O} = x\text{CO} + (a - x)\text{ CO}_2 + (2a - x - c + (b/2))\text{H}_2 \]  
(A.2)
For a miniature power supply, all the water needed for the reforming would likely be carried on the system. The water weight should therefore be included in the energy calculation of the hydrocarbons, as depicted in Table A.2. For comparison purposes, the ideal minimum amount of water required for the hydrocarbon conversion was used in these calculations. The methanol water mixture has an energy density greater than that of the other hydrocarbon/water mixtures.

Table A.2. Fuel processor feed energy density (hydrocarbon + water)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Steam to carbon ratio</th>
<th>Energy (kWt-hr/l)</th>
<th>Energy (kWt-hr/kg)</th>
<th>Reforming Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>1</td>
<td>2.810</td>
<td>3.290</td>
<td>300 – 400</td>
</tr>
<tr>
<td>n-butane</td>
<td>2</td>
<td>2.571</td>
<td>3.110</td>
<td>450 – 650</td>
</tr>
<tr>
<td>n-octane (gasoline)</td>
<td>2</td>
<td>2.670</td>
<td>2.990</td>
<td>550 – 750</td>
</tr>
</tbody>
</table>

Methanol was selected for the initial testing because it reformed at the lowest temperatures. The reforming temperature is important since the heat loss from such a small device is considerable. With methanol selected as the fuel, the reforming reaction can be further simplified to Eq. (A.3):
From the above reaction, it is clear that to maximize the hydrogen production, the carbon monoxide production must be minimized. If no carbon monoxide is produced, the molar ratio of hydrogen produced to methanol fed to the reactor would be 3:1. Carbon monoxide removal is discussed in Section A.2.2.

### A.2.2. Reformate clean-up

The reformate stream is composed of hydrogen, carbon dioxide, and carbon monoxide. Fuel cells operate best on pure hydrogen, but can tolerate carbon dioxide and some other gases such as nitrogen. However, the typical PEM fuel cell can tolerate only 10–20 ppm carbon monoxide [15]. Consequently, researchers are looking at ways to produce PEM fuel cells with a higher CO tolerance [15, 16]. While CWRU has developed a fuel cell that can tolerate up to 5 vol% CO in their hydrogen feed stream, which reduces the clean-up requirements of the reformate stream significantly, for proper fuel cell operation, the carbon monoxide levels in the reformate stream still must be lower than 5 vol% [17]. Typically this clean-up is accomplished in one of two ways. The first method is a multi-step process consisting of water gas shift reactors, combined with selective oxidation and/or carbon monoxide methanation [13]. The second clean-up method is through the use of a hydrogen-permeable membrane [13].
A.3. Experimental results and discussion

Screening tests were conducted to determine which catalyst formulation would offer the best performance for the system. The selected catalyst was then engineered into an integrated steam reformer unit, and a second set of tests was performed to determine the efficiency of the engineered unit.

A.3.1. Catalyst screening tests

The key component of the reformer reactor is the catalyst. Battelle has developed novel ways of engineering catalyst monoliths that allow high mass transfer rates at a low pressure drop [18]. The catalyst supports are specially engineered foam supports from pure metals, alloyed metals, or ceramics. The foams have a very high porosity (10–100 pores/inch) and large pore sizes (<200 µm), which provide the high mass transfer rates. For more conventional catalytic systems, mass transfer is the rate-limiting step, so relatively large devices are required to maximize throughput, and high activity catalysts are not required. By using Battelle’s engineered catalyst monoliths, high activity catalysts can be used to assemble much smaller devices that are capable of maintaining comparable processing rates.

In addition, Battelle has developed its own proprietary Pd/ZnO on Al₂O₃ catalyst for methanol reforming. All catalysts were fabricated in house. The catalyst was tested over a
temperature range of 250–450°C. Distilled de-ionized water was added to the fuel to make a mixture with the desired molar ratio of steam to carbon. The first test was to determine an optimal steam to carbon ratio for methanol processing. The catalysts were tested over a range of molar steam to carbon ratio from 3:1 to pure methanol, and a contact time (CT) of approximately 100 ms, except for the flow of pure methanol (Fig. A.2). The reforming temperature of 360°C at a steam to carbon ratio of 1.8:1 was found to be the lowest temperature required to obtain >99% conversion. No significant change in the reformate composition was observed. The multiple contact times were also tested to determine the effect of longer contact on the reaction. As expected, with an increase in contact time, the temperature required to achieve >99% conversion also decreased (Fig. A.3).

The conversion was calculated by doing a carbon balance on the effluent. A commercial catalyst (Cu/Zn on alumina) was also tested for comparison. Under identical conditions, steam to carbon ratio of 1.8:1 and contact time of 300 ms, the Battelle catalyst was able to convert >99% of the methanol fed to the reactor at a lower temperature of 320°C compared to 420°C required to achieve >99% methanol conversion with the commercial catalyst (Fig. A.4). As well as requiring higher temperatures to obtain >99% conversion, the reformate of the commercial catalyst had much higher CO levels than that from the Battelle catalyst (Table A.3). During the tests, the commercial catalyst produced approximately 2 mols hydrogen for each mol of

---

2 Conversion >100% was sometimes calculated when the carbon did not balance. This was attributed to experimental error and slight variations in flow (pulsing) from the pumps, which was observed.
methanol reacted. In contrast, the reformate from the Battelle catalyst had a significantly higher percentage of hydrogen, a lower percentage of carbon monoxide, and no methane produced. Furthermore, the Battelle Pd/ZnO catalyst resulted in 2.7–2.8 mols of hydrogen produced for each mol methanol reacted, which approaches the ideal of 3 mols as calculated from Eq. (A.3). This higher purity of hydrogen results in superior fuel cell performance over lower purity hydrogen.

![Graph showing the effect of steam to carbon ratio on the Pd/ZnO catalyst performance. The steam to carbon ratio of 1.8:1 appeared to give the best results. (See footnote 2).](image)

Figure A.4. Effect of steam to carbon ratio on the Pd/ZnO catalyst performance. The steam to carbon ratio of 1.8:1 appeared to give the best results. (See footnote 2).

---

3 Methane is produced by the reaction: $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$
Figure A.5. Effect of contact time on methanol reforming with the Pd/ZnO. As expected, longer contact times allowed lower processing temperatures. (See footnote 2).

Table A.3. Typical reformate dry gas composition from Battelle’s Pd/ZnO catalyst and Cu/Zn catalysts with water + methanol (S:C 1.8:1) as fuel

<table>
<thead>
<tr>
<th>Gas</th>
<th>Battelle Pd/ZnO</th>
<th>Cu/Zn on alumina catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H₂)</td>
<td>73.5%</td>
<td>65.9%</td>
</tr>
<tr>
<td>Carbon Dioxide (CO₂)</td>
<td>25.8%</td>
<td>22.5%</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>0.7%</td>
<td>3.1%</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>0.0%</td>
<td>8.5%</td>
</tr>
<tr>
<td>Moles H₂/moles methanol reacted</td>
<td>&gt;2.9</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Figure A.6. Comparison of Pd/ZnO (Battelle’s catalyst) with Cu/Zn on alumina (commercial) catalyst at steam to carbon ratio of 1.8:1 and 300 ms contact time. Lower temperature was required to achieve 100% methanol conversion on the Battelle catalyst compared to the commercial catalyst tested.

A.3.2. Integrated fuel reformer system

The integrated fuel processor test system was built in house and was composed of five unit operations: two vaporizers/preheaters, a reformer, catalytic combustor, and heat exchanger (Fig. A.5). The device was built using 316 stainless steel, but could also be built of high temperature ceramics. The fabrication, assembly and testing were all done in house. The
heat for liquid vaporization, gas preheating, and for the reforming reaction(s) was provided by catalytic combustion of hydrogen or methanol. Both the reformer and the combustor had volumes less than 0.5 cm³. The reformer had a capacity of 200 mW, while the combustor had a capacity of up to 3 W. The oversized combustor capacity allowed a wide range of operating conditions to be examined, and a thermal couple was inserted into the combustor to monitor the device temperature. The total device volume was less than 0.4 cm³. Calculations indicated that a temperature difference between the combustor and steam reformer would be only a couple of °C, which is within the error of the thermocouple.

The system was mounted inside a larger tube for testing. The larger tube provided support to the extremely thin inlet and outlet tubes to the device. Additional equipment was connected to the test stand, including syringe pumps, gas controllers, vapor liquid separation units, and an on-line gas chromatograph (Fig. A.6). The methanol water mixture was fed to the reformer via syringe pumps at rates of 0.02 – 0.1 cm³/hr (20°C basis), and pure methanol to the combustor at rates of 0.1–0.4 cm³/hr (20°C basis). About 8–20 sccm of air were fed to the combustor, depending on the reaction conditions. The product reformate gases were fed to an online micro gas chromatograph (Agilent QuadH), via a Dri-rite tube, which eliminated any water vapor.

The reformer was operated over a wide range of conditions. To achieve 100% conversion, operating temperatures greater than 400°C in the combustor were required. These temperatures were higher than anticipated, and were attributed to the internal flow patterns,
faster contact times than used in the catalyst screening tests, and thermal losses to the environment. Two hundred mWt power was achieved with a thermal efficiency of 9.6%. The thermal efficiency was calculated by dividing the lower heating value of the hydrogen in the reformate stream by the total heating value of the methanol fed the reformer plus the heating value of the fuel fed to the combustor (equation A.4).

\[
\text{Efficiency} = \frac{\Delta H_c \text{ hydrogen}}{\Delta H_c \text{ reformer+combustor methanol feed}} \tag{A.4}
\]

Where \( \Delta H_c \) is the lower heat of combustion of hydrogen or methanol as indicated.

The anticipated electrical power from a fuel cell powered by this stream can be found by multiplying the thermal power by the net fuel cell efficiency. Typical fuel cells operate at 60% efficiency and utilize 80-85% of the H\(_2\) in a reformate stream for a net efficiency of \( \approx 50\% \). Thus, it is anticipated that a fuel cell utilizing the reformate from this device could provide \( \approx 100 \text{ mW} \), and the system (reformer + fuel cell) would have an efficiency of \( \approx 4.8\% \). As the reformer output was decreased, the efficiency also decreased. For example, when the reformer produced 70 mWt (\( \approx 35 \text{ mW} \)), the efficiency decreased to 6% (\( \approx 3\% \) net). This result was expected since the thermal losses as a percent of the total amount of power fed to the device increases as the size is decreased.

In theory, the efficiency of the system could be improved by feeding the unreacted hydrogen from the fuel cell back to the combustor. Yet, the resultant efficiency would be
4.94\% or an increase of only 2.8\% from the original, assuming no additional heat loss due to the extra manifolding required recycle the hydrogen. This small increase in efficiency is not sufficient to make such integration appealing, especially since, in reality, the recycle manifolding would most likely increase the heat loss of the system. Instead, an improved design will more likely provide the efficiency desired. Since the system was operated at temperatures close to the reforming temperature of some hydrocarbons, designing an improved system will include the feasibility of reforming higher hydrocarbons.

Figure A.7. Integrated fuel processor system. It is 0.15” in diameter and 0.25” in length (Appendix G).
A.4. Summary and conclusions

A high-energy power supply is being developed that provides more extended operating times and efficiencies for microelectronic devices than conventional battery technologies. An integrated methanol fuel reformer system has been designed and built. Screening tests were first conducted to determine the best catalyst performance for the reformer. The results from the catalyst testing showed that the Battelle catalyst was superior to the commercial catalyst tested for comparison, Cu/Zn on alumina. Initial testing of the engineered fuel reformer system resulted in the production of 200 mW of hydrogen at a high efficiency of 9% utilizing methanol as fuel. The reformate stream was composed of 73–74% hydrogen, with 25–26% carbon dioxide and carbon monoxide constituting the rest. The device approached the ideal conversion ratio of
3 mols hydrogen produced per mol of methanol reacted. A complete system would consist of liquid and gas delivery systems, valves, packaging, and integration with a fuel cell.

Acknowledgements

This work was supported in part by Defense Advanced Research Projects Agency contract # DABT63-99-C-0039. Their support is gratefully acknowledged.
A.5 References


APPENDIX B. HIGH EFFICIENCY AND LOW CARBON MONOXIDE MICRO-SCALE METHANOL PROCESSORS

J.D. Holladay, E.O. Jones, R.A. Dagle, G. Xia, C. Cao, Y. Wang

aPacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99352, USA
bVoiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA, 99163, USA

Abstract

A micro-scale power supply is being developed to provide an alternative to current secondary batteries for use in microelectronics devices, such as microsensors. The work discussed in this paper expands on this earlier reported sub-watt power generation system. Two designs were evaluated: a processor optimized to improve the thermal efficiency of the methanol reforming reactor from 9 to above 20%, and a system tailored to decrease the carbon monoxide levels to below 500 ppm, preferably lower than 100 ppm. Each design was operated over a range of feed flow rates. Thermal efficiencies up to 33% were demonstrated with the optimized processor, likely as a result of the low operating temperature, high methanol concentration (~60 wt.%) in the feed, and the high hydrogen production. Up to 3.55 sccm hydrogen was produced with

---


2 Corresponding author. Fax: +1-509-376-5106. E-mail address: jamelyn.holladay@pnl.gov (J.D. Holladay)
relatively low carbon monoxide. In the second design, significant decreases in carbon monoxide, in some cases below 100 ppm, were achieved while maintaining reasonable thermal efficiencies of up to 19%.

**Keywords:** Microreactor; Fuel processing; Methanol reformer; Fuel cells

**B.1. Introduction**

In recent years, there has been considerable interest in the development of miniature sub-watt electric power generation using hydrocarbon fuels [1–9]. This research mainly focused on creating a power supply with greater energy density than the secondary batteries currently in microelectronic devices, such as microelectromechanical systems (MEMS) and microsensors. Due to the high energy density of hydrocarbons (e.g., methanol $\sim 5.6$ kWh/kg compared to lithium-ion batteries $\sim 0.12$ kWh/kg), even a very inefficient chemical to electrical energy conversion device could be a significant improvement over the available secondary battery technology [9]. The new technologies range from thermal electric generators embedded in micro-scale combustors to silicon-based MEMS rotary engines [4,6].

In previous papers, we reported the development of a sub-watt power generation system based on a micro-scale methanol processor and a miniature fuel cell [9,10]. The micro-scale processor described previously consisted of two vaporizers, a heat exchanger, a catalytic combustor and a methanol reformer [9]. The methanol reformer reactor was less than 5mm$^3$. The total volume of this device was less than 0.4 cm$^3$, with a weight of less than 1 g, and could
be operated without any external heating. The product gas was composed of 73–74% hydrogen, 25–26% carbon dioxide, and the remainder carbon monoxide. The thermal efficiency was calculated to be approximately 9% by dividing the lower heating value of the product hydrogen by the lower heating value of the methanol fed to the reformer and the fuel fed to the combustor (Eq. (3.1)):

\[
\text{Efficiency} = \frac{\Delta H_c \text{ hydrogen}}{\Delta H_{\text{reformer+combustor methanol feed}}} \tag{B.1}
\]

The major limitation on the thermal efficiency was heat loss due, primarily, to conduction. For a reactor of this small this size, the performance was notable; however, improvements in efficiency and a significant lowering of the carbon monoxide would greatly increase the device’s viability.

This paper discusses the performance of two next-generation micro-scale methanol processors. The first processor consisted of an optimized design to improve the thermal efficiency of the methanol reforming reactor from 9 to above 20%. The second design investigated the possibility of decreasing the carbon monoxide levels from the originally reported 1–2% to below 500 ppm, preferably lower than 100 ppm.
**B.2. Experimental**

**B.2.1. High thermal efficiency micro-scale methanol processor**

The fuel processor, Fig. B.1, was composed of the same unit operations as the earlier device. This second generation processor was constructed of 316 stainless steel, but could also be built of high-temperature ceramics. The fabrication, assembly, and testing were all performed in-house.

The combustor had a volume of less than 5mm$^3$, the reformer had a volume of less than 50mm$^3$, and the fuel processor had a volume of less than 0.4 cm$^3$ with a mass of less than 1 g. Proprietary catalysts developed in-house were used in both the catalytic combustor and reformer. The reformer feed was a methanol–water mixture with a 1:1.2 molar ratio (∼60 wt.% methanol). A 0.01 in. thermocouple was inserted into the combustion reactor to monitor the device operation temperature. Liquid fuel was fed using syringe pumps at rates from 0.03 to 0.2 cc/hr (20 °C basis). At these low flow rates the average flow was consistent, but slight variations of flow (pulsing) were observed. The combustion fuel was either methanol or hydrogen. Between 10 and 25 sccm air was fed to the combustor, depending on the needed reactor temperatures. After water vapor was removed from the reformate, using Dri-rite, the product gases were analyzed with an on-line micro gas chromatograph (Agilent QuadH).
Figure B.1. Second generation micro-scale fuel processor—high efficiency. The diameter is 0.25” and the length is 0.38” (Appendix D). Volume is < 0.4cm³.

B.2.2. Carbon monoxide reduction

The carbon monoxide was removed by selectively reacting it with hydrogen to form methane. A separate reactor was added to the fuel processor for the methanation step (Fig. B.2). The methanation reactor was built of 316 SS and had a volume of less than 0.1 cm³. The total volume of the processor plus methanation reactor was less than 0.5 cm³ and still weighed less than 1 g. A proprietary selective carbon monoxide methanation 3 wt% Ru on Al₂O₃ catalyst was fabricated in-house using a method described in ref [11]. The completed system was composed of six unit operations: two vaporizers, a heat exchanger, a catalytic combustor, a steam reformer, and a methantion reactor. The liquid feeds, gas feeds, and product gas analysis were the same as above. The low carbon monoxide was measured using an infrared gas analyzer (ZRH, California Analytic Instruments).
Figure B.2. Second generation micro-scale fuel processor with CO removal reactor. The methanation section adds 0.075” in length and is 0.028” in diameter (Appendix G). The total volume is <0.5 cm³.

**B.3. Results and discussion**

**B.1. High thermal efficiency micro-scale methanol processor**

The reactor was operated over a wide range of feed flow, i.e., 0.05–0.2 cc/hr. Table B.1 and Fig. B.3 summarize of the reactor performance. At similar feed rates, the new design achieved >99% methanol conversion at significantly lower temperature. The conversion was calculated by performing a carbon balance on the effluent. The capacity of the device was increased by a factor of 4, while still maintaining low temperatures. Low methanol reforming temperatures favor the production of carbon dioxide over carbon monoxide, which was evident in these data.
High thermal efficiencies from 15 to over 30% were achieved. The high efficiencies were ascribed to the lower operating temperatures, the low steam to carbon ratio of 1.2:1 compared to 1.8:1, and the higher capacity. The lower operating temperatures significantly decreased thermal losses, leading to higher efficiencies. The low steam to carbon ratio decreased the amount of water that needed to be vaporized and heated, decreasing the heat duty. Finally, the thermal efficiency increased with higher production as expected. In other words, the thermal losses as a percentage of the thermal power of the hydrogen produced should decrease with increased power.

Figure B.3. High efficiency reactor performance
B.2. Carbon monoxide reduction

The integrated fuel processor/carbon monoxide methanation reactor was operated with feed rates from 0.05 to 0.15 cc/hr. Higher operation temperatures were required to achieve >99% methanol conversion. It was also observed that the carbon monoxide levels did not decrease until >95% conversion was achieved. It is hypothesized that methanol decomposes on the methanation catalyst, thus producing methane, carbon dioxide and carbon monoxide. Table B.2 and Fig. B.4 summarize the results.3

Carbon monoxide reduction was achieved at all flow rates, with <100 ppm CO being achieved at flow rates of 0.05 cc/hr. However, a significant decrease in thermal efficiency also occurred. The efficiency loss was caused by higher operating temperatures and also a loss of hydrogen to methane and water from the carbon monoxide cleanup reactors. The methane levels indicate that some carbon monoxide was being methanated in addition to the carbon monoxide. It is estimated that approximately 13–15% of the hydrogen was consumed in the methanation reactor, much higher than the anticipated 7–10%. The high methane production was likely due to methanator operation at higher than ideal temperatures (220–270 °C) for selective carbon monoxide methantion. A reactor model is being developed to determine the temperature distribution and also to optimize the design.

3 Conversion >100% was sometimes calculated when the carbon did not balance. This calculation was attributed to experimental error and slight variations in flow (pulsing) from the pumps, which was observed.
Table B.1. Fuel processor performance at >99% methanol conversion.

<table>
<thead>
<tr>
<th>Feed Rate (cc/hr)</th>
<th>T (°C)</th>
<th>Reformate Flow (sccm)</th>
<th>Hydrogen (%)</th>
<th>Carbon Monoxide (%)</th>
<th>Carbon Dioxide (%)</th>
<th>Thermal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>255</td>
<td>1.2</td>
<td>73 – 74</td>
<td>0.4 - 0.6</td>
<td>25 – 26</td>
<td>15</td>
</tr>
<tr>
<td>0.08</td>
<td>263</td>
<td>2.0</td>
<td>73 – 74</td>
<td>0.5 – 0.7</td>
<td>24 – 26</td>
<td>21</td>
</tr>
<tr>
<td>0.12</td>
<td>270</td>
<td>3.0</td>
<td>73 – 74</td>
<td>0.5 – 0.6</td>
<td>25 – 26</td>
<td>25</td>
</tr>
<tr>
<td>0.15</td>
<td>313</td>
<td>3.8</td>
<td>72 – 73</td>
<td>0.6 – 0.7</td>
<td>25 – 27</td>
<td>28</td>
</tr>
<tr>
<td>0.2</td>
<td>340</td>
<td>4.9</td>
<td>72 – 73</td>
<td>1.0 – 1.1</td>
<td>25 – 26</td>
<td>33</td>
</tr>
<tr>
<td>Original Processor [9]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>400</td>
<td>1.1</td>
<td>73 – 74</td>
<td>1.0 - 2.0</td>
<td>25 – 26</td>
<td>9</td>
</tr>
</tbody>
</table>

190
Table B.2. Methanol processor with integrated carbon monoxide reactor performance.

<table>
<thead>
<tr>
<th>Feed Rate (cc/hr)</th>
<th>T (°C)</th>
<th>Reformate Flow (sccm)</th>
<th>Hydrogen (%)</th>
<th>Carbon Monoxide (ppm)</th>
<th>Carbon Dioxide (%)</th>
<th>Methane (%)</th>
<th>Thermal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>304</td>
<td>1.0</td>
<td>69 – 70</td>
<td>&lt; 100</td>
<td>25 – 25.5</td>
<td>5.0 – 5.5</td>
<td>9.5</td>
</tr>
<tr>
<td>0.08</td>
<td>323</td>
<td>1.65</td>
<td>69 – 70</td>
<td>&lt; 200</td>
<td>25 – 25.5</td>
<td>6.0 – 6.2</td>
<td>14</td>
</tr>
<tr>
<td>0.10</td>
<td>330</td>
<td>2.1</td>
<td>69 – 70</td>
<td>&lt; 200</td>
<td>25 – 25.5</td>
<td>6.0 – 6.2</td>
<td>17</td>
</tr>
<tr>
<td>0.15</td>
<td>345</td>
<td>3.1</td>
<td>68 – 69</td>
<td>&lt; 300</td>
<td>25 – 26</td>
<td>5.3 – 6.0</td>
<td>19</td>
</tr>
</tbody>
</table>

Figure B.4. Low carbon monoxide fuel processor performance

---

191
B.4. Conclusions

A micro-scale power supply is being developed to power microelectronics such as microsensors. A miniature methanol fuel processor that has thermal efficiencies up to 33% has been demonstrated. It is believed that the low operating temperature, high methanol concentration (\(\sim 60\) wt.\%) in the feed, and the high hydrogen production contributed to the thermal efficiency. The fuel processor was able to produce up to 3.55 sccm hydrogen with relatively low carbon monoxide. For use with conventional fuel cell technology a catalytic carbon monoxide cleanup reactor was integrated onto the fuel processor. Significant decreases in carbon monoxide, in some cases below 100 ppm, were achieved while maintaining reasonable thermal efficiencies of up to 19%.

Acknowledgements

This work was supported in part by Defense Advanced Research Projects Agency contract #DABT63-99-C-0039. Their support is gratefully acknowledged.
B.5 References


APPENDIX C. KINETIC STUDIES OF METHANOL-STEAM REFORMING OVER PD/ZNO CATALYST USING A MICROCHANNEL REACTOR

Chunshe Cao\textsuperscript{a}, Gordon Xia\textsuperscript{a}, Jamie Holladay\textsuperscript{a,b}, Evan Jones\textsuperscript{a}, and Yong Wang\textsuperscript{a,b}

\textsuperscript{a}Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99352

\textsuperscript{b}Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA, 99163, USA

Abstract

A microchannel reactor with effective heat exchange has been developed to evaluate catalyst performance and measure reaction kinetics. The reactor provides an isothermal environment for rate measurement of the endothermic methanol steam reforming reactions over a Pd/ZnO catalyst in a wide temperature range (160°C to 310°C). The apparent activation energy and rate equation have been determined to fit the power law expression:

\[
(-r_A)(\text{mmol/kgcat} \cdot \text{s}) = 2.9047 \times 10^{10} e^{\frac{94800}{RT}} P_{\text{MeOH}}^{0.715} P_{\text{H}_2\text{O}}^{0.088}
\]

\textsuperscript{1} Published in Applied Catalysis. Cao C., G. Xia, J.D. Holladay, E.O. Jones, and Y. Wang. \textbf{2004}. "Kinetic studies of methanol steam reforming over Pd/ZnO catalyst using a microchannel reactor." \textit{Applied Catalysis. A, General} 262(1):19-29
This result provides kinetic data for the design of a miniature fuel processor for small fuel cell applications. The rate equation has been applied to a three-dimensional pseudo homogeneous model to simulate temperature profiles in both microchannel and conventional fixed bed reactors.

Keywords: Kinetics, Methanol steam reforming, Microchannel reactor, Pd/ZnO catalyst

C.1. Introduction

Hydrocarbons such as gasoline, diesel, methanol, and ethanol have much higher energy densities than batteries in powering microelectronic devices[1,2]. However, optimizing the use of these energy sources requires a highly efficient fuel processor that extracts hydrogen from these fuels by processes such as catalytic steam reforming. The technology discussed here centers on the development of a miniature fuel processor for a small fuel cell application (<500mW), whereby a clean hydrogen-rich gas stream is generated with multistage processes (fuel vaporization, steam reforming, carbon monoxide reduction) within the integrated device[3]. For this technology, methanol was selected as the hydrogen source due to its “sweetness” (sulfur free) and readiness of being activated at relatively low temperature (under 250 °C). Low-temperature operation in such a miniature power device reduces the heat loss and insulation, thus improving the power density of the entire system.
As part of the development work, kinetic measurements of the methanol steam reforming reaction were made to provide the direct rate information needed for reactor design and optimization. Kinetic data are conventionally collected from fixed bed reactors, typically a quartz micro-tubular reactor heated in a furnace. However, a significant drawback in such experiments is the non-isothermality of the catalytic bed caused by the strongly endothermic steam reforming reaction. In this paper, a microchannel integral reactor is developed to provide a completely isothermal environment to evaluate catalysts and measure intrinsic kinetics.

In determining kinetics, it is of utmost importance that the catalyst be evaluated at conditions that are free of concentration and temperature gradients in the reactor. However, achieving this goal is often difficult due to substantial heat demands in many exothermic or endothermic chemical reactions. In such cases, a significant degree of coupling of transport phenomena with chemical reactions occurs, which leads to complications and difficulties in characterizing intrinsic catalyst activity. Temperature gradients in a packed bed catalytic reactor with endothermic reactions, known as “cold spots,” usually result in underestimation of the catalyst activity. For highly endothermic chemical reactions, such as steam reforming of methanol, temperature and concentration may vary considerably from point to point in a packed catalyst bed. Typically, a temperature profile in a catalytic reactor shows a large heat sink in the inlet zone of the bed because of a high reaction rate. These local cold spots can cause low local carbon conversion and less hydrogen yield. Analysis of the integrated data obtained from such a system indicates transport limitations and introduces complexity to
intrinsic kinetic measurements. For practical applications such as fuel processing, this also suggests that a tremendous portion of the catalyst in the conventional fixed bed is not utilized efficiently. In such cases, without decreasing the space velocity, the reforming reactor must be operated at high temperature to achieve high conversion. However, in addition to the increased energy loss to the environment and the potential of catalyst deactivation, this high-temperature operation possibly generates more carbon monoxide which is favored at high temperature. The high carbon monoxide concentration in the reformate increases the load to the catalytic carbon monoxide clean-up portion of the device and potentially poisons the fuel cell electrodes. Therefore, maintaining temperature uniformity in this process becomes critical in improving hydrogen one-pass productivity and selectivity.

Previous kinetic studies have mainly focused on Cu-based catalysts[4-9]. It is believed that methanol is dehydrogenated to methyl formate over Cu catalysts[6,7,10-12]. This mechanism seems to explain why Cu catalysts exhibit high selectivity in steam reforming of methanol. However, Cu-based catalysts have poor thermal stability and are pyrophoric, which are not suitable for fuel cell applications. Recent catalyst development in our laboratory[1,13-15] and elsewhere[10-12,16] has verified that Pd supported on ZnO exhibits high activity and selectivity in producing hydrogen with a comparable amount of carbon monoxide formation versus Cu-based catalysts. It is non-pyrophoric and has an advantage in thermal stability over the Cu-based catalyst [13]. Different reaction mechanism in steam reforming of methanol may exist for the Pd/ZnO catalysts [10,12,16]. However, kinetic data for these new catalysts have
not been reported. In this paper, a microchannel reactor is used to provide accurate intrinsic kinetic information without heat and mass transport limitations over the highly active Pd/ZnO catalyst, as well as the empirical rate equation for reactor design.

C.2. Experimental

A microchannel reactor system with active heat exchange has been developed to decouple transport phenomena with chemical reactions for intrinsic kinetics study. The application is especially important to keep isothermal conditions in the catalyst bed for highly endothermic reactions. This reactor provides high heat transfer efficiency, incorporating a built-in preheating zone, and accurate catalyst bed temperature measurement. Figure C.1 shows schematics of the reactor assembly. The catalytic portion of the reactor is a microchannel slot with the gap width of 0.508mm. The catalyst is located in the lower portion of the channel so that the reactants can be preheated to a desired temperature in the upper portion of the channel before entering the catalyst bed. The microchannel is “sandwiched” by two separated oil-heating channels, which are designed to allow oil to circulate at a high rate and maintain a high heat transfer coefficient at the same time.
Figure C.1. Reactor assembly

A schematic of the kinetic testing unit (KTU) system setup is shown in Figure C.2. Pretreatment gases and other carrier/tracer gases can be precisely controlled and delivered into the reactor using mass flow controllers. A liquid methanol and water mixture is pumped into a microchannel vaporizer with precise flowrate settings. The methanol and water vapor are then blended with $N_2$ carrier gas, passing a 25-ml surge tank, where the reactants are preheated to the process temperature and which holds some head pressure for steady operation. Steam reforming reactions take place in the catalyst bed with uniform reactor temperature. Reactor effluent is quenched, and un-reacted methanol and water are collected in a chilled vessel. Gaseous product samples can be taken by a micro gas chromatograph (GC) (Agilent QUADH G2891A) to determine conversion and product selectivity. The micro GC is equipped with Molsieve 5A (10m), PoraPlotQ (8m), OV-1 (2µm, 10m) and OV-1 (1.2µm, 4m)
columns to quantify carbon monoxide, carbon dioxide, hydrogen, methane, ethane, ethylene, propane, and propylene. The analysis of the whole reformer effluent gas products takes less than 2 minutes. Overall carbon balance and hydrogen balance are better than 97%. This reactor unit has efficient collection-bypass, and an instrumentation system for better control and operation. All process data, such as temperature, pressure, and flowrates, are recorded with a LabView 6.2 data acquisition system in a computer and displayed in real time.

(F --- Mass Flow Controller; TC---Thermocouple; A/D---Analog/Digital data acquisition; BPR—Back Pressure Regulator)

Figure C.2. Schematic of reactor system process diagram
The γ-alumina supported Pd/ZnO catalyst was fabricated using an incipient-wetness impregnation method. Neutral γ-alumina (60~120 mesh, Engelhard) was pre-treated at 500°C in air for 2 hours prior to the impregnation. A nitric acid solution of palladium nitrate (Engelhard, 20.19wt% P.M.,) and zinc nitrate hydrate (Aldrich) was introduced onto the γ-Al₂O₃ support in a glass vial, and the sample was shaken at 60°C for 1 hour before being dried in a vacuum oven overnight. The dried sample was calcined at 350°C in air for 3 hours. The final formulated catalyst contains 8.9% Pd by weight, 17.6 wt% ZnO, with a surface area of 168 m²/g and pore volume of 0.48 cm³/g.

The catalyst was activated by flowing 50sccm hydrogen gas through the reactor at 400 °C for 2 hours. The reactor temperature was ramped with a 10°C/min rate from the room temperature.

The methanol used in the entire experiment is from Aldrich with capillary GC grade (99.9+% purity). The experiments were carried out at atmospheric pressure over a wide range of temperature (160°C to 310°C). The steam-to-carbon molar ratio was varied from 0.6 to 1.78. The partial pressure of N₂ varied from 9 to 35 kPa as a carrier gas and a GC internal standard. In this paper, bed residence times are reported as inverse gas hourly space velocity defined as feed flow rate at standard conditions per total reactor volume. The gas hourly velocity ranges from 9,850 to 31,000 hr⁻¹. Carbon processing rate is based on weight of methanol per gram of catalyst per unit time, known as weight hourly space velocity (WHSV). In this study, WHSV
ranges from 2 to 20 gMeOH/gcat/hr. Reforming rate is reported as negative cat-time yield (m-moles methanol converted/kg catalyst/sec), i.e., methanol disappearing rate.

C.3. Results and discussion

C.3.1 Kinetics of steam reforming of methanol

The microchannel reactor presents a highly isothermal environment for the catalyst evaluation, and it is ideal for use in studying reaction kinetics. Traditionally, bed dilution is used to mitigate temperature gradients when the reaction is strongly endothermic or exothermic. However, in addition to the possible influence of the diluting material (usually SiC) on the reaction, catalyst dilution usually changes hydrodynamic behavior and causes a large pressure drop. The global effect is that as the bed volume increases, the space-time-yield decreases due to lower gas hourly space velocity. Moreover, it is not clear whether the longer free distance of molecule collision with a catalytic site in the diluted bed would change product selectivity. Therefore, the microchannel reactor approach provides a unique solution to such problems, in which the catalyst can be kinetically characterized.

Equilibrium calculation showed that the methanol steam reforming reactions have no appreciable thermodynamic limitations. Blank tests were also conducted with a methanol/water mixture fed into the heated microchannel reactor. Results showed that the stainless steel reactor was inactive for reactions between water and methanol over the
temperature range of interest (160°C to 310°C). In addition, pre-experiments varying catalyst loading and methanol-water feed rate showed that external diffusion limitation does not exist over a range of weight hourly space velocity from 2 to 20 gMeOH/gcat/hr. With an average catalyst particle size of 200μm used for the experiments, the effectiveness factor is close to unity due to its small Thiele modulus (less than 0.002). Therefore, the internal diffusion limitation is negligible in this kinetic study.

The activity of the Pd/ZnO catalyst measured by temperature scanning at various weight hourly space velocities is shown in Figure 4.3. The steam-to-carbon molar ratio in this particular run was 1.78, and the initial partial pressure of methanol and water was 25.8 kPa and 45.9 kPa, respectively. Carbon conversion data are collected when the microchannel reactor with active heat exchange is operated at integral mode. It is not unusual that the methanol conversion
decreases with increase of weight hourly space velocity ( WHSV) but not proportionally at a certain temperature, which suggests that the reaction is not zero order to methanol partial pressure. The conversion reaches 100% at 240°C, 260°C, 270°C, and 278°C at WHSV of 4.53, 9.06, 13.59, and 18.12, correspondingly. The residence time distribution (RTD) analysis shows that Peclect numbers are large (>100) in all experimental conditions. Thus, the axial dispersion in the channel is negligible and the flow in the channel is very close to plug flow. Material balance in any differential bed segment of a plug flow reactor (PFR) yields the relationship between the reaction rate and conversion:

\[-r_A dW = F_{A_0} dx_A\]  \hspace{1cm} (C.1)

where \( F_{A_0} \) is the mole flow rate of reactant A, in our case, methanol; \( dW \) is the weight the catalyst element, g; and \((-r_A)\) represents the disappearance of methanol in mole per catalyst weight per unit time. The integral form over the whole reactor is:

\[ \frac{W}{F_{A_0}} = \int_0^x \frac{dX_A}{(-r_A)} \]  \hspace{1cm} (C.2)

Reversing the above equation and then multiplying the molecular weight of the reactant A to both sides of the equation gives the WHSV in the reactor:
Therefore, the methanol conversion is a function of temperature and WHSV when internal and external diffusion are excluded:

\[ X_A = f(T, WHSV) \]  

(C.4)

Plotting experimental data with methanol conversion \( X_A \) vs. space time of methanol, \( 1/\text{WHSV} \), gives isothermal curves, as shown in Figure C.4. The slope at any point on the isothermal curve represents the rate of reaction at that certain condition (\( T \), partial pressure of reactants).

Figure C.4. Isothermal lines of the microchannel reactor with Pd/ZnO catalyst
Polynomial regression of data usually improves precision of curve differential analysis:

\[ x_A = a(1 / \text{WHSV}) + b(1 / \text{WHSV})^2 + c(1 / \text{WHSV})^3 + \ldots \]  \hspace{1cm} (C.5)

The reaction rate then becomes,

\[ (-r_A) = \frac{1}{M_A} \left[ a + 2b(1 / \text{WHSV}) + 3c(1 / \text{WHSV})^2 + \ldots \right] \]  \hspace{1cm} (C.6)

Therefore, the rate at any point on the curve can be determined in such a way. Table C.1 lists partial experimental data of the steam reforming of methanol at four different temperatures.

Table C.1. Measured Reaction Rate of Steam Reforming of Methanol on Pd/ZnO Catalyst

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( P_{\text{MeOH}} ) (Pa)</th>
<th>( P_{\text{H}_2\text{O}} ) (Pa)</th>
<th>( (-r_{\text{MeOH}}) ) mmol/kgcat-s</th>
<th>T (°C)</th>
<th>( P_{\text{MeOH}} ) (Pa)</th>
<th>( P_{\text{H}_2\text{O}} ) (Pa)</th>
<th>( (-r_{\text{MeOH}}) ) mmol/kgcat-s</th>
<th>T (°C)</th>
<th>( P_{\text{MeOH}} ) (Pa)</th>
<th>( P_{\text{H}_2\text{O}} ) (Pa)</th>
<th>( (-r_{\text{MeOH}}) ) mmol/kgcat-s</th>
<th>T (°C)</th>
<th>( P_{\text{MeOH}} ) (Pa)</th>
<th>( P_{\text{H}_2\text{O}} ) (Pa)</th>
<th>( (-r_{\text{MeOH}}) ) mmol/kgcat-s</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>28395</td>
<td>28438</td>
<td>15.6360</td>
<td>210</td>
<td>14712</td>
<td>34809</td>
<td>16.7242</td>
<td>230</td>
<td>4130</td>
<td>24227</td>
<td>15.9968</td>
<td>240</td>
<td>6969</td>
<td>27066</td>
<td>39.1951</td>
</tr>
<tr>
<td>200</td>
<td>28061</td>
<td>28104</td>
<td>15.4810</td>
<td>210</td>
<td>19100</td>
<td>39197</td>
<td>19.8010</td>
<td>230</td>
<td>10909</td>
<td>10952</td>
<td>23.4277</td>
<td>240</td>
<td>11744</td>
<td>31841</td>
<td>52.2594</td>
</tr>
<tr>
<td>200</td>
<td>26072</td>
<td>26115</td>
<td>12.3506</td>
<td>210</td>
<td>20520</td>
<td>40616</td>
<td>21.1594</td>
<td>230</td>
<td>11615</td>
<td>31712</td>
<td>32.9046</td>
<td>240</td>
<td>13680</td>
<td>33777</td>
<td>58.7933</td>
</tr>
<tr>
<td>200</td>
<td>23488</td>
<td>43585</td>
<td>14.0644</td>
<td>210</td>
<td>23678</td>
<td>23722</td>
<td>22.2800</td>
<td>230</td>
<td>14970</td>
<td>35067</td>
<td>40.8728</td>
<td>240</td>
<td>4492</td>
<td>4535</td>
<td>19.9242</td>
</tr>
<tr>
<td>200</td>
<td>22543</td>
<td>42640</td>
<td>12.9670</td>
<td>210</td>
<td>25988</td>
<td>26032</td>
<td>23.9855</td>
<td>230</td>
<td>16363</td>
<td>16407</td>
<td>31.7301</td>
<td>240</td>
<td>11871</td>
<td>11915</td>
<td>49.1613</td>
</tr>
<tr>
<td>200</td>
<td>21046</td>
<td>41143</td>
<td>12.8025</td>
<td>210</td>
<td>26309</td>
<td>26353</td>
<td>25.8756</td>
<td>230</td>
<td>19507</td>
<td>19551</td>
<td>46.1897</td>
<td>240</td>
<td>16844</td>
<td>16888</td>
<td>64.0193</td>
</tr>
</tbody>
</table>
Without a good understanding of the functionality of the Pd-Zn alloy sites in catalyzing steam reforming of methanol reaction, formulating a rate correlation with the traditional Langmuir-Hinshelwood adsorption-reaction model becomes difficult. Since the reaction mechanism of these bi-molecules on supported precious metals can be significantly different from that in the Cu-based catalyst system[10,11], many parameters must be empirically adjusted. Thus, the correlation of rate data in a power-rate law with an Arrhenius expression is practical in reactor design and in predicting the effects of operating condition changes on performance. Now that the rate equation is expressed as

\[ (-r_A) = k_0e^{-\frac{E_a}{RT}} p_A^a p_B^b, \]  

(C.7)

parameters are determined with an optimization method. Assuming the model is linear in the parameters, for n observations of rate (dependent variable),

\[ (-\tilde{r}_A) = \tilde{f}(p_A, p_B)\tilde{g}(a, b, k_0, E_a) + \tilde{\epsilon} \]  

(C.8)

where \( \tilde{f} \) and \( \tilde{g} \) are independent variable and parameter vectors, respectively, and \( \tilde{\epsilon} \) is the experimental error vector associated with the n observations. Parameter \( \tilde{g} \) is determined by minimization of the sum of squares of residuals:

\[ \tilde{\epsilon}^T \tilde{\epsilon} \rightarrow Min \]  

(C.9)
where $\tilde{e}^T$ is the transpose of $\tilde{e}$. The final values of parameters calculated above are tabulated in Table C.2. For $n=158$ experimental observations used in the parameter estimation, the average relative error between the predicted rate and the experimentally measured rate is 5.71%, and the standard deviation is 0.06. Figure C.5 indicates that the determined power law expression is sufficient for representing the kinetics of methanol steam reforming in the reaction rates from 0.5 to 80 mmol/kgcat/s.

Table C.2. Parameters of the Rate Equation

<table>
<thead>
<tr>
<th>$E_a$ (kJ/mol)</th>
<th>$k_0$ (mmol/kgcat/s /kPa$^{0.803}$)</th>
<th>A</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>94.8</td>
<td>$2.9047 \times 10^{10}$</td>
<td>0.715</td>
<td>0.088</td>
</tr>
</tbody>
</table>

Figure C.5. Comparison between predicted rate and measured rate
To test the accuracy of the kinetic rate expression, especially to verify the water partial pressure effect since the 0.088 exponent for water is not statistically different from zero, the KTU was operated at differential mode in which the conversion was controlled below 10%. Methanol partial pressure of 34.2 kPa was maintained and the weight hourly space velocity was 28 gMeOH/gcat/hr. The microchannel reactor was run at 210°C. The steam partial pressure was varied by feeding different methanol-water mixtures: steam to carbon molar ratio 1.8, 1.2, 1.0, and 0.6, respectively. In the differential mode, it is assumed there is no concentration gradient due to the low conversion. The reaction rate is determined by:

\[
(-r_A) = \frac{F_{A0}x_A}{W} = \frac{WHSV}{M_A} x_A
\]  

and the rate is corresponding to half of the conversion measured at the reactor exit \((X_A/2)\). As shown in Figure C.6, in the double log plot of reaction rate versus steam partial pressure, the slope gives the order of reaction to steam as 0.09. This agrees with the results when the reactor is operated in integral mode. Similarly, when the steam pressure remains the same, varying methanol partial pressure in the reactor differential mode, the slope of rate-partial pressure double log plot gives the reaction order of 0.75, which is very close to the integral result.

Therefore, the overall rate equation for steam reforming of methanol is expressed as follows:

\[
(-r_A)\text{ (mmol / kgcat \cdot s)} = 2.9047 \times 10^{10} e^{\frac{94800}{RT}} P_{\text{MeOH}}^{0.715} P_{\text{H}_2\text{O}}^{0.088}
\]  

\[(C.11)\]

210
where methanol and steam partial pressure have units in kPa. The apparent activation energy is 94.8 kJ/mol.

Figure C.6. Steam partial pressure effect on MSR reaction rate in a differential reactor (T=210°C, $P_{\text{MeOH}}=34.2$ kPa)

**C.3.2 Performance comparison between the microchannel reactor and a conventional fixed bed reactor—Evaluate catalyst at isothermal conditions**

Side-by-side comparison experiments were carried out in a ¼-inch quartz tube reactor and the microchannel reactor. Each reactor has a 0.2-gram catalyst loading. The same feedstocks and experimental procedures were applied to both reactors. The conventional fixed bed reactor has the catalyst bed height of 19mm with 4mm ID, while the microchannel reactor
gives a geometry of 0.508mm x 12.7mm x 37.3mm catalyst packing. The microchannel reactor is made of stainless steel.

For the conventional fixed bed reactor testing, the quartz tube reactor was heated by a furnace, while the heat required for the endothermic reaction was supplied with heat transfer fluid in the microchannel reactor. Figure C.7 shows that at the same weight hourly space velocity (WHSV=4.53gMeOH/gcat/hr), the microchannel reactor generally yields higher methanol conversion at the same inlet temperature. This confirms that catalysts in the microchannel reactor “see” higher temperature than in the conventional fixed bed reactor. In another words, the average temperature in the conventional fixed bed reactor is lower than that measured at the reactor inlet due to the endothermic effect. This effect becomes more significant when the conversion is greater than 10% at higher temperature, since high conversion generates more heat sinks and the local conversion at cold spots contribute to low integral total conversion at the reactor exit. Such heat transfer resistance, however, can be significantly reduced or eliminated in a microchannel reactor, in which temperature gradients are minimized.

In order to reveal the temperature profile inside the catalyst bed and further interpret the experimental data obtained from these two reactors, a three-dimensional homogeneous model was developed using the obtained kinetic data to describe the energy transfer and reactions. This model allows adjustment of parameters, such as the pre-exponential term of the intrinsic rate constant, activation energy, effective thermal conductivity and mass diffusivity of
the catalyst bed, so that the reactor performance can be simulated with different catalyst activities and selectivities.

Figure C.7. Performance comparison of the tubular and the microchannel reactors (WHSV=4.53 gMeOH/gcat/hr)

Partial differential equations describing conservation of mass and energy can be expressed as follows:

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot \left( -D_i \nabla c_i + c_i \vec{u} \right) = R_i \tag{C.12}
\]

\[
\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot \left( -k \nabla T + \rho C_p T \vec{u} \right) = Q \tag{C.13}
\]
where $R_i$ is the formation rate of component $i$, which is function of component concentration (or partial pressure) and temperature; $Q$ is the heat generation rate per unit volume of the catalyst bed, which is the function of reaction rate and heat of reaction; $k$ is the effective conductivity of the catalyst bed; $D$ is the effective diffusivity; $\bar{u}$ is linear velocity; $c$ is species concentration; and $T$ is temperature. The reaction rate parameters are determined by independent kinetic measurement with the microchannel reactor, as described in Section C.3.1. The effective diffusivity is a combined effect of the molecular diffusion, Knudsen diffusion, and bed tortuosity[17]. In the model, these parameters are associated with temperature, compositions, and catalyst properties. The effective thermal conductivity of the catalyst bed is of interest primarily for calculating the temperature in the bed during reaction. Supported metal on porous materials presents different thermal conductivity with different loading and synthesis methods. Empirical values from the literature have been taken to evaluate the reforming process[18,19].

The model is constructed and solved with a commercial software FEMLab@ package using the finite element approach. The routine sequence is established in Figure C.8. First, the catalyst bed dimensions are illustrated in the draw mode with the exact reactor geometry. The geometries are meshed according to the calculation tolerance. Jiggle mesh with a growth rate of 1.4 is used to generate meshes in the domain bodies. Then the parameters are filled-in to represent mass and energy principles, in which reaction kinetics and transport properties are taken into account. After assigning boundary conditions and initial value, the routines are set
to converge. Results give the temperature and conversion profiles. Steady state is assumed in this paper, so that the time-dependent terms are dropped to simplify the problem.

Simulation results show that, in general, large temperature gradients exist in the furnace-heated conventional tubular reactor, especially at the high conversion level. Figure C.9 shows that with reactor wall temperature at 220°C, and other conditions the same (steam to carbon molar ratio=1.78, WHSV=4.53 gMeOH/gcat/hr), the tubular reactor has a large heat sink area compared to the microchannel catalyst slab bed. Because the catalysts “see” lower average temperature in the tubular reactor than in the microchannel reactor, a general low

Figure C.8. 3D pseudo-homogenous model simulation sequence for methanol steam reformation

Simulation results show that, in general, large temperature gradients exist in the furnace-heated conventional tubular reactor, especially at the high conversion level. Figure C.9 shows that with reactor wall temperature at 220°C, and other conditions the same (steam to carbon molar ratio=1.78, WHSV=4.53 gMeOH/gcat/hr), the tubular reactor has a large heat sink area compared to the microchannel catalyst slab bed. Because the catalysts “see” lower average temperature in the tubular reactor than in the microchannel reactor, a general low
conversion level in the tubular bed reactor (43%) occurs compared to that in microchannel reactor (60%).

![Figure C.9. Temperature profiles of the tubular reactor and the microchannel catalyst slab bed. (wall temperature at 220°C, WHSV=4.53 gMeOH/gcat/hr).](image)

Such an endothermic effect is not significant when the reactor is operated at low conversion level. However, when the reactor temperature and space velocity increases, leading to high productivity, the catalyst bed temperature gradient becomes large. As shown in Figure C.10, with a fixed WHSV of 4.53 gMeOH/gcat/hr, at a furnace temperature of 180°C, there is only about 1°C temperature gradient in the bed, resulting in an 11% carbon conversion, very close to that in the microchannel reactor. However, when the furnace temperature goes up to 220°C, the coupled endothermic reactions cause a temperature drop as large as 7°C in the bed, resulting in a 43% carbon conversion versus a 60% conversion for the microchannel reactor.
When the furnace temperature is raised to 240°C, the cold spot can be as low as 218°C, resulting in only 66% integral conversion compared to the 100% conversion that should occur in an isothermal reactor. In contrast, simulation results indicate that the microchannel reactor is essentially isothermal. Shown in Figure C.11, even at an extreme condition for the microchannel reactor when the 100% methanol conversion is reached and the degree of heat sink maximizes its value, the maximum possible temperature difference in the bed is only 1.2°C. Experiments have validated such prediction. As shown in Figure C.12, four thermocouple readings in the bed indicate that the maximum temperature difference is 0.8°C. At any other milder conditions (low T, low conversion), such difference is almost invisible (less than 0.1°C). The performance test has demonstrated that this reactor unit provides a very narrow temperature limit for strongly endothermic reactions.

![Temperature profiles of the tubular reactor at different furnace temperatures](image)

Figure C.10. Temperature profiles of the tubular reactor at different furnace temperatures (WHSV=4.53 gMeOH/gcat/hr)
Figure C.11. Temperature profile of the microchannel reactor at high methanol conversion (WHSV=4.53 gMeOH/gcat/hr).

Figure C.12. Temperature distribution along the catalytic bed in the microchannel reactor.
Plugging the rate equation described in Section C.3.1 into the three-dimensional homogeneous model yields local temperature and conversion profiles. The temperature gradient simulated with this kinetics agrees with the experimental observations in both microchannel and conventional tubular fixed bed reactors. The integral conversions based on modeling agree with the experimental data very well. The model is flexible and accurate in any operating conditions in a large space velocity range (WHSV=2 to 20 gMeOH/gcat/hr).

**C.4. Conclusions**

A microchannel reactor has been developed to evaluate catalyst performance and measure reaction kinetics. The reactor can be operated in either integral mode or differential mode with very narrow temperature gradient (<1°C) even for strongly endothermic reactions such as methanol steam reforming. The kinetics of methanol steam reformation over Pd/ZnO catalyst has been studied using a microchannel reactor at atmospheric pressure over a wide temperature range. The apparent activation energy and rate equation have been obtained and applied in the three-dimensional pseudo homogeneous model. The precision of model has been validated with experimental observations.
Acknowledgments

The authors gratefully acknowledge the support of the Defense Advanced Research Projects Agency. This work was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the US Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory in Richland, WA.

C.7 Nomenclature

a: rate equation exponent for reactant A (methanol)
b: rate equation exponent for reactant B (water)
c_i: concentration of component i
D: effective diffusivity
E_a: activation energy, joules/mol/K
\( \vec{e} \): experimental error vector
\( \vec{f} \): independent variable vector
\( \vec{g} \): independent parameter vector
F_{A0}: mole flow rate reactant A which is methanol, mol/s
GC: gas chromatograph
K: effective bed conductivity
KTU: kinetic testing unit

$M_A$: mass of reactant A (methanol), g

$P$: pressure, Pa

PFR: plug flow reactor

$Q$: heat generation, joule/m$^3$

$-r_A$: rate of disappearance of reactant A (methanol), mol/s

$R_i$: formation rate for i

RTD: residence time distribution

$T$: temperature, K

$\bar{u}$: linear velocity

$W$: catalyst weight, g

WHSV: weight hourly space velocity

$X_A$: conversion of reactant A (methanol)
C.5 References


APPENDIX D. COMBUSTION CATALYST FABRICATION

The Pd/Al₂O₃ was the catalyst used in the catalytic combustor. This catalyst was prepared by incipient wetness impregnation of γ-Al₂O₃ (Sasol Puralox 30/140) with solution of Pd nitrate (12.96 wt% in nitric acid) dissolved in deionized water. The metal loading was 10 wt% for all the catalysts. After impregnation, the catalysts were dried at 120°C for 8 hrs and calcined under static air at 500°C for 4 hr.

To achieve low pressure drop and improve heat transfer, porous FeCrAlY foam was used as substrate for the combustion catalyst. The following is the detailed description on preparing structured combustion catalysts. The active components on the combustion catalyst consist of Pd/Al₂O₃ in the powder form, which was prepared as above. The powder catalyst sample was mixed with de-ionized water at ratio of 1:10 by weight, then ball-milled for 24 hr before wash coated onto FeCrAlY foam substrates. The porosity of the foam was 65 PPI (pore openings approximately 200-400μm). Before the catalyst was wash-coated, the foam was cleaned with ethanol and acetone mixture (1:1 by volume) in an ultrasonicated bath for 20 min. After drying 6 hr inside a hood at ambient temperature, the foam was dried at 110°C overnight. The surface of FeCrAlY substrates was thermally treated at 900°C in air for 2 hr. Next, the foam substrate was pre-coated with Al₂O₃ sol–gel to further enhance adhesion and to increase exposed surface area for the subsequent wash coating. Following the surface treatment, these substrates were washcoated with catalyst slurry prepared from ball milled powder catalysts. In order to reach
desired catalyst loading on the substrate, wash-coating process was repeated 4 times. Between each coating step, drying was conducted at 110°C in air. Final calcination was carried out at 400°C for 3 h in air.
A proof-of-concept test of the micro-scale fuel processor coupled with a PBI fuel cell was demonstrated and reported in Holladay et al. 2004 (1) and more details can be found in that paper. For the mesoscale PBI fuel cell, two cells in series, each cell having an area of \( \approx 1 \text{ cm}^2 \), were fabricated. Using two cells in series enabled higher voltages more conducive to operating microsensors and other microelectronics. A series of thick film printing steps were used to deposit current collectors, heaters, and a Pt resistance temperature detector (RTD) on alumina. The heaters were necessary to allow the cells to be tested at the appropriate temperature. Eventually, with the thermal integration of the fuel cell and the fuel processor unit, the heaters can be eliminated. RTD allows the fuel cell temperature to be monitored and the heaters controlled. Using proprietary techniques developed at CWRU, the fuel cell electrodes (two anodes and two cathodes) were printed directly onto a PBI membrane. A porous gas diffusion layer was then printed on the back of each electrode, yielding the final membrane/electrode assembly. The device was assembled by sandwiching a membrane/electrode assembly between two of the current collector plates. A high-temperature adhesive was used to hold the assembly together, and a drop of silver epoxy was used to make the series connection between the cells. The silver epoxy and the high-temperature adhesive were cured at the same time. A fuel manifold (and if desired an air manifold) constructed of alumina with \( 1/16 \text{ in.} \) stainless steel tubing for the gas inlets and outlets was then bonded to the out-side of the fuel cell assembly,
as shown in Figure E.1. Finally, 5-mil-diameter copper wire was bonded to the contact tabs for the fuel cell leads, the heaters, and the RTD using silver epoxy. The completed fuel cell is illustrated in Figure E.2. The fuel cell had an open circuit potential of 1.8V which is lower than the 2.4V expected. This indicated that fuel cell optimization was required.

The output from the baseline design micro-scale fuel processor was fed to the fuel cell as a proof of concept. The fuel cell was heated to 150°C as measured by the RTD. The cathode side was air breathing. As can be seen from Figure E.3, over 23 mW_e of power was generated. This successfully demonstrated a methanol in power out micro-scale power system.

Figure E.1. Assembly of mesoscale fuel cell components. Membrane/electrode assembly (not shown) goes between the two current collector plates. Only one current collector is shown; the other cannot be seen in this view. It is located on the lower side of the first current collector plate. For air-breathing operation, only one manifold is used.
Figure E.2. PBI meso-scale fuel cell

Figure E.3. Bread-boarded fuel processor fuel cell performance.

References

APPENDIX F. CALCULATIONS

In developing the model, there were several important calculations that were done: Mear’s Criterion and Thiele modulus. The Mear’s criterion was used to determine if interparticle heat transport effects within the reactor are significant. Interparticle heat transport effects within the reactor occurring both radially and axially are particularly difficult to evaluate and control\(^{(1)}\). The Thiele Modulus describes the relationship between diffusion and reaction rate in porous catalyst pellets with no mass transfer limitations. It is a way to determine if correlations to account for concentration gradients in the catalyst pellet.

**F.1 Mear’s criterion**

The Mear’s criterion approach followed the development presented by Karim et al. in reference 1. A < 5% difference in reaction rate due to differences between particles can be assumed when:

\[
\frac{|\Delta H_r| \mathcal{R} n f^2}{\lambda_{eff} T_0^2 R / E_a} \left(1 + \frac{4 \lambda_{eff}}{\tau h_w}\right) < 0.4
\]  

\( \text{(F.1)} \)

where \( \Delta H_r \) is the heat of reaction (201.2 kJ mol\(^{-1}\))\(^{(2)}\), \( \mathcal{R} \) is the measured reaction rate per unit bed volume (mol m\(^{-3}\) s\(^{-1}\)); \( \mathcal{R}' = \mathcal{R} \left(\frac{1-\phi}{1-b}\right) \) is the measured reaction rate per unit bed volume (mol m\(^{-3}\) s\(^{-1}\)) with \( \phi \) is the void volume (0.4) and \( b \) is the dilution ratio (ml inert/ml catalyst, which is 0
in this case); $r_t$ is the reactor radius (m), $T_w$ is the wall temperature, $R$ is the ideal gas law, $E_a$ was the activation energy (94,800 J mol$^{-1}$ K$^{-1}$), $h_w$ is the heat transfer coefficient (W m$^{-2}$ K$^{-1}$) and $\lambda_{eff}$ is the effective bed thermal conductivity (W m$^{-1}$ K$^{-1}$).

The heat transfer resistance at the wall is in the second term in equation (F.1), and cannot be neglected at the ratios of tube to particle diameters (~29) in this case. This heat transfer resistance at the wall term and is on the order of 1 at very low flow rates$^{(1)}$. Most experimentalists ignore this term and use 1, but this can be a mistake$^{(1)}$. The formulas proposed by Yagi and Kunii as reported by Karim et al. described in Chapter 3 (equations 3.13 and 3.14) were used.

Equation F.1 was solved at a wall temperature of 590K (approximate average in the bed per Chapter 6) and $\frac{\Delta H_f |9r R_t^2}{\lambda_{eff} T_w^2 R/E_a} \left(1 + \frac{4\lambda_{eff}}{R_t h_w} \right)$ found to be approximately 400 which is much greater than 0.4 indicating that radial interparticle heat transfer effects will have an impact on the reaction rate and which could explain some of the deviation from the experimental data from the numerical simulation in Chapter 3.

**F.2 Thiele modulus**

The Thiele Modulus ($\Phi_s$) was used to determine if significant concentration gradients were occurring within the catalyst pellets. For isothermal systems the smaller the Thiele Modulus is the smaller the concentration gradients through the pellet are. However, for non-
isothermal systems it is more complicated. The calculations followed the approach presented by Scatterfield in ref\(^3\). For non-isothermal systems for there to be minimal concentration gradients in a pellet Thiele Modulus must be:

\[
\Phi_s |\beta| = \frac{r_p^2 (-r) |\Delta H|}{\lambda T_s} < \frac{1}{\gamma} \tag{F.2}
\]

where

\[
\beta = \frac{c_s (-\Delta H) D_{eff}}{\lambda_s T_s} \tag{F.3}
\]

and

\[
\gamma = \frac{E}{R T_s} \tag{F.4}
\]

\(r_p\) is the radius of the particle (cm), \(r\) is the observed reaction rate (mol s\(^{-1}\) cm\(^{-3}\) of catalyst pellet), \(D_{eff}\) is the effective diffusion coefficient for a porous solid based on total cross section normal to direction of diffusion; equal to ratio of flux to concentration gradient (cm\(^2\) s\(^{-1}\)), and \(c_s\) is the concentration at outside particle surface, \(\Delta H\) is the reaction enthalpy (kJ mol\(^{-1}\)), \(\lambda_s\) is the catalyst’s thermal conductivity (W m\(^{-1}\) K\(^{-1}\)), \(E\) is the reaction activation energy, \(R\) is the gas constant, and \(T_s\) temperature at the catalyst surface. For the observed reaction rate equation 4.7 was used by multiplying the equation by the catalyst’s pellet density (~1.04*10\(^{-3}\) kg cm\(^{-3}\) estimated from \(^3\)) and adjusting from mmols to mols. The methanol and water pressures were for the initial concentration to be conservative. The \(D_{eff}\) was determined using equation:

\[
D_{eff} = \left( \frac{1}{D_{K,eff}} + \frac{1}{D_{12,eff}} \right)^{-1} \tag{F.5}
\]
$D_{12,\text{eff}}$ is the effective diffusion coefficient for a porous solid under conditions of bulk or ordinary diffusion based on the total cross section of porous solid normal to diffusion direction\(^{(3)}\). For this case it was methanol in a mixture of water, CO\(_2\), and H\(_2\). $D_{12,\text{eff}} = D_{12} \theta / \tau$ $D_{12}$ was estimated using the Fuller et. al.’s technique as described by Reid, et al. in reference \(^{(4)}\). $\theta$ was the porosity and $\tau$ the tortuosity. Scatterfield recommend that when $\theta$ and $\tau$ were not known they can be assumed to be 0.5 and 4 respectively\(^{(3)}\). The $D_{K,\text{eff}}$ is the effective Knudsen diffusion as:

$$D_{K,\text{eff}} = \frac{9700 r_e \theta}{\tau} \sqrt{\frac{T}{M}}$$  \[ F.6 \]

where $T$ is the temperature, $M$ is the molecular weight of methanol and $r_e$ is the pore radius.

Solving equations F.6 and F.5 resulted in a $D_{\text{eff}} = 4.63 \times 10^{-6}$ m\(^2\) s\(^{-1}\). Substituting into equations F.2-F.4 we find: $\Phi_s |\beta| = 0.07$ and $\frac{1}{\gamma} = 0.052$ therefore $\Phi_s |\beta|$ is slightly more than $\frac{1}{\gamma}$ indicating that we can assume effectiveness is not within 95-105%; however, this was at zero conversion.

At 20% conversion $\Phi_s |\beta|$ is equal to $\frac{1}{\gamma}$ so it is likely that concentration gradients were only significant for a small portion of the reactor.
Table F.1 Thiele modulus parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_p )</td>
<td>0.01 cm</td>
<td></td>
</tr>
<tr>
<td>( C_s )</td>
<td>10 mol m(^{-3})</td>
<td></td>
</tr>
<tr>
<td>( \Delta H )</td>
<td>201.2 kJ mol(^{-1})</td>
<td>(5)</td>
</tr>
<tr>
<td>( T_s )</td>
<td>590K</td>
<td></td>
</tr>
<tr>
<td>( E )</td>
<td>94.8 kJ mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>( R )</td>
<td>8.314 J mol(^{-1}) K(^{-1})</td>
<td>(3)</td>
</tr>
<tr>
<td>( \theta )</td>
<td>0.5</td>
<td>(3)</td>
</tr>
<tr>
<td>( \tau )</td>
<td>4</td>
<td>(3)</td>
</tr>
<tr>
<td>( D_{\text{eff}} )</td>
<td>4.63*10(^{-6}) m(^2) s(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>
References:


APPENDIX G. DEVICE DESIGNS

Generation 1 design:

End View

Cap

Plungers

Generation 2 base design:

End View
Selective methanation reactor attachment

CAP-A

Plungers
Kinetic Testing Unit from Appendix C. It is strongly recommended that in the next generation the top portion be square to make it easier for a wrench to grip.
Any length, 0.25" tubing

OD=0.25"  ID=0.15"

Welding joining

External thread

1.12''  0.28''  0.37''  0.44''

0.50''  0.94''  0.75''  0.18''

OD=0.25''  ID=0.15''

1.03''

60°

Cooling Fluid
APPENDIX H. NSF PROPOSAL: INTEGRATED PULSATING HEAT PIPE MULTIFERROIC DEVICE

This will only include the coversheet, summary, narrative and references. The budget pages and biological sketches are not included.
CERTIFICATION PAGE

Certification for Principal Investigators and Co-Principal Investigators

I certify to the best of my knowledge that:

(1) the statements herein (excluding scientific hypotheses and scientific opinions) are true and complete, and
(2) the text and graphics herein as well as any accompanying publications or other documents, unless otherwise indicated, are the original work of the signatories or individuals working under their supervision. I agree to accept responsibility for the scientific content of the project and to provide the required progress reports if an award is made as a result of this application.

I understand that the willful provision of false information or concealing a material fact in this proposal or any other communication submitted to NSF is a criminal offense (U.S. Code, Title 18, Section 1001).

Name (Typed) | Signature | Date
---|---|---
P/I/PI/Co-P/I/PI | Jamelyn D. Holladay | 09/1/2015

Certification for Authorized Organizational Representative or Individual Applicant

By signing and submitting this proposal, the individual applicant or the authorized official of the applicant institution is: (1) certifying that statements made herein are true and complete to the best of his/her knowledge; and (2) agreeing to accept the obligation to comply with NSF award terms and conditions if an award is made as a result of this application. Further, the applicant is hereby providing certifications regarding Federal debt status, debarment and suspension, drug-free workplace, and lobbying activities (see below), as set forth in the Grant Proposal Guide (GPG), NSF 98-2. Willful provision of false information in this application and its supporting documents or in reports required under an ensuing award is a criminal offense (U.S. Code, Title 18, Section 1001).

In addition, if the applicant institution employs more than fifty persons, the authorized official of the applicant institution is certifying that the institution has implemented a written and enforced conflict of interest policy that is consistent with the provisions of Grant Policy Manual Section 510; that to the best of his/her knowledge, all financial disclosures required by that conflict of interest policy have been made; and that all identified conflicts of interest have been satisfactorily managed, reduced or eliminated prior to the institution's expenditure of any funds under the award, in accordance with the institution's conflict of interest policy. Conflicts which cannot be satisfactorily managed, reduced or eliminated must be disclosed to NSF.

Debt and Debarment Certifications

If answer "yes" to either, please provide explanation.

<table>
<thead>
<tr>
<th>Is the organization delinquent on any Federal debt?</th>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Is the organization or its principals presently debarred, suspended, proposed for debarment, declared ineligible, or voluntarily excluded from covered transactions by any Federal department or agency?</th>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
</table>

Certification Regarding Lobbying

This certification is required for an award of a Federal contract, grant or cooperative agreement exceeding $100,000 and for an award of a Federal loan or a commitment providing for the United States to insure or guarantee a loan exceeding $150,000.

Certification for Contracts, Grants, Loans and Cooperative Agreements

The undersigned certifies, to the best of his or her knowledge and belief, that:

(1) No Federal appropriated funds have been paid or will be paid, by or on behalf of the undersigned, to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with the awarding of any Federal contract, the making of any Federal grant, the making of any Federal loan, the entering into of any cooperative agreement, and the extension, continuation, renewal, amendment, or modification of any Federal contract, grant, loan, or cooperative agreement.

(2) If any funds other than Federal appropriated funds have been paid or will be paid to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, or officer or employee of Congress, or an employee of a Member of Congress in connection with this Federal contract, grant, loan, or cooperative agreement, the undersigned shall complete and submit Standard Form-LLL, "Disclosure of Lobbying Activities," in accordance with its instructions.

(3) The undersigned shall require that the language of this certification be included in the award documents for all subawards at all tiers including subcontractors, subgrants, and contracts under grants, loans, and cooperative agreements and that all subrecipients shall certify and disclose accordingly.

This certification is a material representation of fact upon which reliance was placed when this transaction was made or entered into. Submission of this certification is a prerequisite for making or entering into this transaction imposed by section 1352, title 31, U.S. Code. Any person who fails to file the required certification shall be subject to a civil penalty of not less than $10,000 and not more than $100,000 for each such failure.

AUTHORIZED ORGANIZATIONAL REPRESENTATIVE | SIGNATURE | DATE
---|---|---

TELEPHONE NUMBER | ELECTRONIC MAIL ADDRESS | FAX NUMBER
---|---|---

Page 2 of 2
Summary

We propose the first integration of two novel technologies, pulsating heat pipes (PHPs) with multiferroic power generation, to create an innovative cost effective technology for low temperature waste heat recovery. Energy recovery from waste heat, such as in engine exhaust, can increase the system efficiency by up to 25%. A multiferroic device consists of a specialized magnetic material wrapped in a copper coil. A change in temperature causes this material to change its magnetic field. Thus, rapid temperature swings can cause the magnetic material to oscillate its magnetic field creating an electric current. PHP’s typically have temperature oscillations even at low temperatures making them a natural fit for use with a multiferroic device.

In this proposed work, we will develop improved PHP models and couple those models with a heat sink to simulate the multiferroic device. The validated models will be used to answer some key questions related to PHP materials, number of u-turns, working fluid, etc. as well as ideal position of the multiferroic device.

Intellectual Merit

Intellectual merit will occur in several areas. First, PHP integration with a heat engine (multiferroic device) is not simple and has never been demonstrated. Second, current research
on PHPs is to reduce the oscillation, whereas we will be designing them to increase oscillations both in size ($\Delta T$) and frequency. We will improve upon and exercise PHP models which will ultimately incorporate a multiferroic device. The PHP will be designed to produce 1 Hz temperature $20^\circ \Delta T$ which should be sufficient to create power from the multiferroic device. We will use the model to explore materials, designs, and optimization of where the multiferroic device should be integrated with the PHP. Two or more cases will be used as test scenarios.

**Broader Impacts (Technical)**

This new technology can operate at low temperatures (<150°C) with an order of magnitude increase in power density over traditional thermoelectric generators. Current PHP research is aimed at decreasing temperature oscillations. We will be interested in maximizing temperature oscillation as well as heat energy conduction. The improved PHP models could be used to design PHPs with reduced oscillations for use in the semi-conductor and other industries.

**Broader Impacts (Social)**

Tremendous energy is lost in low temperature exhaust waste heat streams. This new technology may be able to convert this wasted heat to electrical power generation recovering otherwise lost energy in almost any application. In addition, the PI will mentor undergraduate and graduate students. The students will gain experience in modeling and hands on experimental research in microchannel based heat recovery, power generation, and integration
of two novel technologies together. They will gain experience using new exciting technologies that have great promise to better utilize natural resources.
# TABLE OF CONTENTS

For font size and page formatting specifications, see GPG Section II.C.

<table>
<thead>
<tr>
<th>Section</th>
<th>Total No. of Pages in Section</th>
<th>Page No. (Optional)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cover Sheet (NSF Form 1207 - Submit Page 2 with original proposal only)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A  Project Summary (not to exceed 1 page)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>B  Table of Contents (NSF Form 1359)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>C  Project Description (including Results From Prior NSF Support)</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

Please check if Results from Prior NSF Support already have been reported to NSF via the NSF FastLane System, and list the Award Number for that Project

NSF Award No.

| D  References Cited                                                     | 38                           |                      |
| E  Biographical Sketches (Not to exceed 2 pages each)                  | 2                            |                      |
| F  Summary Proposal Budget (NSF Form 1030, including up to 3 pages of budget justification) | 4                            |                      |
| G  Current and Pending Support (NSF Form 1239)                         | 1                            |                      |
| H  Facilities, Equipment and Other Resources (NSF Form 1303)           | 2                            |                      |
| I  Special Information/Supplementary Documentation                      | 0                            |                      |
| J  Appendix (List below)                                               | 0                            |                      |

Include only if allowed by a specific program announcement/solicitation or if approved in advance by the appropriate NSF Assistant Director or designee.

Appendix Items: None.

*Proposers may select any numbering mechanism for the proposal, however, the entire proposal must be columns only if the proposal is numbered consecutively.

NSF Form 1359 (10/97)
Project description

H.1. Introduction

Tremendous energy is lost in the low quality heat in exhaust streams from engines, generators, and boilers. For example, the US Navy has estimated that it could reduce its shipboard logistics fuel consumption by 25% or more by recovering heat from its turbine exhaust\(^1\). On the civilian side, the waste heat of internet servers is a growing problem, with more than 2.5% of the energy budget of the US consumed in data centers. Exascale computers endorsed by the Department of Energy and the National Nuclear Security Administration are projected to consume 100MW/machine. For similar reasons the US DOE Vehicle Technologies program is funding GM, Ford, and GenTherm at $8M/yr to develop heat recovery systems for vehicles.

Recently a new solid state energy conversion device has been discovered called multiferroic power (MFP) which operates at low temperatures and is ideal for many waste heat recovery applications\(^2\). MFP contains materials that go through a reversible phase transformation when heated resulting in a magnetization change. When wrapped in a copper coil, the magnetization change induces an electric current. Small temperature differences on the order of 10-150°C can cause this change in magnetization. By oscillating the temperature back and forth continuous power can be generated\(^2\). At a 1 Hz oscillating \(\Delta T\) of ~20°C, realistic power density of 3 W/cm\(^3\) can be achieved. This is about a 10-100x increase in power density over thermoelectrics with comparable efficiency at an equivalent temperature.
The challenge is to create the thermal cycling at the appropriate frequency. Some options include: spinning aperture radiant heating system, high frequency forced evaporation systems, microchannel heat exchanger or pulsating heat pipe (PHP). Of the options available, a microchannel PHP is extremely attractive since it is passive whereas the others have parasitic power losses. The PHP operation is primarily driven by phenomena occurring in a thin film surrounding the bubbles. This is particularly true for the temperature oscillation magnitude and the speed. The most recent PHP models include this thin film, but have set it to a uniform and arbitrary thickness. This assumption is known to be incorrect. Therefore, inclusion in the models the impact of the thin film thickness especially as the thickness varies due to bubble velocity and evaporation/condensation would be important to predict the performance and design the PHP and therefore the integrated system. We hypothesize that a combined modeling and experimental effort will provide unprecedented understanding of the phenomena involved in MFD and PHD which will guide the selection of appropriate working fluids and operational conditions to enable successful integration of a MFD and PHP. Such a PHP would operate at a low heating temperature of <150°C, with a 0.1 - 1 Hz 20°C ΔT. Based upon the modeling efforts results, an integrated device will be built and proof of concept demonstrated

The proposed work will focus on three main objectives. Objective 1 will be to develop a PHP model and exercise it to find a design with the desired temperature oscillation and frequency. Objective 2 will be to build and test the design developed in Objective 1, thereby
validating the model. Objective 3 will be to integrate the MFP into the design, use modeling to predict the performance, and build and test the device.

**Objective 1. Model and design pulsating heat pipe.**

A PHP model will be used to examine the impact of working fluid choice, pipe diameter, pipe material, pipe length, number of u-turns, and temperature on PHP performance. The goals of this objective are to design a PHP which can achieve the desired $\Delta T$ at the desired frequency. A secondary goal will be to determine the minimal length of the adiabatic section. The PHP operation is dependent on many factors with the thin film surrounding the bubbles one of the primary drivers for the temperature oscillation magnitude, frequency and the heat transfer amount. The film thickness is dependent on the working fluid characteristics, temperature, and bubble speed$^{(3,4)}$. We will examine the effect of the film thickness on performance. In addition, it is believed that a high thermal conductivity is required for proper PHP operation; therefore, we will model a range of thermal conductivities to represent thermally conductive materials such as copper to insulating materials like polyimide (approximately 2 orders of magnitude difference). Finally, the impact of pipe diameters, pipe length and u-turns will be examined.

**Objective 2. Validate pulsating heat pipe model**

Next we will validate the PHP model by building a PHP and comparing the actual performance with that predicted by the model. Model validation is necessary to give us confidence in the model so we can use the model in the next and final objective of including the
MFP in the PHP. We have extensive machining facilities and experience for the system construction.

**Objective 3. Design and build a multiferroic device integrated into a pulsating heat pipe.**

Finally, we will integrate the MFP into the PHP model with the focus on configuration optimization of the PHP with MFP. Two scenarios will be examined. The first will model the MFP integrated into adiabatic portion of the PHP. This section was selected since we believe it will be have the largest temperature swing of any portion of the PHP. However, integrating the MFP into the adiabatic section will change it impacting performance. Thus the second scenario will integrate the MFP in the condenser portion. We will build and test a PHP with a heat load to simulate the MFP to validate the designs.

**H.2. Background**

For most waste heat recovery applications the technology of choice is thermoelectrics (TE). TE’s gained attention in the 1950’s and 60’s when NASA used them in their space program. The critical performance metric for TE’s is the ZT value, and after 50 years of development the ZT values have increased from ~1.0 to 1.2. Similarly the efficiency and power density of TE’s has not significantly increased in the last 50 years despite considerable investment.

Multiferroic power devices are a new alternative to the traditional TE for waste heat recovery\(^{(2)}\). MFP devices have the potential to realistically achieve 3kW/cm\(^3\), which is a factor of 10-100x over TE while still achieving a similar efficiency at the same \(\Delta T\) of 20°C. While the
efficiency for such a $\Delta T$ is small (on the order of 2-4%) the devices may be cascaded to achieve higher efficiencies. To function as a multiferroic material, a material must have two of three magnetic properties: ferromagnetism, ferroelectricity, and/or ferroelasticity. When heated a rapid increase in magnetization occurs which is lost when cooled\textsuperscript{(2)}.

![Graph showing magnetization change in Ni$_{45}$Co$_5$Mn$_{40}$Sn$_{10}$ with changing temperature](image)

Figure H.1 Magnetization change in Ni$_{45}$Co$_5$Mn$_{40}$Sn$_{10}$ with changing temperature\textsuperscript{(5)}

Srivastava et al. (2011) demonstrated a multiferroic power device using Ni$_{45}$Co$_5$Mn$_{40}$Sn$_{10}$ as the material. This alloy is strongly ferromagnetic and also a ferroelastic\textsuperscript{(2)}. When heated the material goes through a phase transformation between two crystalline phases resulting in a strong increase in its magnetic field (Figure H.1). If the temperature increase is continued the magnetization is ultimately lost. As the material is cooled, the magnetization returns, first strongly, and then decreases abruptly. By wrapping the material in a coil of electronically conductive wire such as copper, an electric current is induced by the change in magnetization according to Faraday’s law. Due to hysteresis, the reverse transformation temperature is different than the forward transformation temperature. High
efficiency is achieved by matching the forward and reverse transformation temperatures as close as possible. The Ni$_{45}$Co$_{5}$Mn$_{40}$Sn$_{10}$ has a $\Delta T$ of 20-50°C.

MFP’s power density is proportional to the frequency that the material can be thermally cycled. High frequency thermal cycling is most easily achieved by embedding a mechanism within the MFP to rapidly deliver and remove heat. A simple schematic of this is depicted in Figure H.2 as an array of channels of width $d$ separated by slabs of material of width $2w$. The heat is transferred via convective transport through the channels and conduction through the MFP material. Heat conduction through the material is limited by thermal conductivity and the length scale, $w$. The order of magnitude of the maximum thermal cycle frequency can be estimated by dividing the heating rate by the total heat required to heat the material. Assuming heat conduction is limiting, the maximum cycling frequency scales as

$$f \approx \frac{k_m}{\rho C_p w^2} \quad [H.1]$$

where $\rho$, $k_m$ and $C_p$ are density, thermal conductivity, and specific heat capacity of the multiferroic material, respectively. Using order of magnitude values of $\rho=8000$ kg/m$^3$, $k=75$ W/m-K and $C_p=0.07$ kJ/kg-K, cycling frequency is limited to about 1.2 Hz when $w=1$ cm and 120 Hz when $w=1$ mm. To obtain a 1 kHz cycling frequency, the length-scale of the microstructure
within the material will need to be smaller than 300 microns, which is within the range of typical microchannel devices (Figure H.3).

![Figure H.3 Multiferroic material with embedded heat transfer mechanism](image)

The challenge remains to create the thermal cycling. Some of the options include: spinning aperture radiant heating system, high frequency forced evaporation systems, microchannel heat exchanger or pulsating heat pipe. In the spinning aperture radiant heating design, a radiant beam is directed to the desired surface through a slot in a slowly spinning disk. High frequency forced evaporation is a simpler method than the spinning aperture radiant heating system. Here the MFP is heated by a heat source such as a combustor or from waste heat off an engine, and the temperature oscillations are induced by thin film liquid evaporation. The liquid could be delivered by a piezoelectric pump or acoustic wave mist generator. Again, parasitic loses for the liquid delivery system would be significant.
Two microchannel approaches were considered. The first was a variation of a temperature swing absorption system which was originally designed for NASA\textsuperscript{(6)}. In this system the working fluid flows through microchannels embedded in the MFP. At one end the heat transfer fluid flows through a coil which is externally heated either by a microchannel catalytic combustor or a waste heat stream. Once heated the fluid flows through the microchannels heating the MFP. The fluid is cooled by flowing through a condenser which exchanges heat with the environment. An oscillating piston would be the driving force to move the fluid back and forth with the period determining the thermal cycling frequency and, therefore, the power and efficiency of the MFP. The major challenge for this approach is that the piston would need to be powered imposing a parasitic loss on the system.

The focus of this proposal is the second microchannel approach which is to use a pulsating heat pipe (PHP). PHPs were invented in the 1990’s by Akachi et al\textsuperscript{(7)}. They have a major advantage over other devices since they don’t require a pump or other parasitic load to move the liquid. Like traditional heat pipes, PHP utilize thermal conductivity and phase transformation to rapidly transfer heat between two solid interfaces. Heat pipes operate as follows: At the hot end, liquid is evaporated and absorbs heat from a thermally conductive solid surface. The vapor condenses back into a liquid at the cold end (condenser), releasing the latent heat. The liquid then returns to the evaporator through either capillary or gravity action\textsuperscript{(7)}. In most heat pipes, a wick is used to aid in moving the liquids and to prevent slugging. PHP have three main sections- evaporator, condenser and adiabatic as shown in Figure H.4. Liquid slugging action is used to aid in heat transfer therefore, unlike regular heat pipes, no wick is
used. The PHP is composed of a small tube partially filled with liquid. To minimize the vapor traveling distance and provide some control over the boiling point, the tube is partially evacuated. The PHP operates as follows. Heating the vaporization section causes the liquid to vaporize. In the small capillary tubes, the liquid vaporization results in vapor bubbles and liquid slugs distributed throughout the pipe. The vapor bubbles condense in the cold end. The pressure difference caused by the vaporization in the hot end and the condensing in the cold end pushes the liquid slugs from the heating section to the condenser. The liquid slug movement decreases the pressure in the vaporizing section while increasing it in the condenser. This reversed pressure difference pushes the liquid slug back to the heating section, and oscillatory flow is initiated and sustained. This has been shown to be an effective way of promoting heat transfer, but the temperature in the pipes oscillates\(^7\). One major research area

![PHP schematic showing the main sections: evaporator, adiabatic and condenser](image-url)
in PHP has been minimizing temperature oscillation \(^{(7-25)}\). Unlike current research direction, we will examine how to increase the temperature oscillations to a \(\Delta T\) of 20+°C and increase the oscillation rate to 1Hz. We will design the PHP to be self-sustaining (i.e. unless the proper working fluid and design are chosen the oscillations will stop after some period of time). Figure H.5 shows the schematic for an individual MFP integrated with a PHP and an array.

Research has shown that large swings in temperature can be induced \(^{(5)}\). The challenge will be in obtaining a larger temperature swing at the desired frequency and that is self-sustaining. In addition to temperature, the considerations will include: material, pipe diameter, working fluid type, fill ratio, number of u-turns and pipe length.

One of the keys for proper operation is having an acceptable tube inner diameter. The Bond number (Bo) is used to determine this size. The Bo correlates the surface tension of the liquid slug and gravitational forces in a capillary tube:

\[
\text{Bo} = \frac{d^2 g (\rho_l - \rho_v)}{\sigma}
\]

[H.2]

Figure H.5 A singular MFP \(^{(2)}\) and proposed array of MFP integrated with PHP.
with \( d \) being the diameter, \( g \) being gravitational acceleration, \( \rho_l \) and \( \rho_v \) being the liquid and vapor density and \( \sigma \) is surface tension. Figure H.6 shows the correlation between diameter and Bond number for common working fluids, which show the diameter should be less than 3\text{mm}\(^{5,10,14,23}\). It is not clear how the diameter impacts temperature oscillation. The tube shape has been shown to impact performance with a rectangular shape showing less oscillation than a tubular design\(^{12}\). Maydanik et al. (2009) recommended that PHP inner diameter should be in the range from 0.5 to 3\text{mm}\(^{26}\). Therefore we will start with a tubular design and explore the impact of the diameter over the 0.5 to 3\text{mm} range.

Various working fluids and fill ratios have been explored. Several research groups have compared the performance of PHP using water, methanol, R123, ethanol, and nanofluids\(^{16,19,23,24}\). The data showed that water induced more temperature oscillations than methanol or ethanol\(^{23,24}\). This seems to indicate that fluids with higher boiling points induce larger temperature oscillations. The nanofluids improved heat transfer, but deposited onto the tube walls making them unreliable\(^{19}\), so they will not be examined. Finally, higher fill ratio’s (>60%) have been shown to increase the temperature oscillations.
oscillation, but have decreased heat transfer\(^{(16)}\). Fill ratios of 50% showed good operation in all orientations. Therefore, we will begin with water and fill ratio 50-60% and examine performance using higher boiling point fluids.

Finally, we will use the model to determine the number of u-turns that should be included and the minimum pipe length that can be used in the system. The acceptable number of u-turns depends upon the working fluid, operating temperature, inner diameter of the pipe, PHP orientation, and how the PHP is heated\(^{(15,26-28)}\). For a horizontal PHP, it was determined that a low number of u-turns (<5) would eventually lead to no liquid slugs in the evaporator section. Without a liquid slug in the evaporator, there was no driving force to move the other bubbles and other liquid slugs which would cause the PHP cease functioning\(^{(15,26)}\). The operating time increases with the number of u-turns and at 10 or more u-turns a sustained operation is achieved. The best operation occurred with 26 turns\(^{(28)}\). To achieve orientation independence, ~40 turns are necessary\(^{(27)}\). Therefore we will start with 10 turns in our modeling as a starting point and increase the number of turns as needed. We will use the model to determine if there is a minimum length that is needed to maintain the PHP operation and the impact on the amplitude and frequency of the temperature oscillation.

**PHP model literature review**

The first PHP model was proposed by Miyazaki and Akachi\(^{(29)}\). Based on the oscillating features observed in their experiments, they developed an analytical model of self-exciting oscillation. They later refined the model, by deriving the wave equation of pressure oscillation
in which a reciprocal excitation between pressure oscillation and void fraction was assumed\(^{(30)}\). The model’s predicted wave velocity was in fairly good agreement with experimental results.

Zuo et al. proposed a PHP model which compared the slugging phenomena to an equivalent spring-mass damper system\(^{(31)}\). Their system parameters were affected by heat transfer. The model was flawed in that spring stiffness increased with time which decreased the amplitude of oscillation\(^{(31)}\). This was inconsistent with experimental data\(^{(32)}\).

A purely theoretical model was proposed by Shafii et al. They used the momentum and continuity equations for each of the vapor slugs to balance evaporative fluxes across vapor/liquid interfaces\(^{(33)}\). This model solved for temperature, pressure, plug position and heat transfer rates. But it did not account for the thin liquid film between the pipe wall and vapor slugs, or pressure drops in the u-turns.

Zhang and Faghri developed a model which includes the thin film thicknesses and published the results in a series of papers\(^{(34,35)}\). The initial model considered only the evaporator and condenser and had one open end\(^{(34)}\). The second paper expanded the model to an arbitrary number of turns\(^{(35)}\).

Givler and Martinez applied the commercially available software FLOW-3D to PHP’s. They used this software to predict the performance of simple PHP’s with some success. They recognized the limitation in their approach in two ways. First, they neglected the thin film of liquid that remains on the inside wall of a tube after a vapor bubble has passed. Evaporation of this thin film has been identified as one of the major drivers to pushing slugs through the pipe\(^{(32)}\). The second was pressure drops in the u-turns\(^{(36)}\).
A novel approach for a single bubble PHP was developed by Das et al. They assumed a strong temperature gradient in the vapor bubble and the thin film evaporation–condensation effect was both of which were neglected previously addressed\(^{(17,37)}\). The temperature gradient in the bubble, allowed the bulk temperature gradient to be different than the temperature at saturation pressure. The evaporation–condensation effects accounts for two phase equilibrium that occurs locally at the vapor-liquid interface. Nikolayev reported that the film evaporation-condensation approach including the temperature gradient was validated against experimental results\(^{(17)}\). Nikolayev expanded Das et al.’s model beyond a single bubble PHP to an arbitrary number of bubbles and turns. Both Nikolayev and Das et al. simplified the PHP by using a straight x-axis with a periodic sequence of domains to represent the different heat pipe sections\(^{(17,37)}\). The inclusion of the thin film was key in increasing the model accuracy in terms of allowing large amplitude oscillations and accounted for time varying wetting films through which most of the heat transfer occurs\(^{(3)}\).

A major weakness of the model was the assumption that the thin film thickness was arbitrarily selected and was uniform in thickness\(^{(3,17,37)}\). However, the film thickness \((\delta_f)\) can be approximated as a function of the liquid’s surface tension \((\sigma, \text{N/m})\), dynamic viscosity \((\mu, \text{Pa-s})\), tube radius \((R, \text{m})\), and velocity \((V, \text{m/s})\). Aussilous and Quere\(^{(4)}\) developed a correlation for the thin film thickness based upon the capillary number dimensionless group as follows:

\[
\frac{\delta_f}{R} = \frac{1.34 Ca^\frac{2}{3}}{1+2.5 \left(1.34 Ca^\frac{2}{3}\right)^\frac{2}{3}} \quad [H.3]
\]
Where Ca is the Capillary Number dimensionless group:

\[ Ca = \frac{\mu V}{\sigma} \]  

[H.4]

For PHPs the Ca Number is typically between 0.1 and 0.0001\(^{(3,38)}\). For water at room temperature, the associated velocity would be 0.007 to 7 m/s. As seen in Figure E.7, since the Ca is directly proportional to velocity, as the Ca number (velocity) increases the film thickness increases.

In contrast the film thickness is indirectly proportional to the heat transfer coefficient as shown in equation [H.5].

\[ U = \gamma \frac{\lambda_l}{\delta_f} \]  

[H.5]

Where U is the heat transfer coefficient (W/(K m2)), \( \gamma \) is a coefficient to account for spatial variation in film thickness, \( \lambda_l \) is the heat conductivity of the liquid (W/(m K)), and \( \delta_f \) is the film thickness (m). It should be noted that Nikolev set \( \gamma \) equal to 0.47 and it is not clear the reasoning behind this.
Figure H.7 Film thickness variations with Capillary number using Aussilous and Quere correlation with the typical Ca range for a PHP shown in the grey box. This Ca range is approximately 0.007 to 7 m/s for a water film.

Nikolev studied the impact of thin film thickness by varying the $\delta_f$ from 5µm to >90µm for a water filled PHP with the temperature of the evaporator and condenser set to 35 and 25°C respectively. He reported that at thickness >90µm self-sustained oscillations ceased. The temperature oscillation magnitude increased as the thickness decreased until the thickness reached 5µm. At 5µm, it was surmised that bubble recondensation appears and caused oscillation disruption\(^{[17]}\). This illustrates the importance of better predicting the film thickness.

By comparing equations [H.3] and [H.5] it becomes clear that as the velocity increases the film thickness increases which will negatively impact on heat transfer. Therefore, the working hypothesis is there is an optimum film thickness for desired heat transfer and velocity.
Through integrated theory/modeling and experimental work, we will be able to provide better understanding of the phenomena involved which will be used to design an optimum integration of MFD and PHP.

H.3. Research design and experimental methods

The goal of this research is to use modeling to design the first ever waste heat recovery device that combines two new technologies (1) pulsating heat pipe and (2) multiferroic devices. The primary focus will be to modify evaporator/condenser PHP models to improve their accuracy by accounting for more phenomena and then to include terms to predict MFP performance. The model will be exercised to determine the appropriate temperature, pipe diameter, fill ratio, number of u-turns, working fluid, and pipe length in the adiabatic section between the condenser and evaporator. This research is divided into three objectives (1) model a pulsating heat pipe, (2) validate the model, (3) expand the model to include MFP, predict performance, and build and test an integrated device. The goal the first objective is to improve available PHP models to better account for thin film by using Aussilous and Quere’s (AQ) correlation. This will aid in working fluid selection, tube diameter, and operating conditions. This will enable better prediction of the oscillation magnitude and frequency to enable designing an integrated device. The second objective’s goal is to validate the PHP model against real data to give confidence in the model. The third objective’s goal is to design, build and test an integrated PHP-MFP device. The ultimate goal is to demonstrate the proof-of-concept of the integrated device.
Objective 1. Model a pulsating heat pipe.

1.1 Develop basic PHP model. The first step will be to replicate the thin film evaporation – condensation model described in references[^17,^37] to form a baseline PHP model. As part of this task, the boundary conditions will be defined. Initially, the same boundary conditions as used in literature will be used to enable comparison of model output with experimental results from the literature. This would allow a quick check to ensure the accuracy of the model to this point before adding new phenomena. We will then exercise the model to understand the impact of boundary conditions on the performance.

1.2 Modify model to include additional phenomena. The second sub-task in Objective 1 will be the development and implementation of the AQ correlation to allow the prediction and of the bubble film thickness which will improve the bubble velocity and heat transfer predictions. Inclusion of the AQ correlation will enable better selection of the working fluid and operating conditions. Nikolav

Objective 2. Validate PHP model

2.1 Design PHP device using model. The first step in PHP design will be to calculate the amount of heat that needs to be transported by the PHP to the multiferroic device for the proper device operation. The PHP will be designed to move the appropriate amount of heat at the desired temperature and achieve the desired $\Delta T^\circ C$ of $20^\circ C$. The evaporator side will range from $150^\circ C$
to 250°C. The condenser side will range from 20°C to 40°C to simulate ambient conditions (68°F to 104°F). A wide range of values will be generated to account for variability in device performance. While the model may have the capability to predict the PHP performance at angles, we will assume a single vertical orientation. We will exercise the model, exploring materials of construction, fluid choices, length of tubes, and number of u-turns. Currently the most likely candidates will be water as the working fluid with copper, steel, or polymers tubes as the preferred PHP materials of construction. A flat plate design has been popular in literature, particularly for electronic devices. However, for this application, use of tubes is preferred for ease of integrating the multiferroic device, particularly the copper wire winding (~2000 turns).

2.2 Build and test PHP device. We will then build the PHP device designed in sub-task 2.1. Depending on the materials of construction, diameter, number of u-turns, etc, the PHP may be a challenge to build particularly should a small diameter be preferred. A ceramic material would require casting and be difficult to ensure proper flow. Simply bending a metal or plastic pipe may result in kinks. It is desirable to have a smooth inner surface which makes adhering two etched plates together potentially a challenge. In addition, constructing the device to allow integration of the multiferroic power device needs to be considered. It is anticipated that the magnet portion of the multiferroic power device will be a clam shell that can be clamped onto the tube. The copper wire will be wrapped around the magnets. Should a flat plate design prove to be the best, integration of the components of the multiferroic power device will be
more difficult. One option is to design the plate with gaps where the magnet can be clamped into place and the copper wire wound.

Figure H.8. Test stand set-up. Thermocouples will be connected to each loop at the condenser, adiabatic, and evaporator sections.

The PHP will be tested over a range of temperatures. The experimental set-up is shown in Figure H.8. The condenser side will be room temperature, but the evaporator will range from 150°C to 250°C. We will measure the change in temperature, oscillations, and heat transfer rates. A hot bath will be used to heat the evaporator section, a separate cooling box charged with water will be used for the condenser section. Thermocouples will be attached on the outside tube of the evaporator section, adiabatic section, and condenser section. Additional thermocouples will be used on the heating box and cooling box to monitor temperature changes. In addition to measuring the temperature oscillations, the average heat transfer rate and effective thermal conductivity which is often used to determine the heat transfer
performance of the heat pipe will be measured. The average heat transfer rate will be
determined the change in temperature of the water charge in the cooling box using eqn:

\[ Q = C_p m \Delta T/t \quad [H.6] \]

Where \( Q \) is the average heat transfer rate, \( C_p \) is the specific heat of the water charge, \( m \) is the
mass of the water charge, \( \Delta T \) is the change in temperature of the water charge and \( t \) is the
change in time. The effective thermal conductivity (\( \lambda_{eff} \)) is calculated:

\[ \lambda_{eff} = \frac{Q \cdot l}{A_c (T_{evap} - T_{cond})} \quad [H.7] \]

Where \( l \) is the length between the evaporator and the condenser sections, \( A_c \) is the total cross
section area of the heat pipe, and \( T_{evap} \) and \( T_{cond} \) are the mean wall temperatures at the
evaporator and condenser sections respectively. These values will be compared to the
predicted performance and to the performance of the PHP with the integrated MFP.

2.3 Adjust PHP model if necessary. The results of sub-task 2.2 will be analyzed and compared
to the PHP model predicted results. Should it be necessary, some of the model parameters may
be adjusted to better fit the data.
Objective 3. Design and build a mfp integrated into a pulsating heat pipe.

3.1 Integrate MFP into the PHP model. Once the PHP model has been validated, we will add additional complexity to represent the multiferroic power device. We believe that the adiabatic section will have the largest temperature swing in the PHP. For this reason, we will include a MFP modeled as an additional heat loss on the adiabatic section with power production based upon literature. With a heat loss, the adiabatic section will no longer be adiabatic, and there is concern that the PHP will no longer function without a true adiabatic section. Next we will move the MFP to the condenser section. While temperature swings may not be as large as in the adiabatic section, there is less concern that the additional heat loss from the MFP will cause the PHP to function poorly. Finally, we will compare the results of the two positions and design an integrated device.

3.2 Build and test MFP-PHP system. The final task will be to build and test the MFP-PHP system. The multiferroic material, Ni$_{45}$Co$_{3}$Mn$_{40}$Sn$_{10}$, will be provided by Dr. Jun Cui of the Pacific Northwest National Laboratory. We will modify the MFP design for integration with the PHP. It is anticipated that the PHP tube will be circular. The fabrication of the integrated PHP-MFP device will be as follows. We will make the multiferroic and the permanent magnetic material in a clam shell which can be clamped onto the PHP (Figure H.9). For example, if a copper tube is
determined to be the material of choice, prior to bending the tube, the permanent magnetic and multiferroic material clamshell will be attached into the predetermined places. Fine insulated copper wire will be wound around (1000-2000 turns) the multiferroic material clamshell. This winding may be done by a machine or by hand. At this point the tube will be bent into the desired shape for the PHP. Should a ceramic material be chosen, then the fabrication may be different. In this case it is likely that a tube will not be circular, but square. In this scenario, for a ceramic or silicon based PHP, the PHP will be formed first with slots or areas where the clamshell can be inserted and the copper wire can be wound (Figure H.10). The copper wire will need to be wound by hand.

The test stand set-up (Figure H.11) will be almost the same as for the PHP alone. The difference will be inclusion of a resistor and testing for power generation. A 10k Ω resistor will be placed between the coil ends. An amp-meter will be placed in line to measure current. A voltmeter will be used to measure the voltage. We will test it over the same temperature range and conditions identified in sub-task 3.1. The PHP performance will be
measured similar to task 2.2 and compared to the PHP results from task 2.2. The results of the testing will be analyzed and compared to the model reports to determine the model accuracy.

Figure H.11. MFD-PHP integrated device test stand set-up. Thermocouples will be connected to each loop at the condenser, adiabatic, and evaporator sections. The MFD will be connected to a load (resistor) and voltmeter to measure power veneration.

The work plan is presented in a project Gantt chart. Each objective will take approximately 12 months. The plan is laid out to achieve each objective and to build upon each accomplishment to achieve the ultimate goal of demonstrating the integration of the pulsating heat pipe and multi-ferroic device for low temperature heat conversion to power.
Project Gantt Chart.

<table>
<thead>
<tr>
<th>Activity</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q1</td>
<td>Q2</td>
<td>Q3</td>
</tr>
<tr>
<td>Objective 1 Model a Pulsating Heat Pipe</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 Develop Basic PHP Model</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2 Modify Model to include additional Phenomena</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Objective 2. Validate PHP Model</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 Design PHP Device using Model</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2 Build and Test PHP Device</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.3 Adjust PHP Model if necessary</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Objective 3. Design and Build a MFP Integrated with a PHP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1 Integrate MFP into PHP Model</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2 Build and Test MFP-PHP System</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

H.4. Nomenclature and references

Nomenclature

\( A_c = \) total cross sectional area of the PHP

\( \text{Bo} = \) Bond number

\( \text{Ca} = \) Capillary number

\( \text{Cp} = \) specific heat capacity

\( d = \) tube diameter

\( f = \) frequency

\( g = \) gravity acceleration

\( k_m\text{-} = \) thermal conductivity multiferroic material

\( l = \) length
m = mass of vapor by default

MFP = Multiferroic power

PHP = pulsating heat pipe

Q = heat exchange rate

R = Radius

T = temperature

$T_{\text{cond}}$ = condenser temperature

$T_{\text{evap}}$ = evaporator temperature

t = time

TE = thermoelectric

U = heat transfer coefficient (of film transfer if no indices)

US DOE = United States Department of Energy

V = velocity

w = width

Z = thermoelectric figure of merit. It is the electrical conductivity times Seeback coefficient squared, divided by the thermal conductivity

Greek Symbols

$\Delta$ = difference

$\delta_l$ = liquid film thickness

$\lambda_{\text{eff}}$ = effective heat conductivity of the PHP
\( \lambda_l = \text{heat conductivity of the liquid} \)

\( \gamma = \text{coefficient to account for spatial variation in film thickness} \)

\( \mu = \text{dynamic viscosity} \)

\( \rho = \text{density} \)

\( \rho_l = \text{liquid density} \)

\( \rho_v = \text{vapor density} \)

\( \sigma = \text{surface tension} \)

References


