A Numerical Study of Catalytic Light-Off Response

THESIS

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in the Graduate School of The Ohio State University

By

Wenbo Jia, BS

Graduate Program in Mechanical Engineering

The Ohio State University

2016

Master's Examination Committee:

Professor Mei Zhuang, Advisor
Professor Xiaodong Sun
Abstract

The performance of a three-way catalytic converter is studied numerically using commercial computational fluid dynamics (CFD) software Fluent™ 15.0 and MATLAB/Simulink programs. At first a cold flow simulation is performed to study the effects of converter geometric parameters on flow distributions at the monolith inlet. The effectiveness of the heat transfer from exhaust gases to the monolith through convective heat transfer is then investigated without consideration of the chemical reactions. The kinetics model proposed by Holder et al. is implemented into the 1D channel model and a 2D axisymmetric model is developed combining 2D axisymmetric heat conduction with the 1D channel model. The effects of cell density, catalyst loading, flow and temperature distributions at the monolith inlet on conversion efficiencies are examined.

The results show that the flow and temperature distribution and the pressure drop across the monolith are strongly affected by converter geometric parameters such as the pipe/diffuser angle $\theta$, the substrate length to diameter ratio $L/D$, and the inlet gas temperature and mass flow rate. The flow at the monolith inlet becomes more non-uniform with increasing of the angle $\theta$, the mass flow rate, and the inlet gas temperature and decreasing of the ratio $L/D$. The temperature at the monolith inlet becomes more uniform with increasing of the mass flow rate and decreasing of the inlet gas temperature. The pressure drop across the monolith increases with increasing of the mass flow rate, the
inlet gas temperature, the angle $\theta$, and the ratio L/D. The results also suggest that a substrate with a larger cell density and heavier loaded catalyst in the front gives better conversion efficiencies. The conversion efficiencies are not affected much by a change of thermal conductivity of the converter insulation mat up to 10%. Furthermore uniform flow and temperature distributions at the monolith inlet give rise to the best conversion efficiencies for a converter with a given flow condition. For a given temperature distribution at the monolith inlet, the effects of the flow distribution at the inlet on the conversions are negligible. The conversion efficiencies decrease as the temperature distribution at the monolith inlet becomes more non-uniform.
Acknowledgments

First I would like to thank my advisor, Dr. Mei Zhuang, for the opportunity to work in The Ohio State University Simulation Innovation and Modeling Center (SIMCenter). You were always glad to share your abundant experience, to show me the proper direction and to help me revise the paper work. Besides the academic aspect, you also encouraged me when I faced difficulties. You gave me confidence and a grateful heart.

I also would like to thank Dr. Xiaodong Sun for sharing his knowledge and suggestions in the heat transfer and fluid dynamics field.

This thesis would not have been possible without the financial support from Tenneco Inc. and the technical support from Michael Bradford, Nagoor-Gani Mohamed, Stephen Thomas and Paul Majewski of Tenneco. I greatly appreciate Michael Bradford’s knowledge and the sharing of his expertise in chemical kinetics. Nagoor-Gani Mohamed served as the project manager. I am grateful for his support of the project and suggestions on CFD simulations. I am also grateful for the feedback provided by Stephen Thomas on CFD simulations. Paul Majewski provided us the experimental test data from Tenneco.

At last I would also like to thank Dr. Deborah Petrone for helping me to edit the thesis. Dr. Petrone was the English teacher when I first arrived U.S. She is always nice
and happy to help her students. She accepted my request of paper editing in the final hours before the deadline and did a great job.
Vita

December 1991.................................Born—Jinan, Shandong, China

May 2014........................................B.S. Mechanical Engineering, The Ohio
                                            State University

August 2014-Present..........................Graduate Research Associate, The Ohio
                                            State University

Fields of Study

Major Field: Mechanical Engineering
Table of Contents

Abstract ................................................................................................................................. ii

Acknowledgments .............................................................................................................. iv

Vita ..................................................................................................................................... vi

List of Tables .................................................................................................................... xi

List of Figures .................................................................................................................. xiv

Nomenclature .................................................................................................................. xxi

Chapter 1  Introduction ................................................................................................... 1

Chapter 2  Cold Flow and Light-off Simulations of the Catalytic Converters without
Chemical Reactions ........................................................................................................ 6

  2.1 Problem Statement .................................................................................................. 6

    2.1.1 Objective of Research .................................................................................... 8

    2.1.2 Scopes of Research .................................................................................... 8

    2.1.3 Geometry Modeling ................................................................................... 9

    2.1.4 Material Properties .................................................................................. 11

  2.2 CFD Simulation Set Up .................................................................................... 16
2.2.1 Finite Volume Method and a Porous Media ........................................16

2.2.2 Mesh Generation ..................................................................................18

2.2.3 Model Verification ..............................................................................21

2.2.4 Test Cases ..........................................................................................22

2.3 CFD Simulation Results and Discussions ..............................................25

2.3.1 Base Case Results and Discussions ....................................................25

2.3.2 Effects of the Geometric Parameters and the Inlet Conditions on Flow Index .50

2.3.3 Effects of the Inlet Conditions and Cell Density on Temperature Index ....55

2.3.4 Effects of the Geometric Parameters and the Inlet Conditions on the Pressure Drop ..................................................................................58

Chapter 3 1D Model for Catalytic Converters .............................................63

3.1 Problem Statement .................................................................................63

3.1.1 Objectives of Research ......................................................................63

3.1.2 Scope of Study ....................................................................................64

3.1.3 Substrate and Exhaust Gas Properties .................................................64

3.2 Model Construction ................................................................................65

3.2.1 TWC Module ....................................................................................65

3.2.2 Catalyst Module ................................................................................68

3.2.3 Reactions Module ..............................................................................75
3.2.4 Thermal Module ................................................................. 83
3.3 Model Set Up ................................................................. 85
3.4 The Effects of the Substrate Cell Densities on the Conversion Efficiencies ........... 85
3.5 The Effects of the Catalyst Loadings on the Conversion Efficiencies ................. 90
3.6 Model Tuning ................................................................. 93

Chapter 4 2D Axisymmetric Model ............................................. 107
4.1 Formulation ................................................................. 108
4.2 Data Structure and Transfer ........................................... 110
4.3 2D Axisymmetric Model Set Up ....................................... 115
4.4 Results Using GM FTP Data ........................................... 116
4.5 Effects of Thermal Insulation of Catalytic Converters on Conversion Efficiencies ................................................................. 119
4.6 Effects of Inlet Flow Non-uniformity on Conversion Efficiencies ................. 122

Chapter 5 Conclusions ............................................................. 125

References .............................................................................. 129

Appendix A: User Defined Function .............................................. 133

Appendix B: Code for the MATLAB/Simulink Programs ......................... 140

Appendix B-1: MATLAB Code of Input Parameter for the 1D Channel Model .... 140
Appendix B-2: MATLAB Code of Input Data File Generator for the 2D Axisymmetric Model

Appendix B-3: MATLAB Code of Input Parameter for the 2D Axisymmetric Model

Appendix C: Data for Calculating Diffusion Coefficients

Appendix C-1: Collision Diameters and Energy of Interaction [26]

Appendix C-2: Collision Integral [26]

Appendix C-3: Diffusion Volumes [27]
List of Tables

Table 1 Properties of monoliths with 3 different cell densities ........................................... 16
Table 2 Summary of the Fluent 15.0 Setup ................................................................................. 16
Table 3 Nusselt number for Laminar flows in square tubes with different boundary conditions [20] ......................................................................................................................... 18
Table 4 Summary of inflation layer setup .................................................................................... 18
Table 5 Different mesh size options for mesh independence study ........................................... 19
Table 6 Comparisons of flow and temperature indices ............................................................... 21
Table 7 Group I - Effect of L/D in cold flow simulation ............................................................. 22
Table 8 Group II - Effect of the angle $\theta$ in cold flow simulation ............................................. 22
Table 9 Group III – Light-off simulation with various inlet mass flow rate ................................. 23
Table 10 Group IV – Light-off simulation with various inlet gas temperature ......................... 23
Table 11 Group V – Light-off simulation with various cell density ............................................. 24
Table 12 Detailed conditions for the cold flow base case (case 2 in group I) ............................. 25
Table 13 Detailed conditions for the light-off base case (case 4 in group IV) .............................. 29
Table 14 Detailed conditions of the light-off case with a ramp inlet gas temperature (case 6 in group IV) ........................................................................................................................................... 39
Table 15 Flow index for group V (L/D = 0.5, $\theta = 40.8^\circ$ at t=120s) ....................................... 54
Table 16 Temperature index for group V (L/D = 0.5, $\theta = 40.8^\circ$ at t = 120s) ....................... 57
Table 39 Properties for substrates with different catalyst loadings ...........................................91
Table 40 Substrate properties used in the MATLAB/Simulink program [14] .........................94
Table 41 Reactions that consume CO, CH₄, C₃H₆ and NO ..................................................99
Table 42 Table of pre-exponential coefficient A and activation energy E before and after tuning. ..................................................................................................................100
Table 43 Signals in the Emissions in and Emissions out .........................................................110
Table 44 Signals in the Exhaust in and Exhaust out .................................................................111
Table 45 Inputs of the 2D axisymmetric model .......................................................................112
Table 46 Emissions out and Exhaust out of the 2D axisymmetric model ............................113
Table 47 T_mon of TWC the 2D axisymmetric model ..............................................................113
Table 48 Parameters to set up the 2D axisymmetric model ..................................................115
Table 49 Cases with different thermal conductivity kmat ......................................................119
Table 51 Performance rank for cases with different flow index and temperature index .122
List of Figures

Figure 1 Schematic of the catalytic converter with flow deflectors [2] ......................... 2
Figure 2 Pressure drop as a function of diffuser angle at different gas hourly space velocity (GHSV). The monolith was a 400/7 with an L/D of 1.11 [7]. ......................... 4
Figure 3 Schematic of a typical catalytic converter ..................................................... 7
Figure 4 Catalytic converter provided by Tenneco [15] ............................................. 10
Figure 5 Converter geometry used in base cases (unit: mm) .................................... 10
Figure 6 A geometric view of the converter in Design Modeler ................................. 11
Figure 7 Density of the air as a function of temperature [16] .................................... 12
Figure 8 Specific heat of the air as a function of temperature [16] ............................. 12
Figure 9 Thermal conductivity of the air as a function of temperature [16] .......... 13
Figure 10 Kinematic viscosity of the air as a function of temperature [16] ............. 13
Figure 11 Thermal conductivity of the substrate as a function of temperature [15] ...... 15
Figure 12 Mesh of the catalytic converter (base geometry): (a) Overall view (b) Section view .................................................................................................................. 20
Figure 13 Pressure contours at the symmetry plane for the cold flow base case (case 2 in group I) ........................................................................................................ 26
Figure 14 Pressure contours at the substrate-inlet surface for the cold flow base case (case 2 in group I) ....................................................................................................... 26
Figure 26 Local mass flow contours at the substrate-inlet surface for the light-off base case (case 4 in group IV) .................................................................35
Figure 27 Local mass flow profile at the substrate-inlet surface for light-off base case (case 4 in group IV) .................................................................36
Figure 28 Volume averaged temperature (K) in the substrate vs. time (s) for the light-off base case (case 4 in group IV) ..................................................................................37
Figure 29 Temperature index vs. time (s) for light-off base case (case 4 in group IV) ....38
Figure 30 A ramp inlet gas temperature vs. time for the light-off case (case 6 in group IV) ............................................................................................................39
Figure 31 Pressure contours at the symmetry plane for the light-off case with a ramp inlet gas temperature (case 6 in group IV) ..................................................................................40
Figure 32 Pressure contours at the substrate-inlet surface for the light-off case with a ramp inlet gas temperature (case 6 in group IV) ..................................................................................40
Figure 33 Local mass flow contours at the symmetry plane for the light-off case with a ramp inlet gas temperature (case 6 in group IV) ..................................................................................41
Figure 34 Local mass flow contours at the substrate-inlet surface for the light-off case with a ramp inlet gas temperature (case 6 in group IV) ..................................................................................41
Figure 35 Temperature contours at the symmetry plane for the light-off case with a ramp inlet gas temperature (case 6 in group IV) ..................................................................................42
Figure 36 Temperature contours at the substrate-inlet surface for the light-off case with a ramp inlet gas temperature (case 6 in group IV) ..................................................................................42
Figure 37 Volume averaged temperature (K) in the substrate vs. time (s) for the light-off case with a ramp inlet gas temperature (case 6 in group IV) ...........................................43

Figure 38 Temperature index vs. time (s) for the light-off case with a ramp inlet gas temperature (case 6 in group IV) .................................................................43

Figure 39 Inlet gas temperature vs. time for the light-off case with the experimental data provided by Tenneco ..........................................................................................45

Figure 40 Total mass flow rate vs. time for the light-off case with the experimental data provided by Tenneco ..........................................................................................45

Figure 41 Flow index vs. time for the light-off case with the experimental data provided by Tenneco .................................................................................................46

Figure 42 Temperature index vs. time for the light-off case with the experimental data provided by Tenneco ..........................................................................................47

Figure 43 Temperature index vs. time for the light-off case with the experimental data provided by Tenneco ..........................................................................................48

Figure 44 Pressure drop vs. time for the light-off case with the experimental data provided by Tenneco .................................................................................................49

Figure 45 Flow index vs. L/D ratio for group I (θ = 40.8°, CPSI = 400, T_{g,in} = 300 K) ..........................................................50

Figure 46 Flow index vs. θ for group II (L/D = 0.5, CPSI = 400, T_{g,in} = 300 K) ........................................51

Figure 47 Flow index vs. inlet gas temperature for group IV (L/D = 0.5, θ = 40.8°, m_{in} = 64.5 g/s, CPSI = 400, at t = 120 s) ..................................................................................52

Figure 48 Flow index vs. mass flow rate for group III (L/D = 0.5, θ = 40.8°, CPSI = 400, T_{g,in} = 650K at t = 120 s) ..................................................................................................53
Figure 49 Temperature index vs. inlet gas temperature for group IV (L/D = 0.5, θ = 40.8°, \(\dot{m}_{in} = 64.5\) g/s, CPSI = 400, and \(t = 120\)s) ..........................................................55

Figure 50 Temperature index vs. mass flow rate for group III (L/D = 0.5, θ = 40.8°, CPSI = 400, \(T_{g, in} = 650\) K at \(t = 120\)s) ..........................................................56

Figure 51 Pressure drop across the monolith vs. L/D ratio for group I (θ = 40.8°, CPSI = 400, \(T_{g, in} = 300\) K) .................................................................................58

Figure 52 Pressure drop across the monolith vs. θ for group II (L/D = 0.5, CPSI = 400, \(T_{g, in} = 300\) K) .................................................................................59

Figure 53 Pressure drop across the monolith vs. inlet gas temperature for group IV (L/D = 0.5, θ = 40.8°, \(\dot{m}_{in} = 64.5\) g/s at \(t = 120\)s) ..........................................................60

Figure 54 Pressure drop across the monolith vs. mass flow rate for group III (L/D = 0.5, θ = 40.8°, \(T_{g, in} = 650\) K at \(t = 120\)s) .................................................................................61

Figure 55 Overview of the 1D TWC model .................................................................................65

Figure 56 Code for 1D catalyst module .................................................................................68

Figure 57 GM FTP cycle: inlet gas temperature vs. time .................................................87

Figure 58 Mass flow rate of GM FTP cycle data as a function of time .........................87

Figure 59 CO conversion efficiency for substrates with different cell densities ..........88

Figure 60 CH₄ conversion efficiency for substrates with different cell densities ..........89

Figure 61 C₃H₆ conversion efficiency for substrates with different cell densities ..........89

Figure 62 NO conversion efficiency for substrates with different cell densities ..........90

Figure 63 CO conversion efficiency using 1D model GM FTP cycle data for substrates with different catalyst loadings .................................................................92
Figure 64 $CH_4$ conversion efficiency using 1D model GM FTP cycle data for substrates with different catalyst loadings ................................................................. 92

Figure 65 $C_3H_6$ conversion efficiency using 1D model GM FTP cycle data for substrates with different catalyst loadings ................................................................. 93

Figure 66 NO conversion efficiency using 1D model GM FTP cycle data for substrates with different catalyst loadings ................................................................. 93

Figure 67 Relationship among pre-exponential coefficient A, temperature and conversion .................................................................................................................... 95

Figure 68 Relationship among activation energy E, temperature and conversion ........ 95

Figure 69 Conversion efficiencies and mass flow rate plots for cast manifold data before tuning ........................................................................................................... 96

Figure 70 Conversion efficiencies and mass flow rate plots for fabricated manifold data before tuning ........................................................................................................... 97

Figure 71 Conversion efficiencies and mass flow rate plot for cast manifold data after tuning ........................................................................................................... 102

Figure 72 Conversion efficiencies and mass flow rate plot for fabricated manifold data after tuning ........................................................................................................... 103

Figure 73 Conversion efficiencies for cast manifold data ($E1 = E4 = 6000, E5 = 8000$) ....................................................................................................................... 105

Figure 74 Monolith Temperature vs. Time at Node 10, 30, 54 for cast manifold data ($E1 = E4 = 6000, E5 = 8000$) ....................................................................................................................... 106

Figure 75 Schematic of 10 layers 2D axisymmetric model ......................................... 108
Figure 76 Schematic of the thermal circuit used to calculate $h_{eff}$ ........................................ 109

Figure 77 Mask for sub model layer 8 .................................................................................. 114

Figure 78 Comparisons of conversion efficiencies using GM FTP cycle data (uniform distribution of mass flow rate and temperature at inlet surface) among the 1D model, layer 1 and layer 10 in the 2D axisymmetric model .............................................................................. 117

Figure 79 Contours of monolith temperature using GM FTP cycle data at different times ............................................................................................................................ 118

Figure 80 Temperature Contours of the three cases at 300 seconds ............................. 120

Figure 81 Comparisons of overall conversion efficiencies with different thermal conductivity of mat $k_{mat}$ ......................................................................................................................... 121

Figure 82 Comparisons of overall conversion efficiencies with different inlet flow and temperature distributions .......................................................................................................................... 123

Figure 83 Monolith temperature distributions of different 4 inlet conditions at 50 seconds .............................................................................................................................................. 124
Nomenclature

Roman
A  
Monolith frontal area (m$^2$)
BiFo  
Biot Fourier number
C$_g$  
Gas phase concentration (kmol/m$^3$)
C$_s$  
Surface concentration (kmol/m$^3$)
C$_p$  
Specific heat capacity (J/kg·K)
CPSI  
Cells per square inch
D  
Diameter of substrate (m)
D$_x$  
Molecular diffusivity of species x (m$^2$/s)
d$_h$  
Hydraulic diameter of square cells in substrate (m)
e  
Monolith void fraction
E  
Activation energy
f$_{ox}$  
Availability of oxidising species
f$_{red}$  
Availability of reducible species
G$_a$  
Geometric surface area per unit volume (1/m)
h  
Heat transfer coefficient (W/m$^2$·K)
h$_{eff}$  
Effective heat transfer coefficient (W/m$^2$·K)
IAD  
Interfacial area density (1/m)
K$_p(T)$  
Chemical equilibrium constant
k  
Thermal conductivity (W/m·K)
k$_r$  
Radial thermal conductivity
k$_z$  
Axial thermal conductivity
k$_{mat}$  
Thermal conductivity of the fibrous insulation mat
k$_{steel}$  
Thermal conductivity of steel
k$_m$  
Species mass transfer coefficient
K$_{eq}$  
Equilibrium constant
L  
Length of the substrate (m)
M$_x$  
Molecular weight of species x (kmol/kg)
m  
Mass (kg)
m$_{solid}$  
Mass of the solid element (kg)
m  
Mass flow rate (g/s)
m$_{in}$  
Inlet mass flow rate (g/s)
Nu$_d$  
Nusselt number
P  
Pressure (N/m$^2$)
Pr  
Prandtl number
$q_{cond}$  
Conduction heat flow (J/s)
$q_{conv}$  
Convection heat flow (J/s)
$q_{reaction}$  
Reaction heat flow (J/s)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_i$</td>
<td>Reaction rate (kmol/m$^3$)</td>
</tr>
<tr>
<td>$R_f$</td>
<td>Forward reaction rate (kmol/m$^3$)</td>
</tr>
<tr>
<td>$R_n$</td>
<td>Net reaction rate (kmol/m$^3$)</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant (J/kmol·K)</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>$Sh$</td>
<td>Asymptotic Sherwood number</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature of air (K)</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Gas temperature (K)</td>
</tr>
<tr>
<td>$T_{g,in}$</td>
<td>Inlet gas temperature (K)</td>
</tr>
<tr>
<td>$T_s$</td>
<td>Solid temperature (K)</td>
</tr>
<tr>
<td>$t$</td>
<td>Time (s)</td>
</tr>
<tr>
<td>$v_g$</td>
<td>Gas velocity (m/s)</td>
</tr>
<tr>
<td>$\Sigma V_i$</td>
<td>Diffusion volumes</td>
</tr>
<tr>
<td>$x$</td>
<td>Segment axial distance (m)</td>
</tr>
<tr>
<td>$[X]$</td>
<td>Molar concentration of $X$ (kmol/m$^3$)</td>
</tr>
</tbody>
</table>

Greek

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
<td>Collision diameter (Å)</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Temperature-dependent collision integral</td>
</tr>
<tr>
<td>$\theta$</td>
<td>The angle between walls of diffuser and substrate</td>
</tr>
<tr>
<td>$\theta_{rh}$</td>
<td>Fraction of oxidised rhodium sites</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Dynamic viscosity (kg/m·s)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density (kg/m$^3$)</td>
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Chapter 1  Introduction

The three-way catalytic converter is an emissions control device that combines carbon monoxide (CO) with unburned hydrocarbons (HC) to produce carbon dioxide (CO₂) and water (H₂O) and also reduces oxides of nitrogen (NOₓ). According to the study by Rodriguez et al. [1], more than 90% of the total unburned hydrocarbons emissions occur during the cold-start period. Therefore the fundamental understanding of complex processes occurred in the converter during this time period is critical for improving the converter light-off performance.

A lot of research has been done to reduce pressure drop and improve conversion efficiency of the three-way catalytic converter. It can be divided into two aspects: converter designs and laboratory tests, mathematical/numerical models and chemical kinetics.

The research in the converter designs and laboratory tests discussed below gives suggestions in converter design to improve the converter’s performance. Hirata [2] used flow deflectors placed inside the converter diffuser region as shown in Figure 1 to reduce the pressure drop and improve the flow distribution. Santos et al. [3] found that at low space velocities, the ceramic substrate presents better conversions, particularly for HC and CO, as compared to the metallic substrate, possibly because of its lower thermal
conductivity which facilitates local ignition. At high space velocities, the metallic substrate presents better conversions, as compared to the ceramic substrate, mainly because of its larger geometric surface area and lower transverse Peclet number. Konstantas et al. [4] found the oxygen storage capacity is essential for increased efficiency of the catalytic converters and is correlated with precious metal implementation in the washcoat.

Figure 1 Schematic of the catalytic converter with flow deflectors [2]

The research in mathematical/numerical models and chemical kinetics make it possible to develop a model and simulate the performance of the converter and save huge experimental expense. Amirnordhin et al. [5, 6] used an adapted sub-grid scale modeling to predict the pressure loss and chemical performance of square- and hexagonal-cell-
shaped honeycomb monoliths. A hexagonal-shaped cell gives a better mechanical performance (lower pressure drop) than a square-shaped cell. On the other hand, a square-shaped cell performs better chemically (higher specific surface area) than a hexagonal-shaped cell. Hayes et al. [7] performed a self-consistent parametric study of a catalytic converter in a 2-d configuration and found the monolith substrate configuration had a significant impact on flow, temperature distributions and the pressure drop, and on the resulting chemical reactions. Figure 2 shows the effect of diffuser angle at three GHSV on the pressure drop for the standard monolith size, with a cell density of 400 CPSI and a 7 mil (0.007 inch) wall thickness (denoted as 400/7). Marghmaleki [8] developed a transient heterogeneous 2D model to study the influence of geometry on performance of catalytic converter. Marghmaleki found the monolith with 400 CPSI and thin walls warmed up faster than other CPSI configurations in transient cold start simulations. Loya [9] added considerations of viscosity, conductivity and diffusion in the bulk gas phase to the classical 1D model and made the model more accurate than the classical model.
In the current study, a systematic numerical investigation is conducted for the performance of a three-way catalytic converter during the cold start. The effects of various factors on flow and temperature distributions at the monolith inlet and the conversion efficiencies are studied. The objectives of the study are to:

a. Conduct a cold flow simulation to characterize the flow distributions in catalytic converters.

b. Investigate the effectiveness of the heat transfer from exhaust gases to the monolith through convective heat transfer.

c. Develop simulation tools of a combined 2D axisymmetric CFD with 1D channel models for the optimum converter design in terms of flow distribution, cell densities and catalyst loadings.
CFD simulations without considerations of chemical kinetics are performed to investigate the effects of geometry and inlet conditions to the flow distribution and thermal response of the catalytic converter. A global reaction mechanism [10] for three-way catalytic converters is implemented into a 1D channel model in MATLAB/Simulink programs. The reaction reversibility of certain reactions is added, and the Chapman-Enskog theory and Fuller correlation are used as the diffusion mechanism for a better description of the actual physical processes involved. The kinetic parameters (pre-exponential coefficient and activation energy) are tuned to match the conversion efficiencies from Tenneco test data. The 1D model is then extended to 2D axisymmetric model by combining 2D axisymmetric CFD with the 1D channel model. The effects of the thermal insulation on the conversion efficiency are also studied. GM FTP cycle data [11] and Tenneco manifolds experimental data [12-14] were used in this study.

The thesis is organized as follows. The cold flow and light-off simulations without consideration of chemical reactions are carried out in chapter 2. In chapter 3, the 1D channel model with Holder et al’s reaction mechanism is implemented and the effects of cell density and catalyst loading on the conversion efficiency are investigated. In chapter 4, the 2D-axisymmetric model is developed. The effects of the thermal insulation and the flow and temperature non-uniformity at the substrate inlet on the performance of catalytic converters are studied. In chapter 5, the conclusions of the investigations are summarized, and the remarks with regard to various aspects on model construction and execution strategies and future work are discussed.
Chapter 2  Cold Flow and Light-off Simulations of the Catalytic Converters without Chemical Reactions

2.1 Problem Statement

For a set of cold flow conditions, the CFD simulations will be performed for a Tenneco catalytic converter. Since the flow distribution at the inlet of the catalytic converter is unknown, a uniform velocity profile at the inlet is assumed. A schematic of the catalytic converter solution domain is shown in Figure 3. The effects of various operating parameters such as inlet mass flow rate, the angle $\theta$ and the L/D ratio on the flow distribution and the pressure drop across the monolith will be studied. To quantify the flow mal-distribution, a flow index as shown in Equation (1) (defined as the ratio of the mass flow rate through the center core of the monolith which corresponding to one quarter of the monolith volume to the total mass flow rate) will be used. A flow index of 25% will guarantee the mass flow through the converter is uniformly distributed thus the catalyst can be used more efficiently to generate better conversion efficiency. The results of the simulations will be analyzed and used to identify important geometric features that lead to efficient catalytic converters.

$$\text{flow index} = \frac{m_{\text{center}}}{m_{\text{total}}}$$  \hspace{1cm} (1)
To understand how effectively heat is transferred from gases to the monolith through convection, a set of simulations will be performed to study the temperature and flow distributions for a number of selected converters (from the earlier study) without considering the chemical reactions. The inlet gas temperature is increased initially with time and then kept as a constant to mimic to cold-start condition. The inlet velocity, as a function of temperature, is increased such that the mass flow rate remains a constant. In simulations, a uniform inlet velocity profile is assumed. The ambient temperature is given, e.g., 300K. The overall heat transfer coefficients for the monolith and pipe/diffuser walls need to be estimated and given as inputs for the simulations. The convective boundary conditions for the pipe and diffuser walls will be applied. Similar to the flow index, a temperature index as shown in Equation (2) (defined as the thermal energy contained within the central volume fraction equal to 0.25 compared to the overall energy within the monolith) will be used to quantify the temperature distribution during cold-
start without considering the chemical reactions (By definition, a temperature index of 25% means the temperature in core region and other region are the same) The effectiveness of the heat transfer from exhaust gases to the monolith through convective heat transfer can therefore be examined. The results will provide some directions on the design of efficient converters.

\[
\text{temperature index} = \frac{T_{\text{center}}}{4 \cdot T_{\text{total}}}
\]  

(2)

2.1.1 Objective of Research

Three-dimensional CFD simulations will be performed to evaluate the flow distribution, thermal response and pressure drop along substrate. The flow index and temperature index will be calculated from CFD solutions and compared among different cases to assess the effects of the geometry, the mass flow rate and the inlet gas temperature on the flow and temperature fields.

2.1.2 Scopes of Research

The scope of this research is as follows:

i. Conduct a cold flow simulation to characterize the flow distributions in catalytic converters.

ii. Conduct a light-off simulation to characterize the flow and temperature distributions in catalytic converters.
iii. Investigate the effects of geometry (the angle $\theta$ and L/D), the inlet mass flow rate, the inlet gas temperature on flow distribution and thermal response of the catalytic converter.

2.1.3 Geometry Modeling

The catalytic converter studied in this report is the top part of the whole converter from Tenneco’s company as shown in Figure 4 [15]. The outlet diffuser is adjacent to the substrate as shown in Figure 4 and there are many parts that are irrelevant to this research. To simplify the model and keep it complete, the geometry shown in Figure 5 is used. The inlet pipe diameter, inlet pipe length, half angle $\theta$, length and diameter of substrate, gap between inlet diffuser and thickness of steel layer and mat are all measured from Tenneco’s model. The outlet pipe and outlet diffuser are created the same as the inlet pipe and inlet diffuser. The geometry is saved in STEP AP214 format and imported in ANSYS Workbench shown in Figure 6. The green high-lighted surface in Figure 6 is defined as “substrate-inlet surface” in this thesis.
Figure 4 Catalytic converter provided by Tenneco [15]

Figure 5 Converter geometry used in base cases (unit: mm)
2.1.4 Material Properties

Temperature dependent air properties are provided by Tenneco [16] and shown in Figures 7-10. The properties of air are coded as a user-defined function under material browser in Fluent™ 15.0.
Figure 7 Density of the air as a function of temperature [16]

Figure 8 Specific heat of the air as a function of temperature [16]
Figure 9 Thermal conductivity of the air as a function of temperature [16]

Figure 10 Kinematic viscosity of the air as a function of temperature [16]
Below are the expressions used in Figures 7-10:

\[ \rho = 360.77819^{-1.00336} \]  
(3)

\[ c_p = 1.9327 \times T^4 - 7.9999 \times 10^{-7} \times T^3 + 1.1407 \times 10^{-3} \times T^2 - 4.489 \times 10^{-1} \times T + 1.0575 \times 10^3 \]  
(4)

\[ k = 1.5207 \times 10^{-11} \times T^3 - 4.857 \times 10^{-8} \times T^2 + 1.0184 \times 10^{-4} \times T - 3.9333 \times 10^{-4} \]  
(5)

\[ v = -1.1555 \times 10^{-14} \times T^3 + 9.5728 \times 10^{-11} \times T^2 + 3.7604 \times 10^{-8} \times T - 3.4484 \times 10^{-6} \]  
(6)

The properties of the steel from the fluent database are used for the steel layers:

\[ \rho = 8030 \text{ kg/m}^3, \quad c_p = 502.48 \text{ J/kg} \cdot \text{K}, \quad k = 16.27 \text{ W/m} \cdot \text{K}. \]

The thermal conductivity of the mat provided by Tenneco is used [15]:

\[ k_{\text{mat}} = 10^{-4}T^2 + 0.028T + 67.241 \text{ mW/m} \cdot \text{K} \]  
(7)

The density and specific heat of the mat considered are from Chen et al. [17]:

\[ \rho = 1000 \text{ kg/m}^3, \quad c_p = 600 \text{ J/kg} \cdot \text{K}. \]
The thermal conductivity of the substrate provided by Tenneco is used as shown in Figure 11. The expression of Figure 11 is as follows:

\[ k = 2 \times 10^{-12} T^3 + 3 \times 10^{-9} T^2 - 4 \times 10^{-6} T + 0.0041 \text{ mW/m} \cdot \text{K} \]  

(8)

The density, specific heat, inertial resistance and viscous resistance and open frontal area (OFA) of the substrate are provided by Tenneco [15]. The cell diameter of the monolith with 400 CPSI is provided by Tenneco and the other two cell diameters for monoliths with CPSI of 600 and 900 are obtained from Hayes et al. [7].

The density and specific heat of the substrate used are:

\[ \rho = 279 \text{ kg/m}^3, \quad c_p = 500 \text{ J/kg} \cdot \text{K}. \]

The properties of monoliths with different cell densities are listed in Table 1:
Table 1 Properties of monoliths with 3 different cell densities

<table>
<thead>
<tr>
<th>CPSI/Wall thickness (mm)</th>
<th>Inertial resistance (/m)</th>
<th>Viscous resistance (/m²)</th>
<th>Cell diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400/4.5</td>
<td>13.4597</td>
<td>3.34297 × 10⁷</td>
<td>1.1557</td>
</tr>
<tr>
<td>600/3.5</td>
<td>13.911</td>
<td>5.18257 × 10⁷</td>
<td>0.948</td>
</tr>
<tr>
<td>900/2.5</td>
<td>14.1177</td>
<td>7.89841 × 10⁷</td>
<td>0.783</td>
</tr>
</tbody>
</table>

2.2 CFD Simulation Set Up

2.2.1 Finite Volume Method and a Porous Media

The Finite Volume Method (FVM) is the most popular numerical method used in CFD and Computational Heat Transfer (CHT). Compared to Finite Difference Method (FDM) and Finite Element Methods (FEM), both local and global conservation are inherently built into FVM, which is the most important issue in CFD and CHT. Table 2 shows the summary of the Fluent™ 15.0 Setup. For thermal condition of walls, both convection and radiation boundary conditions are employed to simulate the real situation.

Table 2 Summary of the Fluent 15.0 Setup

<table>
<thead>
<tr>
<th>Analysis type</th>
<th>Steady state for cold flow simulation, transient for light off simulation (time step 1s until 120s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbulence model</td>
<td>k-ε realizable model non-equilibrium wall functions</td>
</tr>
<tr>
<td>Walls (mixed thermal conditions)</td>
<td>Heat transfer coefficient=10 W/m² · K, Free stream temperature=300 K, External emissivity=0.35, External radiation temperature = 300 K.</td>
</tr>
<tr>
<td>Inlet type</td>
<td>Mass-flow-inlet</td>
</tr>
<tr>
<td>Outlet type</td>
<td>Pressure-outlet, zero gauge pressure</td>
</tr>
<tr>
<td>Solution methods</td>
<td>SIMPLE scheme</td>
</tr>
<tr>
<td>Default setting for spatial discretization</td>
<td></td>
</tr>
</tbody>
</table>
In both cold flow and light-off simulations, the porous media is used to model the substrate properties. The porous media option simplifies the calculation on monolith. The heat transfer coefficient of porous media is calculated by combining the solid-phase heat transfer coefficient and gas-phase heat transfer coefficient in proportion of open frontal area. The pressure drop in the channel of porous media is calculated only in the axial direction and has contributions from viscous and inertial resistances. In the light-off simulations, the Non-Equilibrium Thermal Model is used in porous media. In such an approach, a solid zone that is spatially coincident with the porous fluid zone is defined, and this solid zone only interacts with the fluid with regard to heat transfer. The conservation equations for energy are solved separately for the fluid and solid zones [18]. Equations (9) and (10) [19] are employed in user defined functions (given in Appendix A) to compute the heat transfer coefficient for each mesh cell. The Nusselt number is used to calculate the heat transfer coefficient:

\[ h = \frac{k}{d_h} Nu_d \]  \hfill (9)

The values of Nusselt number are different depending on the Reynolds number and the shape of tubes. For cases in this report, the Reynolds number of square tubes in the substrate is around 100, which is less than 2300. The flow is therefore laminar:

\[ Re = \frac{pv d_h}{u} \]  \hfill (10)

Table 3 shows the Nusselt number for laminar flows in square tubes with different boundary conditions. Also a constant uniform wall temperature boundary condition is used.
Table 3 Nusselt number for Laminar flows in square tubes with different boundary conditions [20]

<table>
<thead>
<tr>
<th>Boundary condition</th>
<th>Nusselt number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant uniform wall temperature, both axially and peripherally</td>
<td>2.976</td>
</tr>
<tr>
<td>Constant axial wall heat flux with uniform peripheral wall temperature</td>
<td>3.6</td>
</tr>
<tr>
<td>Constant axial wall heat flux with uniform peripheral wall heat flux</td>
<td>3.091</td>
</tr>
</tbody>
</table>

2.2.2 Mesh Generation

The first step in the FVM is mesh generation, which is to divide the computational domain into a number of small control volumes. The accuracy of the CFD results is determined by the quality of the mesh and the turbulence model that are employed. Since the gradients of fluid velocity and often the temperature are large near the wall, prism layers are added to allow a sufficiently fine mesh to adequately capture the flow features in the near wall region. Such prism layers are called inflation layers in Fluent settings. Several inflation options were tested and the chosen settings shown in Table 4 were based on mesh quality, computational efficiency and accuracy. The total thickness of an inflation layer is defined by the values of the number of layers, growth rate and maximum thickness.

Table 4 Summery of inflation layer setup

<table>
<thead>
<tr>
<th>Inflation option</th>
<th>Number of layers</th>
<th>Growth ratio</th>
<th>Max thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total thickness</td>
<td>5</td>
<td>1.2</td>
<td>5</td>
</tr>
</tbody>
</table>
Also the inlet part of the converter needs to be finely meshed since it will influence the accuracy of the flow distribution at the substrate-inlet surface. However, as the total number of mesh cells increases, the CPU usage increases. Therefore, a mesh independence study was conducted to find the trade-off between the accuracy and the computational cost. Since the mesh generated by ANSYS Workbench is unstructured, the size of each cell in mesh is not the same; the values of the max size, max face size and local max size can be used to control the total number of the cells. The max size and max face size are global settings for all the cells in the geometry and the local max size is a local setting for a certain part in the geometry.

Table 5 Different mesh size options for mesh independence study

<table>
<thead>
<tr>
<th>Case #</th>
<th># of cells</th>
<th>Max size (mm)</th>
<th>Max face size (mm)</th>
<th>Local max size at inlet part (mm)</th>
<th>Flow index (%)</th>
<th>Temperature index (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>87511</td>
<td>20</td>
<td>14</td>
<td>no</td>
<td>26.92</td>
<td>25.33</td>
</tr>
<tr>
<td>2</td>
<td>125906</td>
<td>20</td>
<td>10</td>
<td>no</td>
<td>26.78</td>
<td>25.26</td>
</tr>
<tr>
<td>3</td>
<td>260146</td>
<td>14</td>
<td>10</td>
<td>no</td>
<td>26.76</td>
<td>25.25</td>
</tr>
<tr>
<td>4</td>
<td>388297</td>
<td>14</td>
<td>10</td>
<td>7</td>
<td>26.15</td>
<td>25.28</td>
</tr>
<tr>
<td>5</td>
<td>489301</td>
<td>14</td>
<td>10</td>
<td>6</td>
<td>26.13</td>
<td>25.27</td>
</tr>
<tr>
<td>6</td>
<td>692519</td>
<td>14</td>
<td>10</td>
<td>5</td>
<td>26.11</td>
<td>25.27</td>
</tr>
</tbody>
</table>

The mesh independence study was performed for the light-off case with the inlet gas temperature of 464K and inlet mass flow rate of 64.5 g/s. As shown in Table 5, a set of six different mesh size options was considered. From the table, we can see that there is only 0.04% change in the flow index and 0.01% change in the temperature index between case 4 and case 6. However, the total number of the cells used in case 4 was only
about 56% of that in case 6. Therefore, the mesh settings used in case 4 were employed for the cases in this study. The final mesh for the base geometry is shown in Figure 12.

Figure 12 Mesh of the catalytic converter (base geometry): (a) Overall view (b) Section view
2.2.3 Model Verification

As mentioned in the introduction, the CFD model is verified against a similar 2D CFD study on the effects of geometry on flow distribution and thermal response of converters by Hayes et al. [7]. The same mesh generation approach and Fluent settings are used in cases for comparisons with Hayes’ results. The converter geometric parameters are diffuser angle of 40, L/D ratio of 1, CPSI of 400. The inlet conditions are GHSV of 25000 h$^{-1}$, 300 K for the cold flow simulations and GHSV of 25000 h$^{-1}$, 700 K for the light-off simulations. The results are shown in Table 6 below.

<table>
<thead>
<tr>
<th>Case</th>
<th>Flow index (%)</th>
<th>Temperature index (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold flow simulation - Hayes et al.</td>
<td>29</td>
<td>NA</td>
</tr>
<tr>
<td>Cold flow simulation – current study</td>
<td>28.74</td>
<td>NA</td>
</tr>
<tr>
<td>Light-off simulation - Hayes et al.</td>
<td>30.50</td>
<td>25.30</td>
</tr>
<tr>
<td>Light-off simulation- current study</td>
<td>28.33</td>
<td>25.37</td>
</tr>
</tbody>
</table>

The flow index of the cold flow simulation and the temperature index of the light-off simulation agree well between our results and that of Hayes. Compared with the cold flow simulation, the flow index of the light-off simulation decreased slightly, instead of the slight increase in Hayes’ result. The difference here could be caused by the fact that in Hayes’ study a 2D geometry and a constant density were assumed. In current study, a 3D geometry and temperature dependent air density were used.
2.2.4 Test Cases

2.2.4.1 Test Cases for Cold Flow Simulation

Tenneco has provided ranges of interest for the angle $\theta$ (20° - 70°), and L/D ratio (0.35 - 1.5). The study of the effects of the geometric parameters on the flow distribution is only considered in cold flow simulation cases (see Tables 7 and 8) with the inlet gas temperature at 300K. When changing the L/D ratio, the volume of monolith is kept as a constant to make sure the expense of precious metals remain the same. And the length of the inlet and outlet pipes are adjusted to keep the overall length of the converter the same as the base case. Each case of the cold flow simulation includes six different mass flow rates: 40 g/s, 64.5 g/s, 80 g/s, 150 g/s, 250g/s and 400g/s.

Table 7 Group I - Effect of L/D in cold flow simulation

<table>
<thead>
<tr>
<th>Case #</th>
<th>L/D</th>
<th>$\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.35</td>
<td>40.8</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>40.8</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>40.8</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>40.8</td>
</tr>
</tbody>
</table>

Table 8 Group II - Effect of the angle $\theta$ in cold flow simulation

<table>
<thead>
<tr>
<th>Case #</th>
<th>L/D</th>
<th>$\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>40.8</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>70</td>
</tr>
</tbody>
</table>
2.2.4.2 Test Cases for Light-off Simulation

For light-off simulation cases, the effects of the mass flow rate, inlet gas temperature and cell density on the flow and temperature distributions and the pressure drop across the monolith are studied. The base geometry as shown in Figure 5 is employed in cases of groups III, IV and V (see Tables 9 – 11).

Table 9 Group III – Light-off simulation with various inlet mass flow rate

<table>
<thead>
<tr>
<th>Case #</th>
<th>$\dot{m}_{in}$ (g/s)</th>
<th>$T_{g,in}$ (K)</th>
<th>CPSI/Cell wall thickness (mil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>650</td>
<td>400/4.5</td>
</tr>
<tr>
<td>2</td>
<td>64.5</td>
<td>650</td>
<td>400/4.5</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>650</td>
<td>400/4.5</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>650</td>
<td>400/4.5</td>
</tr>
<tr>
<td>5</td>
<td>250</td>
<td>650</td>
<td>400/4.5</td>
</tr>
<tr>
<td>6</td>
<td>400</td>
<td>650</td>
<td>400/4.5</td>
</tr>
</tbody>
</table>

Table 10 Group IV – Light-off simulation with various inlet gas temperature

<table>
<thead>
<tr>
<th>Case #</th>
<th>$\dot{m}_{in}$ (g/s)</th>
<th>$T_{g,in}$ (K)</th>
<th>CPSI/Cell wall thickness (mil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>64.5</td>
<td>464</td>
<td>400/4.5</td>
</tr>
<tr>
<td>2</td>
<td>64.5</td>
<td>500</td>
<td>400/4.5</td>
</tr>
<tr>
<td>3</td>
<td>64.5</td>
<td>600</td>
<td>400/4.5</td>
</tr>
<tr>
<td>4</td>
<td>64.5</td>
<td>650</td>
<td>400/4.5</td>
</tr>
<tr>
<td>5</td>
<td>64.5</td>
<td>700</td>
<td>400/4.5</td>
</tr>
<tr>
<td>6</td>
<td>64.5</td>
<td>300 to 700 with slope of 20/s</td>
<td>400/4.5</td>
</tr>
</tbody>
</table>
Table 11 Group V – Light-off simulation with various cell density

<table>
<thead>
<tr>
<th>Case #</th>
<th>$\dot{m}_{in}$ (g/s)</th>
<th>$T_{g,in}$ (K)</th>
<th>CPSI/Cell wall thickness (mil)</th>
<th>OFA</th>
<th>Interfacial area density (1/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>64.5</td>
<td>650</td>
<td>400/4.5</td>
<td>0.828</td>
<td>3461</td>
</tr>
<tr>
<td>2</td>
<td>64.5</td>
<td>650</td>
<td>600/3.5</td>
<td>0.836</td>
<td>4219</td>
</tr>
<tr>
<td>3</td>
<td>64.5</td>
<td>650</td>
<td>900/2.5</td>
<td>0.855</td>
<td>5108</td>
</tr>
</tbody>
</table>

For Group V, three cases of CPSI with a given cell wall thickness, 400/4.5 (used in Tenneco’s catalytic converter), 600/3.5 and 900/2.5 are considered. The OFA (see below for definition) and interfacial area density are calculated based on CPSI, cell diameter and cell wall thickness using Equations (11) and (12). The results are listed in Table 11.

The cells in the substrate are rectangular channels with a square cross-section. The interfacial area density is calculated using Equation (11).

$$IAD = \frac{A}{V} = \frac{4}{d_h}$$

(11)

The open frontal area is the percentage of the open area of the cross-section of a monolith and is calculated using Equation (12) [21]:

$$OFA = \frac{CPSI \cdot d_h}{25.4^2}$$

(12)

The last light-off case considered is based on the experimental data provided by Tenneco. The mass flow rate and inlet gas temperature from the experimental data were used to simulate the real light-off case without chemical reactions. The base geometry ($L/D = 0.5, \theta = 40.8^\circ, \text{CPSI} = 400$) was employed in this case.
In the thesis, the results from the base cases (case 2 in Group I for cold flow simulation and cases 4 and 6 in Group IV for light-off simulation and the case with experimental data) are discussed in details. Other cases are included to complete a systematic investigation on the effects of the geometric parameters, the flow conditions and the monolith cell density on the flow and temperature indices and the pressure drop across the monolith.

2.3 CFD Simulation Results and Discussions

2.3.1 Base Case Results and Discussions

2.3.1.1 The Cold Flow Base Case and Discussions

Case 2 in Group I is selected as the base case for cold flow simulation. The detailed conditions are shown in Table 12. Figures 13 – 17 are contour plots and charts of the simulation results. In Figure 13 and Figure 15, the inlet pipe is on the left, the exhaust gas flows from the left to right. All the pressure shown in the contours in this thesis is gage pressure.

<table>
<thead>
<tr>
<th>$\dot{m}_{in}$ (g/s)</th>
<th>$T_{g,in}$ (K)</th>
<th>CPSI/Cell wall thickness (mil)</th>
<th>L/D</th>
<th>$\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.5</td>
<td>300</td>
<td>400/4.5</td>
<td>0.5</td>
<td>40.8</td>
</tr>
</tbody>
</table>
Figure 13 Pressure contours at the symmetry plane for the cold flow base case (case 2 in group I)

Figure 14 Pressure contours at the substrate-inlet surface for the cold flow base case (case 2 in group I)
Figure 15 Local mass flow contours at the symmetry plane for the cold flow base case (case 2 in group I)

Figure 16 Local mass flow contours at the substrate-inlet surface for the cold flow base case (case 2 in group I)
The region with the highest pressure is at the center of the substrate-inlet surface (see Figures 13 and 14) because part of the exhaust gas is blocked in front of the substrate. The pressure then decreases as the gas flows through the substrate to the outlet. The major pressure loss occurs across the substrate and is of 73.46 Pa in this case.

By definition, the mass flow rate is calculated using Equation (13).

\[ \dot{m} = \int \rho \cdot u \, dA \]  

(13)
It is difficult to show the mass flow rate in a contour plot, the local mass flow (the mass flow rate per unit area) contour defined as $\rho \cdot u$ is shown instead in Figures 15 and 16. The flow in the inlet region is turbulent. The mass flow rate per unit area is larger in the inlet pipe and the center part of the inlet diffuser compared to that of the near wall region of the diffuser as a result of the passage of the diffuser. The flow in substrate is laminar and the differences of the local mass flow in the substrate are much smaller than those in the inlet region. The local mass flow through the center core of the substrate is larger than that in the near wall region of the substrate. The flow index for this case is 27.744%. Since it is a cold flow simulation, the air density will not be effected by the temperature, the velocity profile shown in Figure 17 also illustrate that there is more air flow in the center region of the monolith.

2.3.1.2 The Light-off Base Case with Steady Inlet Gas Temperature and Discussions

Case 4 in Group IV is selected as the base case for light-off simulation with a steady inlet gas temperature. The detailed conditions are shown in Table 13. The simulation results of the contour plots and charts at the time of 120 seconds are shown in Figures 18 – 28. The temperature index vs. time is given in Figure 29.

<table>
<thead>
<tr>
<th>$\dot{m}_{in}$ (g/s)</th>
<th>$T_{g, in}$ (K)</th>
<th>CPSI/Cell wall thickness (mil)</th>
<th>L/D</th>
<th>$\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.5</td>
<td>650</td>
<td>400/4.5</td>
<td>0.5</td>
<td>40.8</td>
</tr>
</tbody>
</table>
Figure 18 Pressure contours at the symmetry plane for the light-off base case (case 4 in group IV)

Figure 19 Pressure contours at the substrate-inlet surface for the light-off base case (case 4 in group IV)
Figure 20 Temperature contours at the symmetry plane for the light-off base case (case 4 in group IV)

Figure 21 Temperature contours at the substrate-inlet surface for the light-off base case (case 4 in group IV)
Figure 22 U-velocity contours at the substrate-inlet surface for the light-off base case (case 4 in group IV)
Figure 23 U-velocity profile at the substrate-inlet surface for the light-off base case (case 4 in group IV)
Figure 24 Density profile at the substrate-inlet surface for the light-off base case (case 4 in group IV)
Figure 25 Local mass flow contours at the symmetry plane for the light-off base case (case 4 in group IV)

Figure 26 Local mass flow contours at the substrate-inlet surface for the light-off base case (case 4 in group IV)
Figure 27 Local mass flow profile at the substrate-inlet surface for light-off base case (case 4 in group IV)

The pressure contour plots (see Figures 18 and 19) are similar to that of the cold flow base case (see Figures 13 and 14), while the pressure drop across the monolith is larger for the light-off case. The pressure drop through the substrate for the light-off base case is 245.8 Pa.

It can be seen from the temperature contours in Figures 20 and 21 that the gas is much hotter in the center at the substrate-inlet surface. The temperature index of this case
is 26.058%. The heat loss through convection, conduction and radiation is considered at the converter walls.

From Figures 22 and 23, the velocity in the center region is higher than that in the near-wall region. Because of the high temperature in the center region of the substrate-inlet surface, the density there is lower than that in the outer region of the surface (see Figure 24), thus the local mass flow in the center for the light-off case (see Figures 25 and 26) is smaller than that in the cold flow case (see Figures 15 and 16). As a result, the flow is more uniform for the light-off case (see Figures 27 and 17). The flow index of the light-off case is 24.959%, which is very close to a uniform flow (the flow index = 25%).

Figure 28 Volume averaged temperature (K) in the substrate vs. time (s) for the light-off base case (case 4 in group IV)
Figure 28 shows that the average temperature of the substrate keeps increasing as time elapses. From Figures 29 we can see that the temperature index at the substrate-inlet surface increases for the first 12 seconds as the hot gas flows into the converter, which causes the temperature mal-distribution. As the time increases beyond 12 seconds, the temperature index decreases as the entire converter is warmed up.

2.3.1.3 The Light-off Base Case with a Ramp Inlet Gas Temperature and Discussions

Case 6 in Group IV is selected as the base case for the light-off simulation with a ramp inlet gas temperature. As shown in Figure 30, the inlet gas temperature increases evenly from 300K to 700K in the first 20 seconds and is kept at 700K until the time of 120 seconds. The detailed conditions are shown in Table 14. The ramp inlet gas
temperature represents the cold start condition more accurately. All the figures in this section are based on the CFD solution at the time of 120 seconds.

![Figure 30 A ramp inlet gas temperature vs. time for the light-off case (case 6 in group IV)](image)

Table 14 Detailed conditions of the light-off case with a ramp inlet gas temperature (case 6 in group IV)

<table>
<thead>
<tr>
<th>$\dot{m}_{in}$ (g/s)</th>
<th>$T_{g,in}$ (K)</th>
<th>CPSI/Cell wall thickness (mil)</th>
<th>L/D</th>
<th>$\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.5</td>
<td>300 to 700 with slope of 20/s</td>
<td>400/4.5</td>
<td>0.5</td>
<td>40.8</td>
</tr>
</tbody>
</table>
Figure 31 Pressure contours at the symmetry plane for the light-off case with a ramp inlet gas temperature (case 6 in group IV)

Figure 32 Pressure contours at the substrate-inlet surface for the light-off case with a ramp inlet gas temperature (case 6 in group IV)
Figure 33 Local mass flow contours at the symmetry plane for the light-off case with a ramp inlet gas temperature (case 6 in group IV)

Figure 34 Local mass flow contours at the substrate-inlet surface for the light-off case with a ramp inlet gas temperature (case 6 in group IV)
Figure 35 Temperature contours at the symmetry plane for the light-off case with a ramp inlet gas temperature (case 6 in group IV)

Figure 36 Temperature contours at the substrate-inlet surface for the light-off case with a ramp inlet gas temperature (case 6 in group IV)
Figure 37 Volume averaged temperature (K) in the substrate vs. time (s) for the light-off case with a ramp inlet gas temperature (case 6 in group IV)

Figure 38 Temperature index vs. time (s) for the light-off case with a ramp inlet gas temperature (case 6 in group IV)
The contour plots of the pressure (Figures 31 and 32), local mass flow (Figures 33 and 34), temperature (Figures 35 and 36) are similar to those shown in section 2.3.1.2.

The pressure drop across the substrate of this case is 245.9Pa, and the flow index is 24.959%.

Figures 37 and 38 show the average temperature of the substrate and the thermal response of the substrate. The thermal response is slower than the cases with steady inlet gas temperature because it takes about 20 seconds for the inlet gas temperature to reach 700K. The peak of temperature index occurs at about 20 seconds and then the temperature index decreases to 26.175% at 120 seconds.

2.3.1.4 The Light-off Case with Input from the Experimental Data Provided by Tenneco

The experimental data provided by Tenneco were used as input in this light-off case to simulate the real cold start condition. The inlet gas temperature and the mass flow rate vs. time are shown in Figures 39 and 40. The base geometry with the L/D ratio of 0.5, the angle $\theta$ of 40.8° and the monolith with CPSI of 400 was used in this case.
Figure 39 Inlet gas temperature vs. time for the light-off case with the experimental data provided by Tenneco

Figure 40 Total mass flow rate vs. time for the light-off case with the experimental data provided by Tenneco
Figure 41 Flow index vs. time for the light-off case with the experimental data provided by Tenneco.

Figure 41 shows the change of the flow index as time elapses. The flow index is affected by the mass flow rate and the inlet gas temperature. Since the relative change of the mass flow rate (see Figure 40) is much larger than that of the inlet gas temperature (see Figure 39) during the time period, the mass flow rate, therefore, has a greater influence on the flow index. As a result the trend of the flow index vs. time is similar to the trend of the mass flow rate vs. time (see Figure 40).
Figure 42 shows the change of the temperature index as a function of time. As the time increases, the substrate is warmed up more uniformly, and the temperature index decreases, and then level off after about 12 minutes.
To show the temperature distribution within the monolith, the temperature index was calculated at the substrate-inlet surface, the substrate-outlet surface and three interior surfaces, parallel to the inlet and outlet surfaces, at 1/4, 1/2 and 3/4 of the substrate length from the inlet surface. Figure 43 shows the temperature index for the above five surfaces vs. time. Initially the temperature distribution in the substrate is not uniform and the temperature indices for the five surfaces differ significantly. As time elapses, the temperature distribution becomes more uniform and the temperature indices of the five surfaces become nearly the same.

Figure 43 Temperature index vs. time for the light-off case with the experimental data provided by Tenneco
Figure 44 shows the change of pressure drop as time elapses. Similar to the flow index discussed above, the pressure drop is also affected by the mass flow rate and the inlet gas temperature. From Figures 39 and 40, we can see that the relative change of the mass flow rate is much larger than that of the inlet gas temperature. As a result, the trend of the pressure drop vs. time is similar to the trend of the mass flow rate vs. time (see Figure 40).
2.3.2 Effects of the Geometric Parameters and the Inlet Conditions on Flow Index

The effects of the geometry parameters (such as the angle $\theta$ and the L/D ratio) and inlet conditions (such as the inlet mass flow rate and the inlet gas temperature) on the flow index are investigated.

As shown in Figure 45, the flow index decreases as the L/D ratio becomes larger. The flow index decreases about 4.5% from the L/D ratio of 0.35 to 1.5. When L/D = 1.5, the flow index is 25.792%, for the mass flow rate of 64.5g/s and the angle $\theta$ of 40.8°, which is close to a uniform flow (the flow index of 25%). Also, the flow index increases as the mass flow rate increases.

Figure 45  Flow index vs. L/D ratio for group I ($\theta = 40.8^\circ$, CPSI = 400, $T_{g, in} = 300$ K)
As shown in Figure 46, the flow index increases as $\theta$ increases. Larger $\theta$ means a sharp change in geometry along the flow path which results in the flow mal-distribution at the substrate-inlet surface. In addition, the flow index increases with an increase of the mass flow rate for a given $\theta$. 

Figure 46 Flow index vs. $\theta$ for group II (L/D = 0.5, CPSI = 400, $T_{g,in} = 300$ K)
As mentioned in 2.3.1.1, the mass flow rate is expressed as Equation (13). With the inlet gas temperature increases, the temperature index increases and the density difference between the center and the near wall region of the converter increases. As a result the mass flow rate in the center of the converter decreases, thus the flow index decreases. In Figure 47, it shows that the flow index indeed decreases as the inlet gas temperature increases. The flow index can reach below 0.25 because the air in the center region with higher temperature leads to a lower density compared to the air in the near-wall region.

Figure 47 Flow index vs. inlet gas temperature for group IV (L/D = 0.5, θ = 40.8°, \(\dot{m}_{\text{in}} = 64.5\) g/s, CPSI = 400, at t = 120 s)
It is shown in Figure 48 that the flow index increases as the mass flow rate increases. This is in an agreement with the cold flow cases shown in Figures 45 and 46.
Table 15 Flow index for group V (L/D = 0.5, $\theta = 40.8^\circ$ at t=120s)

<table>
<thead>
<tr>
<th>Case #</th>
<th>$m_{in}$ (g/s)</th>
<th>$T_{g, in}$ (K)</th>
<th>CPSI/Cell wall thickness (mil)</th>
<th>OFA</th>
<th>Interfacial area density (/m)</th>
<th>Flow index (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>64.5</td>
<td>650</td>
<td>400/4.5</td>
<td>0.828</td>
<td>3461</td>
<td>24.959</td>
</tr>
<tr>
<td>2</td>
<td>64.5</td>
<td>650</td>
<td>600/3.5</td>
<td>0.836</td>
<td>4219</td>
<td>24.632</td>
</tr>
<tr>
<td>3</td>
<td>64.5</td>
<td>650</td>
<td>900/2.5</td>
<td>0.855</td>
<td>5108</td>
<td>24.46</td>
</tr>
</tbody>
</table>

From Table 15, the flow index decreases about 0.5% when the CPSI increases from 400 to 900. As the CPSI increases, the OFA increases from 0.828 to 0.855. This results in a more uniform u-velocity distribution at the substrate-inlet surface; coupled with the mal-distribution of the density caused by the temperature difference at the substrate-inlet surface, the flow index at the surface decreases slightly. The effect of the cell density on the flow index is small compared to that of the other geometric parameters such as the L/D ratio, the angle $\theta$, and the inlet mass flow rate.
2.3.3 Effects of the Inlet Conditions and Cell Density on Temperature Index

As shown in Figure 49, the temperature index increases as the inlet gas temperature increases. At the time of 120 seconds, it has been shown earlier that the simulation has not yet reached a steady state. With the inlet gas temperature of 464 K at the time of 120 seconds, the temperature index is 25.68%, which is still larger than that of the steady state value of 25.28% as shown in Table 5 (case 4). With the inlet gas temperature increases, the temperatures of both the center and the near-wall regions of
the converter increase. The temperature difference between the near-wall region and the environment increases which leads to an increase in the heat loss caused by convection, conduction and radiation. As a result, the temperature difference between the center and the near-wall regions of the converter increases, thus the temperature index increases.

As shown in Figure 50, the temperature index decreases as the mass flow rate increases. As mentioned earlier that the simulation has not yet reached a steady state at the time of 120 seconds. However, a larger mass flow rate allows the entire converter to

Figure 50 Temperature index vs. mass flow rate for group III (L/D = 0.5, $\theta = 40.8^\circ$, CPSI = 400, $T_{g,\text{in}} = 650$ K at $t = 120s$)
be heated up quickly so that a more uniform temperature distribution can be obtained. As a result, the temperature index decreases.

Table 16 Temperature index for group V (L/D = 0.5, \( \theta = 40.8^\circ \) at \( t = 120s \))

<table>
<thead>
<tr>
<th>Case #</th>
<th>( \dot{m}_{\text{in}} ) (g/s)</th>
<th>( T_{g,\text{in}} ) (K)</th>
<th>CPSI/Cell wall thickness (mil)</th>
<th>OFA</th>
<th>Interfacial area density (/m)</th>
<th>Temperature index (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>64.5</td>
<td>650</td>
<td>400/4.5</td>
<td>0.828</td>
<td>3461</td>
<td>26.058</td>
</tr>
<tr>
<td>2</td>
<td>64.5</td>
<td>650</td>
<td>600/3.5</td>
<td>0.836</td>
<td>4219</td>
<td>26.05</td>
</tr>
<tr>
<td>3</td>
<td>64.5</td>
<td>650</td>
<td>900/2.5</td>
<td>0.855</td>
<td>5108</td>
<td>26.04</td>
</tr>
</tbody>
</table>

As shown in Table 16, the temperature index is not much affected by the cell density and the cell wall thickness without consideration of the chemical reactions. While the effects of the cell density and the cell wall thickness become important if the chemical reactions are considered [22]. As stated in Mohiuddin’s work [22], a catalytic converter with a higher cell density and slightly thinner wall thickness allows more precious metal catalysts to be loaded hence increasing reaction surface areas for better conversion efficiency. Also a higher cell density provides a higher exhaust flow velocity and promotes chemical reactions with catalysts.
2.3.4 Effects of the Geometric Parameters and the Inlet Conditions on the Pressure Drop

As shown in Figure 51, the pressure drop across the monolith increases as the L/D ratio increases. As the L/D ratio changes from 0.35 to 1.5, the pressure drop increases up to about 600% for the cases studied. The pressure drop increases as the mass flow rate increases. In ANSYS Fluent, the pressure drop through porous media is governed by Darcy’s Law [18]. The cases shown in Figure 51 (group I) are for cold flow simulations, thus the density is the same for all the cases. Therefore a larger mass flow rate means a
larger velocity which results in a larger pressure drop via the monolith. In addition the pressure drop increases significantly with increasing the L/D ratio for a larger mass flow rate.

Figure 52 Pressure drop across the monolith vs. $\theta$ for group II (L/D = 0.5, CPSI = 400, $T_{g,\text{in}} = 300$ K)

As shown earlier that the flow index at the substrate-inlet surface increases as the angle $\theta$ increases (see Figure 46). The flow mal-distribution at the surface becomes significant for a larger $\theta$. As a result, the pressure drop increases across the monolith as the angle $\theta$ increases. Since the pressure drop across the monolith is the major contributor for the overall pressure drop over the converter, only the pressure drop across the
monolith was shown (see Figure 52). It can be seen from Figure 52 that the slope of the curves becomes steeper as the mass flow rate increases.

![Graph showing pressure drop across the monolith vs. inlet gas temperature for group IV (L/D = 0.5, $\theta = 40.8^\circ$, $m_{in} = 64.5$ g/s at $t = 120s$)](image)

Figure 53 Pressure drop across the monolith vs. inlet gas temperature for group IV ($L/D = 0.5, \theta = 40.8^\circ, \dot{m}_{in} = 64.5 \, \text{g/s at } t = 120s$)

A larger inlet gas temperature leads to a smaller density and therefore a larger velocity (for a given mass flow rate) in the center core of the monolith. As a result, the pressure drop across the monolith increases as the inlet gas temperature increases. From Figure 53, the relationship between the inlet gas temperature and the pressure drop is almost linear.
In the light-off cases as shown in Figure 54, as expected a larger mass flow rate leads to a larger pressure drop across the monolith for a given inlet gas temperature. The relation between the mass flow rate and the pressure drop is almost linear.
Table 17 Pressure drop for group V (L/D = 0.5, $\theta = 40.8^\circ$ at $t = 120s$)

<table>
<thead>
<tr>
<th>Case #</th>
<th>$m_{in}$ (g/s)</th>
<th>$T_{g,in}$ (K)</th>
<th>CPSI/Cell wall thickness (mil)</th>
<th>OFA</th>
<th>Interfacial area density (/m)</th>
<th>Pressure drop (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>64.5</td>
<td>650</td>
<td>400/4.5</td>
<td>0.828</td>
<td>3461</td>
<td>245.8183</td>
</tr>
<tr>
<td>2</td>
<td>64.5</td>
<td>650</td>
<td>600/3.5</td>
<td>0.836</td>
<td>4219</td>
<td>411.67</td>
</tr>
<tr>
<td>3</td>
<td>64.5</td>
<td>650</td>
<td>900/2.5</td>
<td>0.855</td>
<td>5108</td>
<td>609.383</td>
</tr>
</tbody>
</table>

As shown in Table 17, the effect of the cell density on the pressure drop is enormous. The monolith with a larger cell density has a larger inertial resistance and a larger viscous resistance, which leads to a larger pressure drop.
Chapter 3  1D Model for Catalytic Converters

3.1 Problem Statement

A numerical study of the start-up transient phase of a catalytic converter with time dependent inlet exhaust gas conditions is performed. The 1D channel model includes the chemical kinetics as well as convective and conduction heat transfer inside the monolith channel. The numerically predicted time-dependent conversion of the pollutants is compared with experimental data from Tenneco.

3.1.1 Objectives of Research

A global reaction mechanism from Holder et al’s model will be implemented in MATLAB/Simulink for 1D channel model of catalytic converters. The parameters of chemical reaction kinetics will be calibrated to match experimental data from Tenneco. The conversion efficiencies and the substrate temperature of Tenneco converters will be evaluated. In addition, the effects of substrate cell densities and catalyst loadings on the conversion efficiencies will be studied.
3.1.2 Scope of Study

The scope of this research is as follows:

i. Implement Holder et al’s model in MATLAB/Simulink
ii. Perform a numerical simulation using Tenneco data
iii. Calibrate the parameters of reaction kinetics to match Tenneco data
iv. Study the effects of substrate cell densities and catalyst loadings on the conversion efficiencies

3.1.3 Substrate and Exhaust Gas Properties

The substrate studied in the thesis is the cylindrical part of the entire catalytic converter from Tenneco. The monolith length and the monolith frontal area are listed in Table 18 along with other substrate properties provided by Tenneco.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Tenneco substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolith density (kg/m³)</td>
<td>1622</td>
</tr>
<tr>
<td>Monolith length (m)</td>
<td>0.1524</td>
</tr>
<tr>
<td>Cell hydraulic radius (m)</td>
<td>0.00057785</td>
</tr>
<tr>
<td>CPSI</td>
<td>400</td>
</tr>
<tr>
<td>Void fraction of the monolith</td>
<td>0.828</td>
</tr>
<tr>
<td>Monolith frontal area (m²)</td>
<td>0.072966</td>
</tr>
<tr>
<td>Noble metal loading (g/ft³)</td>
<td>35</td>
</tr>
<tr>
<td>Dispersion</td>
<td>0.07</td>
</tr>
<tr>
<td>Substrate thermal conductivity (W/m·K)</td>
<td>3</td>
</tr>
<tr>
<td>Exhaust specific heat (J/kg·K)</td>
<td>1089</td>
</tr>
<tr>
<td>Monolith specific heat (J/kg·K)</td>
<td>500</td>
</tr>
<tr>
<td>Initial monolith temperature (K)</td>
<td>293</td>
</tr>
</tbody>
</table>
3.2 Model Construction

This section analyzes the model, by looking at the individual code blocks or modules that make up the three-way catalytic converter (TWC) model. Then it describes how to set up the model and run the simulation.

3.2.1 TWC Module

![Diagram of TWC model]

Figure 55 Overview of the 1D TWC model

The TWC model simulates a gasoline three-way catalyst converter. As shown in Figure 55, the TWC model has been broken down into several Simulink™ modeling blocks that are explained individually in the following sections (3.2.2 - 3.2.4). The TWC model has 14 input variables and 14+n (n is the number of elements that a substrate is divided) output variables.
Both the inputs and outputs of TWC module include two parts: Emissions in/out and Exhaust in as shown in/out Table 19 and Table 20.

Table 19 Inputs of TWC module

<table>
<thead>
<tr>
<th>No.</th>
<th>Variable</th>
<th>Bus Width</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Emissions in</td>
<td>11×1</td>
<td>Model input of the exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>2</td>
<td>Exhaust in</td>
<td>3×1</td>
<td>Model input of exhaust parameters</td>
<td>Various</td>
</tr>
</tbody>
</table>

Table 20 Outputs of TWC module

<table>
<thead>
<tr>
<th>No.</th>
<th>Variable</th>
<th>Bus Width</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Emissions out</td>
<td>11×1</td>
<td>Output of predicted exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>2</td>
<td>Exhaust out</td>
<td>3×1</td>
<td>Output of predicted exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>3</td>
<td>T_Mon</td>
<td>n×1</td>
<td>Vector of monolith temperatures</td>
<td>K</td>
</tr>
</tbody>
</table>
The detailed signals in the Emissions in and Emissions out buses are listed in Table 21.

<table>
<thead>
<tr>
<th>Line</th>
<th>Variable</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M_NO</td>
<td>Mass flow rate nitric oxide</td>
<td>kg/s</td>
</tr>
<tr>
<td>2</td>
<td>M_NO2</td>
<td>Mass flow rate nitrogen dioxide</td>
<td>kg/s</td>
</tr>
<tr>
<td>3</td>
<td>M_N2O</td>
<td>Mass flow rate nitrous oxide</td>
<td>kg/s</td>
</tr>
<tr>
<td>4</td>
<td>M_N2</td>
<td>Mass flow rate nitrogen</td>
<td>kg/s</td>
</tr>
<tr>
<td>5</td>
<td>M_CO</td>
<td>Mass flow rate carbon monoxide</td>
<td>kg/s</td>
</tr>
<tr>
<td>6</td>
<td>M_CO2</td>
<td>Mass flow rate carbon dioxide</td>
<td>kg/s</td>
</tr>
<tr>
<td>7</td>
<td>M_CH4</td>
<td>Mass flow rate methane (slow burn HC)</td>
<td>kg/s</td>
</tr>
<tr>
<td>8</td>
<td>M_C3H6</td>
<td>Mass flow rate propene (fast burn HC)</td>
<td>kg/s</td>
</tr>
<tr>
<td>9</td>
<td>M_H2</td>
<td>Mass flow rate hydrogen</td>
<td>kg/s</td>
</tr>
<tr>
<td>10</td>
<td>M_H2O</td>
<td>Mass flow rate water</td>
<td>kg/s</td>
</tr>
<tr>
<td>11</td>
<td>M_O2</td>
<td>Mass flow rate oxygen</td>
<td>kg/s</td>
</tr>
</tbody>
</table>

The detailed signals in the Exhaust in and Exhaust out buses are listed in Table 22.

<table>
<thead>
<tr>
<th>Line</th>
<th>Variable</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M_ExhGas</td>
<td>Mass flow rate of the exhaust</td>
<td>kg/s</td>
</tr>
<tr>
<td>2</td>
<td>T_ExhGas_in</td>
<td>Temperature of the exhaust</td>
<td>K</td>
</tr>
<tr>
<td>3</td>
<td>P_ExhGas</td>
<td>Pressure of the exhaust</td>
<td>Pa</td>
</tr>
</tbody>
</table>

A MATLAB M file was written according to the substrate and exhaust properties shown in Table 18 and the chemical kinetics to initialize the parameters in the model (see Table 23).
Table 23 Initialization M file in 1D TWC model

<table>
<thead>
<tr>
<th>Variable</th>
<th>Type</th>
<th>Description</th>
<th>Units/Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initialization</td>
<td>M_file</td>
<td>M-file to load the TWC input physical and chemical variables used within the model (see Appendix B)</td>
<td>Varied</td>
</tr>
</tbody>
</table>

3.2.2 Catalyst Module

The catalyst module (see Figure 56) deals with the mass transfer onto and off the monolith surface to predict the surface concentrations of the emissions. The surface concentration is then used to calculate the reaction rate and hence the emissions downstream of the monolith.

Figure 56 Code for 1D catalyst module
The TWC model has been developed with an option for the user to set the number of discretized elements the monolith is broken down into. This discretization number of elements (n) can be set to between 2 and 100 elements in the input file.

The inputs, outputs and constants of catalyst module are listed in Tables 24-26.

### Table 24 Inputs of catalyst module

<table>
<thead>
<tr>
<th>No.</th>
<th>Variable</th>
<th>Bus Width</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Emissions in</td>
<td>11×1</td>
<td>Vector of emission species</td>
<td>kg/s</td>
</tr>
<tr>
<td>2</td>
<td>P_ExhGas</td>
<td>1×1</td>
<td>Exhaust pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>3</td>
<td>M_ExhGas</td>
<td>1×1</td>
<td>Exhaust mass flow rate</td>
<td>kg/s</td>
</tr>
<tr>
<td>4</td>
<td>T_Mon</td>
<td>n×1</td>
<td>Monolith segment temperatures</td>
<td>K</td>
</tr>
<tr>
<td>5</td>
<td>T_ExhGas</td>
<td>n×1</td>
<td>Monolith exhaust gas temperatures</td>
<td>K</td>
</tr>
</tbody>
</table>

### Table 25 Outputs of catalyst module

<table>
<thead>
<tr>
<th>No.</th>
<th>Variable</th>
<th>Bus Width</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Emissions out</td>
<td>11×1</td>
<td>Vector of emissions species</td>
<td>kg/s</td>
</tr>
<tr>
<td>2</td>
<td>Q_Reac</td>
<td>n×1</td>
<td>Rate of heat produced by chemical reaction per monolith segment</td>
<td>J/s</td>
</tr>
</tbody>
</table>
The code solves the following equations to predict the surface and exhaust gas concentrations [23]:

The gas phase species equation:

\[
(e \frac{\partial C_g}{\partial t} + v \frac{\partial C_g}{\partial z}) = -k_m G_u (C_g - C_s) \quad (14)
\]

The surface species equation:

\[
(1 - e) \frac{\partial C_s}{\partial t} = k_m G_u (C_g - C_s) - R \cdot N \quad (15)
\]

For this calculation, the accumulation of mass in the gas phase was neglected, that is:

\[
\frac{\partial C_g}{\partial t} = 0 \quad (16)
\]

This is acceptable since the gas phase time constants are typically much smaller than those of the surface response [24]. This quasi-steady approach allows us to describe the gas concentration as the differential equation:
\[ v_g \frac{\partial C_g}{\partial z} = -k_m G_a (C_g - C_s) \]  

(17)

This allows the Euler method to be used:

\[ \frac{dC_g}{dz} = \frac{C_{g,\text{out}} - C_{g,\text{in}}}{L} \]  

(18)

\[ \frac{C_{g,\text{out}} - C_{g,\text{in}}}{L} = -k_m G_a (C_g - C_s) \]  

(19)

To determine the mass transfer to the surface, within an element the gas concentration term, \( C_g \), is taken to be the outlet gas concentration simulating an element as a continuously stirred reactor.

\[ \frac{C_{g,\text{out}} - C_{g,\text{in}}}{L} = -k_m G_a (C_g - C_s) \]  

(20)

Since surface concentration is a function of one independent variable, it can be integrated:

\[ C_s = \int \frac{1}{1 - e^{-[k_m G_a (C_g - C_s) - R \cdot N]}} \]  

(21)

The last term \( R \cdot N \) in Equations (15) and (21) represents production or depletion of the species through chemical reactions. The instantaneous value for \( R \) is calculated in the reactions module.

From Equation (21), a small change in the gas or surface concentration has a large effect on the surface concentration. It takes a long time to reach a stable solution in Simulink. The interaction has very stiff dynamics. As shown in Figure 56, two “Lag” blocks (first order delay) have been used in the feedback loop. These blocks filter out
high frequency oscillations and allow for slower responses. The default value for these two delays is 0.1 s. Since the system (governing equations) is very stiff, the numerical method must take very small steps to achieve satisfactory results. Unfortunately sometimes the time settings for the “Lag” blocks must be decreased to keep the numerical method working. This could result in capturing unwanted fast dynamics (high frequency oscillations).

The $k_m$ term is the mass transfer coefficient (m/s) for the gas species passing onto the substrate. From Chan et al.’s [25] paper, the following equation was used to calculate the value of $k_m$:

$$k_m = \frac{Sh \cdot D_s}{d_h}$$

(22)

The asymptotic Sherwood number has been used to calculate $k_m$ and is a parameter in the input file.

As shown in Table 27, originally the species diffusivity was calculated relative to oxygen (1.35 cm$^2$/s) using the following estimation when the value is unknown. The diffusion mechanism was revised using Chapman-Enskog theory [26] and Fuller correlation [27] to model the physics more accurately.
Table 27 Comparison of Original and revised diffusion mechanisms

<table>
<thead>
<tr>
<th>Original diffusion mechanism</th>
<th>Revised diffusion mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D = \frac{T^{1.75}}{P}D_x$, $D_x = 1.35 \times \sqrt{\frac{32}{M_x}}$</td>
<td>Chapman-Enskog theory for NO, CH$_4$ and C$_3$H$_6$</td>
</tr>
<tr>
<td></td>
<td>Fuller correlation for other gas species</td>
</tr>
</tbody>
</table>

In the original diffusion mechanism, the diffusion coefficient was calculated using Equations (23) and (24).

$$D = \frac{T^{1.75}}{P}D_x$$  \hspace{1cm} (23)

It uses Oxygen as a reference where $D_{O_2} = 1.35$ cm$^2$/s, and for other species $X$ with molecular weight $M_x$

$$D_x = 1.35 \times \sqrt{\frac{32}{M_x}}$$  \hspace{1cm} (24)

where, $T$ is the absolute temperature (K), $M_x$ is the molar mass (g/mol) and $P$ is the pressure (atm).

This diffusion mechanism is an approximation compared to Oxygen and can be revised to be more scientific using Chapman-Enskog theory and Fuller correlation.

The diffusion coefficient based on the Chapman-Enskog theory is calculated as:

$$D_{12} = \frac{1.858 \times 10^{-3} T^2}{P\sigma_{12}^2 \Omega} \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{\frac{3}{2}}$$  \hspace{1cm} (25)
where 1 and 2 index the two kinds of molecules present in the gaseous mixture, $T$ is the absolute temperature (K), $M$ is the molar mass (g/mol), $P$ is the pressure (atm), $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$ is the average collision diameter (Å), can be found in table (see Appendix C-1) and $\Omega$ is a temperature-dependent collision integral, can be found in table (see Appendix C-2).

The diffusion coefficient based on the Fuller correlation is given as

$$D_{ij} = \frac{10^{-3}T^{1.75}}{P} \left[ \sum \frac{1}{M_i} \right]^{\frac{1}{2}} \left[ \frac{1}{M_1} + \frac{1}{M_2} \right]^{-\frac{1}{2}}$$

(26)

where 1 and 2 index the two kinds of molecules present in the gaseous mixture, $T$ is the absolute temperature (K), $M$ is the molar mass (g/mol), $P$ is the pressure (atm) and $V_i$ is the diffusion volumes, can be found in table (see Appendix C-3). Here, the species 1 refers to the specific gas species (NO, CO etc), species 2 refers to air.

Although Fuller correlation (~3% error) is more accurate than Chapman-Enskog theory (~8% error), the diffusion volumes for NO, CH$_4$ and C$_3$H$_6$ are not listed in the reference [27]. Thus Chapman-Enskog theory was used to predict the diffusion coefficient of these three species and Fuller correlation was employed to predict the diffusion coefficient of the other species.

The comparisons of conversion efficiencies curves between the case with original diffusion mechanism and the case with revised diffusion mechanism shows that the one with new diffusion mechanism are slightly lower than the original ones. Since the
original one also takes temperature and pressure into consideration, the difference is small.

To model the chemical storage of oxygen, two additional surface species are required \(Ce_2O_3\) and \(CeO_2\). The ceria species remain on the surface of the catalyst and do not diffuse on or off, thus their diffusivity is set to zero.

The model is coded to allow the users to change the size of monolith discretization. This has been done using variable size bus widths in the MATLAB/Simulink code. The emissions enter the catalyst module as an 11 species wide bus. This bus is expanded to give one species per element modeled. For example if 10 elements were used the species bus in the model would be 130 wide (11 gas species plus two storage species multiplied by number of elements). The discretization code works by stepping the emission signals through the elements so the gas comes into the first element and the element exit exhaust composition is calculated, this is then fed into the second element (done in the emissions transfer block) and the output from this element is calculated and so on until the last monolith segment, where the emissions downstream of the catalyst exit the monolith.

3.2.3 Reactions Module

The reactions module predicts the rate of change of surface concentration as a result of the certain chemical kinetics. The chemical kinetics from Holder et al’s paper [10] is coded in the 1D TWC model and is revised to include reversibility to reactions 6, 8 and 9.
The inputs, outputs of 1D reaction module are of the same form and listed in Tables 28-30.

Table 28 Inputs of reaction module

<table>
<thead>
<tr>
<th>No.</th>
<th>Variable</th>
<th>Bus Width</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cs</td>
<td>13n×1</td>
<td>Substrate surface concentration of species</td>
<td>Various</td>
</tr>
<tr>
<td>2</td>
<td>T_Mon</td>
<td>n×1</td>
<td>Monolith segment temperatures</td>
<td>K</td>
</tr>
</tbody>
</table>

Table 29 Surface concentration signals Cs

<table>
<thead>
<tr>
<th>Line</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Concentration of nitric oxide</td>
<td>mole fraction</td>
</tr>
<tr>
<td>2</td>
<td>Concentration of nitrogen dioxide</td>
<td>mole fraction</td>
</tr>
<tr>
<td>3</td>
<td>Concentration of nitrous oxide</td>
<td>mole fraction</td>
</tr>
<tr>
<td>4</td>
<td>Concentration of nitrogen</td>
<td>mole fraction</td>
</tr>
<tr>
<td>5</td>
<td>Concentration of carbon monoxide</td>
<td>mole fraction</td>
</tr>
<tr>
<td>6</td>
<td>Concentration of carbon dioxide</td>
<td>mole fraction</td>
</tr>
<tr>
<td>7</td>
<td>Concentration of methane (slow burn HC)</td>
<td>mole fraction</td>
</tr>
<tr>
<td>8</td>
<td>Concentration of propene (fast burn HC)</td>
<td>mole fraction</td>
</tr>
<tr>
<td>9</td>
<td>Concentration of hydrogen</td>
<td>mole fraction</td>
</tr>
<tr>
<td>10</td>
<td>Concentration of water</td>
<td>mole fraction</td>
</tr>
<tr>
<td>11</td>
<td>Concentration of oxygen</td>
<td>mole fraction</td>
</tr>
<tr>
<td>12</td>
<td>Concentration of CeO₂</td>
<td>kmol/m³</td>
</tr>
<tr>
<td>13</td>
<td>Concentration of Ce₂O₃</td>
<td>kmol/m³</td>
</tr>
</tbody>
</table>

Table 30 Outputs of reaction module

<table>
<thead>
<tr>
<th>No.</th>
<th>Variable</th>
<th>Bus Width</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R</td>
<td>13n×1</td>
<td>Rate of change of surface concentration</td>
<td>kmol/(m³·s)</td>
</tr>
<tr>
<td>2</td>
<td>Q_Reac</td>
<td>n×1</td>
<td>Rate of heat produced by chemical reaction per monolith segment</td>
<td>J/s</td>
</tr>
</tbody>
</table>
There are 21 reactions in Holder et al.'s model (see below) since $C_3H_8$ is not considered in the current study, Reaction 3 and 7 which are related to $C_3H_8$ are not modeled in MATLAB/Simulink program. All other 19 reactions are considered. Reaction 6, 8 and 9 are coded as reversible reactions.

Reaction 1 $CO + 0.5O_2 \rightarrow CO_2$

Reaction 2 $H_2 + 0.5O_2 \rightarrow H_2O$

Reaction 3 $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ (not coded in the MATLAB/Simulink model)

Reaction 4 $C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O$

Reaction 5 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Reaction 6 $CO + H_2O \leftrightarrow CO_2 + H_2$

Reaction 7 $C_3H_8 + 3H_2O \leftrightarrow 3CO + 7H_2$ (not coded in the MATLAB/Simulink model)

Reaction 8 $C_3H_6 + 3H_2O \leftrightarrow 3CO + 6H_2$

Reaction 9 $CH_4 + H_2O \leftrightarrow CO + 3H_2$

Reaction 10 $CO + NO \rightarrow CO_2 + 0.5N_2$

Reaction 11 $H_2 + NO \rightarrow H_2O + 0.5N_2$

Reaction 12 $C_3H_6 + 9NO \rightarrow 3H_2O + 3CO_2 + 4.5N_2$

Reaction 13 $H_2 + 2NO \rightarrow H_2O + N_2O$
Reaction 14 \( N_2O + H_2 \rightarrow H_2O + N_2 \)

Reaction 15 \( CO + 2NO \rightarrow CO_2 + N_2O \)

Reaction 16 \( N_2O + CO \rightarrow CO_2 + N_2 \)

Reaction 17 \( H_2 + 2CeO_2 \rightarrow Ce_2O_3 + H_2O \)

Reaction 18 \( Ce_2O_3 + H_2O \rightarrow H_2 + 2CeO_2 \)

Reaction 19 \( CO + 2CeO_2 \rightarrow CO_2 + Ce_2O_3 \)

Reaction 20 \( CO_2 + Ce_2O_3 \rightarrow CO + 2CeO_2 \)

Reaction 21 \( 0.5O_2 + Ce_2O_3 \rightarrow 2CeO_2 \)

The constants used in the reaction module are listed in Table 31.

<table>
<thead>
<tr>
<th>Name</th>
<th>Size</th>
<th>Description</th>
<th>Units/Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_X )</td>
<td>1×1</td>
<td>Natural logarithm of pre-exponential factors, ( \ln(A) ), for reactions 1-21.</td>
<td>See Appendix B</td>
</tr>
<tr>
<td>( E_X )</td>
<td>1×1</td>
<td>Activation energy ( E ) divided by universal constant ( R ) for reactions 1-21.</td>
<td>See Appendix B</td>
</tr>
<tr>
<td>( A_{I_X} )</td>
<td>1×1</td>
<td>Pre-exponential factors for inhibition terms 1-7.</td>
<td>See Appendix B</td>
</tr>
<tr>
<td>( E_{I_X} )</td>
<td>1×1</td>
<td>Activation energy for inhibition terms 1-7.</td>
<td>See Appendix B</td>
</tr>
</tbody>
</table>

The reaction rate is expressed as

\[
R = \frac{Ae^{-E/RT}}{F} \prod_{k=1}^{n}[\text{reactant}]_k
\]  

(27)
where $F$ is for inhibition terms.

$$F_1 = T \left(1 + K_{a,1}[CO]^{0.2} + K_{a,2}[C_3H_6]^{0.7} + K_{a,3}[NO]^{0.7}\right)^2$$  \hspace{1cm} (28)

$$F_2 = T \left(1 + K_{a,4}[CO] + K_{a,5}[C_3H_6] + K_{a,6}[NO]^{0.7}\right)^2$$  \hspace{1cm} (29)

and $K_{a,x}$ represents the Arrhenius form.

$F_1$ and $F_2$ are used separately in the expression of the reaction rates for reactions 1-16 (not include reactions 3 and 7). Details can be found in Table 32.

<table>
<thead>
<tr>
<th>Inhibition term</th>
<th>Reaction No. that used this inhibition term</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_1$</td>
<td>1,2,4,5</td>
</tr>
<tr>
<td>$F_2$</td>
<td>6, 8-16</td>
</tr>
</tbody>
</table>

Reactions 6, 8 and 9 are considered as reversible reactions. Reactions 6 and 8 are modeled based on several references [28-33].

Reaction 6 is the water gas shift reaction. With rhodium being the active metal, the fraction of rhodium sites that are oxidized (active) is defined as $\theta_{Rh}$. The rate of oxidation and reduction of the rhodium is defined by

$$R_{ox} = (1 - \theta_{Rh})k_{Rh,ox}f_{ox}$$  \hspace{1cm} (30)

$$R_{red} = \theta_{Rh} k_{Rh,red}f_{red}$$  \hspace{1cm} (31)

where $k$ represents the Arrhenius form.

$$f_{ox} = 2[CO_2] + [NO]$$  \hspace{1cm} (32)

$$f_{red} = [CO] + [H_2] + 2[C_3H_6] + 4[CH_4]$$  \hspace{1cm} (33)

The rate of change of $\theta_{Rh}$ with time is defined by the equation
Given this calculation of $\theta_{Rh}$, Reaction 6 proceeds according to the following reaction rate equation:

$$\frac{d\theta_{Rh}}{dt} = R_{ox} - R_{red}$$  \hspace{1cm} (34)$$

where

$$R_b = \theta_{Rh} \left( \frac{[H_2O][CO]}{G_x} \right) \left( 1 - \frac{[CO_2][H_2]}{[CO][H_2O]K_{p}^1(T)} \right)$$ \hspace{1cm} (35)$$

and

$$G_x = T \left\{ 1 + C_1 e^{\frac{D_1}{T}} [CO] + E_1 e^{\frac{F_1}{T}} [C_3H_6] \right\}^2 \left\{ 1 + G_1 e^{\frac{H_1}{T}} [CO]^2 [C_3H_6]^2 \right\} \left( 1 + I_1 e^{\frac{J_1}{T}} [NO]^{0.7} \right)$$ \hspace{1cm} (36)$$

$K_{p}^1(T)$ is the chemical equilibrium constant for the reaction.

The values for the constant are entered in the model as shown in Table 33:

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_{p}^1(T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.01E-5</td>
</tr>
<tr>
<td>500</td>
<td>0.0077584</td>
</tr>
<tr>
<td>700</td>
<td>0.1229268</td>
</tr>
<tr>
<td>800</td>
<td>0.2914794</td>
</tr>
<tr>
<td>900</td>
<td>0.570485</td>
</tr>
<tr>
<td>1000</td>
<td>0.9645616</td>
</tr>
<tr>
<td>1100</td>
<td>1.4614117</td>
</tr>
<tr>
<td>1200</td>
<td>2.0910517</td>
</tr>
<tr>
<td>1300</td>
<td>2.7924972</td>
</tr>
</tbody>
</table>

Reaction 8 is the steam reforming reaction and the reaction rate is described by
\[ R_s = \frac{k_s [C_3H_6][H_2O]}{G_X} \left( 1 - \frac{[CO_2]^3[H_2]^9}{[C_3H_6][H_2O]^9} K^2_p(T) \right) \] (37)

with the value of \( K^2_p(T) \) listed in Table 34.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( K^2_p(T) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.765E-37</td>
</tr>
<tr>
<td>500</td>
<td>4.944E-11</td>
</tr>
<tr>
<td>700</td>
<td>6.9437131</td>
</tr>
<tr>
<td>800</td>
<td>21143.918</td>
</tr>
<tr>
<td>900</td>
<td>10830468</td>
</tr>
<tr>
<td>1000</td>
<td>1.593E+09</td>
</tr>
<tr>
<td>1100</td>
<td>9.455E+10</td>
</tr>
<tr>
<td>1200</td>
<td>2.842E+12</td>
</tr>
<tr>
<td>1300</td>
<td>5.059E+13</td>
</tr>
</tbody>
</table>

The details of the formulation on reversible reaction 9 are given in the following:

**Reaction 9** \( CH_4 + H_2O \leftrightarrow CO + 3H_2 \)

The equilibrium constant is given as [34]:

\[ K = \frac{Y_{CO}^3 Y_{H_2}^3}{Y_{CH_4}Y_{H_2O}} P^2 \] (38)

where \( Y_X \) is mole fraction of \( X \) and \( P \) is the pressure (atm).

The temperature dependent critical equilibrium constant is expressed as [34]:

\[ K_{eq} = 1.198 \times 10^{13} e^{-26830/T} \] (39)

where \( T \) is the absolute temperature (K).

From Holder et al’s paper, we have an expression for reaction rate, \( R_f \), which is the forward reaction rate. The net reaction rate of the reversible reaction is given as
\[ R_n = R_f \left( 1 - \frac{K}{K_{eq}} \right) \]  

(40)

The Equations (38-40) used for this reaction are similar to those of propylene’s steam reforming reaction, Equations (36) and (37), that we have already coded for Reaction 8 \( C_3H_6 + 3H_2O \leftrightarrow 3CO + 6H_2 \)

The kinetic parameter set of the reaction rate constants are given according to the reaction rate expression and \( A' = \ln A \). The values of the constants are listed in Appendix B.

Inputs and outputs of the module are shown in Tables 35 and 36.

<table>
<thead>
<tr>
<th>No.</th>
<th>Variable</th>
<th>Bus Width</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M_Exh</td>
<td>1×1</td>
<td>Mass flow of the exhaust</td>
<td>kg/s</td>
</tr>
<tr>
<td>2</td>
<td>T_Exh</td>
<td>1×1</td>
<td>Exhaust temperature upstream of the TWC module</td>
<td>K</td>
</tr>
<tr>
<td>3</td>
<td>Q_Heat</td>
<td>n×1</td>
<td>Heat released during chemical reactions per element</td>
<td>W</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Variable</th>
<th>Bus Width</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T_ExhGas_out</td>
<td>1×1</td>
<td>Exhaust temperature downstream of the TWC module</td>
<td>kg/s</td>
</tr>
<tr>
<td>2</td>
<td>T_Mon</td>
<td>n×1</td>
<td>Substrate temperatures along the brick</td>
<td>K</td>
</tr>
<tr>
<td>3</td>
<td>T_ExhGas</td>
<td>n×1</td>
<td>Exhaust temperature in element</td>
<td>W</td>
</tr>
</tbody>
</table>
3.2.4 Thermal Module

The exhaust thermal module simulates the heat transfers occurring in the TWC monolith. Heat transfer is based on conduction, convection and the heat released by the chemical reactions. The module is used to predict temperatures in the brick, in order to achieve accurate simulation of chemical reactions and heat release.

This quasi steady state model is based on the assumption that the characteristic time constant of the flow rate and temperature is much higher than the residence time of the flow [35, 36].

The convective heat transfer rate is calculated from the average gas temperature across the element and the average solid temperature during a time step.

The average gas temperature across an element becomes:

\[
\bar{T}_g = \bar{T}_s + (T_{g,0} - \bar{T}_{s(i)}) \varepsilon_s \tag{41}
\]

where \(\varepsilon_s = \frac{1-e^{-NTU}}{NTU} \) and \(NTU = \frac{hA}{mc_p} \) subscript 0 means the inlet face of the first element and the subscript \(i\) means the outlet face of the \(i^{th}\) element.

The average solid temperature during a time step is given by:

\[
\bar{T}_s = \bar{T}_g + (T_{s,0} - \bar{T}_{s(i)}) \varepsilon_t \tag{42}
\]

where \(\varepsilon_t = \frac{1-e^{-BiFo}}{BiFo} \) and \(BiFo = \frac{hA\Delta t}{m_{solid}c_{psolid}}\).

Equations (41) and (42) give a convective heat transfer rate of:
\[ q_{\text{conv}} = hA \left[ T_{g,0} \frac{\varepsilon_s}{1 + \frac{\varepsilon_s - \varepsilon_t}{\varepsilon_t}} - T_{s,0} \frac{\varepsilon_t}{1 + \frac{\varepsilon_s - \varepsilon_t}{\varepsilon_s}} \right] \]  

(43)

From this, the gas temperatures within a monolith element are calculated for the whole system at each time step using Equation (44).

\[ T_{g,x} = T_{g,0} - NTU \left[ T_{g,0} \frac{\varepsilon_s}{1 + \frac{\varepsilon_s - \varepsilon_t}{\varepsilon_t}} - T_{s,0} \frac{\varepsilon_t}{1 + \frac{\varepsilon_s - \varepsilon_t}{\varepsilon_s}} \right] \]  

(44)

The heat transfer rate is then modified by adding in the terms for conduction within the monolith.

The heat transfer by conduction within the monolith is calculated with the 1D conduction Equation (45):

\[ \frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \]  

(45)

where \( \alpha = \frac{kA\delta x}{m_{\text{solid}} c_{\text{solid}}} \).

This gives a discretized approximation using the second order central difference scheme:

\[ q_{\text{cond}} = \frac{kA}{\delta x} \left( T_{i+1} - 2T_i + T_{i-1} \right) \]  

(46)

The heat released by chemical reactions \( q_{\text{reaction}} \) is calculated from the reaction module.

The total heat term becomes:

\[ \Sigma q = q_{\text{conv}} + q_{\text{cond}} + q_{\text{reaction}} \]  

(47)

The new solid temperature can then be calculated from this heat transfer rate:
\[ T_{n,\Delta} = \frac{1}{m_{\text{solid}} c_{\text{psolid}}} \int_{}^{} q dt \]  

(48)

3.3 Model Set Up

Table 37 lists all the input parameters that are found in the input file to the model (see Appendix B). These inputs need to be set according to the properties of the substrate and the exhaust gas.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>n_elements</td>
<td>Number of elements to simulate the monolith</td>
<td></td>
</tr>
<tr>
<td>Sh_{inf}</td>
<td>Asymptotic Sherwood number</td>
<td>-</td>
</tr>
<tr>
<td>Dens_{ECT_mon}</td>
<td>Monolith substrate density</td>
<td>kg/m³</td>
</tr>
<tr>
<td>L_{ECT_mon}</td>
<td>Total monolith length</td>
<td>m</td>
</tr>
<tr>
<td>hydraulic_radius</td>
<td>Cell hydraulic radius</td>
<td>m</td>
</tr>
<tr>
<td>N_{ECT_CPSI}</td>
<td>Cell density of monolith</td>
<td>Cells per square inch (CPSI)</td>
</tr>
<tr>
<td>E</td>
<td>Monolith void fraction</td>
<td>-</td>
</tr>
<tr>
<td>A_{ECT_Mon}</td>
<td>Monolith frontal area</td>
<td>m²</td>
</tr>
<tr>
<td>ox_storage_capacity</td>
<td>Oxygen storage capacity</td>
<td>kmol/m³</td>
</tr>
<tr>
<td>Noble_metal_Loading</td>
<td>Noble metal loading</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Dispersion</td>
<td>Noble metal dispersion</td>
<td>-</td>
</tr>
<tr>
<td>LBA_Monol</td>
<td>Substrate thermal conductivity</td>
<td>J/(m·s·K)</td>
</tr>
<tr>
<td>Nu_{inf}</td>
<td>Asymptotic Nusselt number</td>
<td>-</td>
</tr>
<tr>
<td>initial_mono_temp</td>
<td>Initial monolith temperature</td>
<td>K</td>
</tr>
<tr>
<td>cp_exhgas</td>
<td>Exhaust specific heat</td>
<td>J/(kg·K)</td>
</tr>
<tr>
<td>cp_monolith</td>
<td>Monolith specific heat</td>
<td>J/(kg·K)</td>
</tr>
</tbody>
</table>

3.4 The Effects of the Substrate Cell Densities on the Conversion Efficiencies

To examine the effects of the substrate cell densities on the conversion efficiencies, substrates with different cell densities are simulated using 1D channel model. GM FTP cycle data [11] is used in this section. The detailed properties of
substrate with different cell densities are listed in Table 38. All the properties of these three substrates are the same except the cell hydraulic radius, the CPSI and the void fraction of the monolith.

Table 38 Properties for substrates with different cell densities

<table>
<thead>
<tr>
<th>Properties</th>
<th>GM substrate</th>
<th>Substrate with CPSI of 600</th>
<th>Substrate with CPSI of 900</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolith density(kg/m3)</td>
<td>1720</td>
<td>1720</td>
<td>1720</td>
</tr>
<tr>
<td>Monolith length(m)</td>
<td>0.2286</td>
<td>0.2286</td>
<td>0.2286</td>
</tr>
<tr>
<td>Cell hydraulic radius(m)</td>
<td>0.000524</td>
<td>0.0004385</td>
<td>0.000363</td>
</tr>
<tr>
<td>CPSI</td>
<td>400</td>
<td>600</td>
<td>900</td>
</tr>
<tr>
<td>Void fraction of the monolith</td>
<td>0.681</td>
<td>0.7153</td>
<td>0.7353</td>
</tr>
<tr>
<td>Monolith frontal area(m²)</td>
<td>0.008775</td>
<td>0.008775</td>
<td>0.008775</td>
</tr>
<tr>
<td>Noble metal loading(g/ft³)</td>
<td>225 for the first inch, 120 for the other</td>
<td>225 for the first inch, 120 for the other</td>
<td>225 for the first inch, 120 for the other</td>
</tr>
<tr>
<td>Dispersion</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Substrate thermal conductivity(W/m·K)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Exhaust specific heat(J/kg·K)</td>
<td>1089</td>
<td>1089</td>
<td>1089</td>
</tr>
<tr>
<td>Monolith specific heat(J/kg·K)</td>
<td>1020</td>
<td>1020</td>
<td>1020</td>
</tr>
<tr>
<td>Initial monolith temperature(K)</td>
<td>293</td>
<td>293</td>
<td>293</td>
</tr>
</tbody>
</table>

The inlet gas temperature of GM FTP cycle data as a function of time is shown in Figure 57.
The average mass flow rate of GM FTP cycle data is shown in Figure 58.

At a given time, the conversion efficiency of species X is defined as:
conversion efficiency = \left( 1 - \frac{\dot{m}_{outX}}{\dot{m}_{inX}} \right) \times 100\% \quad (49)

where \( \dot{m}_{outX} \) is the total mass flow rate of species X at the outlet and \( \dot{m}_{inX} \) is the total mass flow rate of species X at the inlet.

The conversion efficiencies for the exhaust gas are shown in Figures 59-62. With CPSI increased from 400 to 900, the conversion efficiencies for all these four species increase slightly and the overall trend remains the same. Therefore, a substrate with a larger cell density gives better conversion efficiencies.

Figure 59 CO conversion efficiency for substrates with different cell densities
Figure 60 \( \text{CH}_4 \) conversion efficiency for substrates with different cell densities

Figure 61 \( \text{C}_3\text{H}_6 \) conversion efficiency for substrates with different cell densities
3.5 The Effects of the Catalyst Loadings on the Conversion Efficiencies

To examine the effects of the catalyst loadings on the conversion efficiencies, substrates with different catalyst loadings are simulated using 1D channel model. GM FTP cycle data [11] is used in this section. The detailed properties of substrate with different catalyst loadings are listed in Table 39. All the properties of these three substrates are the same except the catalyst loadings. To make sure the expenses of the precious metals remain the same, the total catalyst loading of these three substrates are kept as a constant. The first substrate is the one used in the original GM cycle test, the second one is revised with uniform catalyst loading, the third substrate has a catalyst loading reverse to the GM substrate (the first one). The information about GM FTP cycle data is shown in section 3.4.
Table 39 Properties for substrates with different catalyst loadings

<table>
<thead>
<tr>
<th>Properties/Substrate</th>
<th>GM substrate</th>
<th>Substrate with uniform loading</th>
<th>Substrate with loading reverse to GM substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate No.</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Monolith density(kg/m³)</td>
<td>1720</td>
<td>1720</td>
<td>1720</td>
</tr>
<tr>
<td>Monolith length(m)</td>
<td>0.2286</td>
<td>0.2286</td>
<td>0.2286</td>
</tr>
<tr>
<td>Cell hydraulic radius(m)</td>
<td>0.000524</td>
<td>0.000524</td>
<td>0.000524</td>
</tr>
<tr>
<td>CPSI</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Void fraction of the monolith</td>
<td>0.681</td>
<td>0.681</td>
<td>0.681</td>
</tr>
<tr>
<td>Monolith frontal area(m²)</td>
<td>0.008775</td>
<td>0.008775</td>
<td>0.008775</td>
</tr>
<tr>
<td>Noble metal loading(g/ft³)</td>
<td>225 for the first inch, 120 for the other</td>
<td>155</td>
<td>120 for the first two inches, 225 for the other</td>
</tr>
<tr>
<td>Dispersion</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Substrate thermal conductivity(W/m·K)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Exhaust specific heat(J/kg·K)</td>
<td>1089</td>
<td>1089</td>
<td>1089</td>
</tr>
<tr>
<td>Monolith specific heat(J/kg·K)</td>
<td>1020</td>
<td>1020</td>
<td>1020</td>
</tr>
<tr>
<td>Initial monolith temperature(K)</td>
<td>293</td>
<td>293</td>
<td>293</td>
</tr>
</tbody>
</table>

The conversion efficiencies for the exhaust gas are shown in Figures 63-66. From substrate 1 to 3, the conversion efficiencies for all these four species decrease slightly and the overall trend remains the same. Therefore, a substrate with more catalyst loaded in the front part gives better conversion efficiencies.
Figure 63 CO conversion efficiency using 1D model GM FTP cycle data for substrates with different catalyst loadings

Figure 64 CH₄ conversion efficiency using 1D model GM FTP cycle data for substrates with different catalyst loadings
Figure 65 $C_3H_6$ conversion efficiency using 1D model GM FTP cycle data for substrates with different catalyst loadings

Figure 66 NO conversion efficiency using 1D model GM FTP cycle data for substrates with different catalyst loadings

3.6 Model Tuning

The chemical reaction coefficients of the MATLAB/Simulink model were tuned according to Tenneco experimental data [12-14]. Since the gas concentrations of $NO_2$, 93
\( N_2O \) and \( C_2H_6 \) are less than 10 ppm in input data (and there are many negative values in these data), the gas concentrations of these three gas species are treated as 0 ppm. The total hydrocarbon THC is treated as a combination of \( CH_4 \) and \( C_3H_6 \). Table 40 shows the converter properties used in MATLAB/Simulink program.

Table 40 Substrate properties used in the MATLAB/Simulink program [14]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Tenneco substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolith density (kg/m(^3))</td>
<td>920</td>
</tr>
<tr>
<td>Monolith length (m)</td>
<td>0.0889</td>
</tr>
<tr>
<td>Cell hydraulic radius (m)</td>
<td>0.000363</td>
</tr>
<tr>
<td>CPSI</td>
<td>900</td>
</tr>
<tr>
<td>Void fraction of the monolith</td>
<td>0.7353</td>
</tr>
<tr>
<td>Monolith frontal area (m(^2))</td>
<td>0.011</td>
</tr>
<tr>
<td>Noble metal loading (g/ft(^3))</td>
<td>163, = 5.76 kg/m(^3)</td>
</tr>
<tr>
<td>Dispersion</td>
<td>0.05</td>
</tr>
<tr>
<td>Catalytic surface area per unit reactor volume (1/m)</td>
<td>59501</td>
</tr>
<tr>
<td>Substrate thermal conductivity (W/m·K)</td>
<td>2.4</td>
</tr>
<tr>
<td>Exhaust specific heat (J/kg·K)</td>
<td>1089</td>
</tr>
<tr>
<td>Monolith specific heat (J/kg·K)</td>
<td>500</td>
</tr>
<tr>
<td>Initial monolith temperature (K)</td>
<td>295</td>
</tr>
</tbody>
</table>

A reaction rate constant \( k \) is dependent on the temperature and the activation energy. It is expressed as an Arrhenius like term

\[
k = A e^{-E/RT}
\]

where \( A \) is pre-exponential coefficient and \( E \) is activation energy and \( R \) is the universal gas constant.

These kinetic parameters (pre-exponential coefficient \( A \) and activation energy \( E \)) can be tuned to match experimentally measured light-off data. The following diagrams
Figures 67 and 68 show how A and E affect the reactions occurring in the reaction module:

Figure 67 Relationship among pre-exponential coefficient $A$, temperature and conversion

Figure 68 Relationship among activation energy $E$, temperature and conversion

Figures 69 and 70 show the conversion efficiencies and mass flow rate plots for the cast and fabricated manifold data before tuning. The simulation results of cast manifold and fabricated manifold data show similar conversion efficiencies. The simulation results show that the conversion for $NO$ can reach 100%. The conversion of
simulation result for $CO$, $CH_4$ and $C_3H_6$ are very low compared to the those of the experimental result.

Figure 69 Conversion efficiencies and mass flow rate plots for cast manifold data before tuning
Figure 70 Conversion efficiencies and mass flow rate plots for fabricated manifold data before tuning
Table 41 shows the reactions that consume $CO$, $CH_4$, $C_3H_6$ and $NO$. Pre-exponential coefficient $A$ and activation energy $E$ of corresponding reactions will be tuned to let the simulation results fit the experimental results better.

The method of tuning is stated as follows. Firstly only consider the major oxidation reactions (reactions 1, 2, 4, 5) and deactivate other reactions. Tune the coefficients of these 4 reactions to match the experimental data. Then turn on all other reactions that consume $CO$, $CH_4$, $C_3H_6$ and tune the coefficients to fit the experimental data. Thirdly take $NO$ into considerations, keep all the reactions on and deactivate reactions 10, 11, 12, 13 and 15 one by one to find the major reaction that consumes $NO$. Tune its coefficient to match the $NO$ conversion in experimental data. Lastly keep all the reactions on and tune their coefficients slightly to match the experimental data better.

After lots of trials, reaction 1, 4, 5 and 8 were tuned to fit the experimental data. Table 42 shows the pre-exponential coefficient $A$ and activation energy $E$ before and after tuning.
Table 41 Reactions that consume CO, CH\textsubscript{4}, C\textsubscript{3}H\textsubscript{6} and NO

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Reactions</th>
</tr>
</thead>
</table>
| **CO**     | Reaction 1 \( CO + 0.5O_2 \rightarrow CO_2 \)  
              Reaction 6 \( CO + H_2O \leftrightarrow CO_2 + H_2 \)  
              Reaction 10 \( CO + NO \rightarrow CO_2 + 0.5N_2 \)  
              Reaction 15 \( CO + 2NO \rightarrow CO_2 + N_2O \)  
              Reaction 16 \( N_2O + CO \rightarrow CO_2 + N_2 \) |
| **CH\textsubscript{4}** | Reaction 5 \( CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \)  
                           Reaction 9 \( CH_4 + H_2O \leftrightarrow CO + 3H_2 \) |
| **C\textsubscript{3}H\textsubscript{6}** | Reaction 4 \( C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O \)  
                                Reaction 8 \( C_3H_6 + 3H_2O \leftrightarrow 3CO + 6H_2 \)  
                                Reaction 12 \( C_3H_6 + 9NO \rightarrow 3H_2O + 3CO_2 + 4.5N_2 \) |
| **NO**     | Reaction 10 \( CO + NO \rightarrow CO_2 + 0.5N_2 \)  
              Reaction 11 \( H_2 + NO \rightarrow H_2O + 0.5N_2 \)  
              Reaction 12 \( C_3H_6 + 9NO \rightarrow 3H_2O + 3CO_2 + 4.5N_2 \)  
              Reaction 13 \( H_2 + 2NO \rightarrow H_2O + N_2O \)  
              Reaction 15 \( CO + 2NO \rightarrow CO_2 + N_2O \) |
Table 42 Table of pre-exponential coefficient $A$ and activation energy $E$ before and after tuning.

<table>
<thead>
<tr>
<th>No. of Reaction</th>
<th>$ln(A)$</th>
<th>$E$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original</td>
<td>After tuning</td>
</tr>
<tr>
<td>1, $CO + 0.5O_2 \rightarrow CO_2$</td>
<td>35.6</td>
<td>36.6</td>
</tr>
<tr>
<td>2, $H_2 + 0.5O_2 \rightarrow H_2O$</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>4, $C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O$</td>
<td>35.3</td>
<td>36.3</td>
</tr>
<tr>
<td>5, $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$</td>
<td>28</td>
<td>36</td>
</tr>
<tr>
<td>6, $CO + H_2O \leftrightarrow CO_2 + H_2$</td>
<td>13.3</td>
<td>11</td>
</tr>
<tr>
<td>8, $C_3H_6 + 3H_2O \leftrightarrow 3CO + 6H_2$</td>
<td>14.69</td>
<td></td>
</tr>
<tr>
<td>9, $CH_4 + H_2O \leftrightarrow CO + 3H_2$</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>10, $CO + NO \rightarrow CO_2 + 0.5N_2$</td>
<td>28.6</td>
<td></td>
</tr>
<tr>
<td>11, $H_2 + NO \rightarrow H_2O + 0.5N_2$</td>
<td>25.28</td>
<td></td>
</tr>
<tr>
<td>12, $C_3H_6 + 9NO \rightarrow 3H_2O + 3CO_2 + 4.5N_2$</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>13, $H_2 + 2NO \rightarrow H_2O + N_2O$</td>
<td>29.8</td>
<td></td>
</tr>
<tr>
<td>14, $N_2O + H_2 \rightarrow H_2O + N_2$</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>15, $CO + 2NO \rightarrow CO_2 + N_2O$</td>
<td>27.2</td>
<td></td>
</tr>
<tr>
<td>16, $N_2O + CO \rightarrow CO_2 + N_2$</td>
<td>25.8</td>
<td></td>
</tr>
<tr>
<td>17, $H_2 + 2CeO_2 \rightarrow Ce_2O_3 + H_2O$</td>
<td>7.35</td>
<td></td>
</tr>
<tr>
<td>18, $Ce_2O_3 + H_2O \rightarrow H_2 + 2CeO_2$</td>
<td>-6.28</td>
<td></td>
</tr>
<tr>
<td>19, $CO + 2CeO_2 \rightarrow CO_2 + Ce_2O_3$</td>
<td>9.03</td>
<td></td>
</tr>
<tr>
<td>20, $CO_2 + Ce_2O_3 \rightarrow CO + 2CeO_2$</td>
<td>5.38</td>
<td></td>
</tr>
<tr>
<td>21, $0.5O_2 + Ce_2O_3 \rightarrow 2CeO_2$</td>
<td>-12.02</td>
<td></td>
</tr>
</tbody>
</table>
Figures 71 and 72 show the conversion efficiencies and mass flow rate plots for the cast and fabricated manifold data after tuning. The simulation results of cast manifold and fabricated manifold data after tuning show similar conversion efficiencies. The simulation results show that the conversion for NO still can reach 100%. The conversion of CO and CH₄ became higher than the cases before tuning and fit experimental data better. The conversion of C₃H₆ is still very low compared to the experimental data at the first 200 seconds.
Figure 71 Conversion efficiencies and mass flow rate plot for cast manifold data after tuning
Figure 7.2 Conversion efficiencies and mass flow rate plot for fabricated manifold data after tuning.
As shown in Figures 73, the predicted conversion for $CO$, $CH_4$ and $C_3H_6$ can be much improved during a preliminary study if the activation energies $E1,E4$ are adjusted to 6000 and $E5$ is modified to 8000 (reactions R1, R4 and R5 are activated only). However, these values are not in the commonly used range for the reactions (typically, $E1\sim12500$, $E4\sim12500$ and $E5\sim14500$) and make the system really stiff. As a result, the time setting of “Lag” blocks are decreased to 0.002 s. As shown in Figure 74, the simulation captured unwanted fast dynamics. The monolith temperature can be as high as 9000 K which is not possible in real situation. Further systematic investigations on tuning the kinetic data for matching measured conversion efficiencies are needed.
Figure 73 Conversion efficiencies for cast manifold data ($E1 = E4 = 6000, E5 = 8000$ and $A5 = 35.30$)
Figure 74 Monolith Temperature vs. Time at Node 10, 30, 54 for cast manifold data ($E1 = E4 = 6000, E5 = 8000$)
Chapter 4  2D Axisymmetric Model

In this chapter a 2D axisymmetric model is developed by coupling 2D axisymmetric flow and heat transfer with the 1D channel model. The data structure and transfer within the model are discussed. The effects of thermal insulation, the flow and temperature non-uniformity at the substrate inlet on monolith temperature and conversion efficiencies are studied.
4.1 Formulation

A schematic of 10 layers 2D axisymmetric model is shown in Figure 75.

The governing equation for 2D axisymmetric heat conduction is used as:

\[
q_{\text{cond}} = V_{\text{cond}} \left( k_r \frac{1}{r} \frac{\partial T}{\partial r} + k_r \frac{\partial^2 T}{\partial r^2} + k_z \frac{\partial^2 T}{\partial z^2} \right) \tag{51}
\]

where \( V_{\text{cond}} = V_{\text{seg}} (1 - e) \).

At the center axis where \( r = 0 \),

\[
\frac{\partial T}{\partial r} = 0 \tag{52}
\]
At outer boundary where \( r=R \), both convection and radiation are taken into considerations as

\[-k_r \frac{\partial T}{\partial r} = h_{\text{eff}} (T - T_{\text{amb}}) + \varepsilon \sigma (T^4 - T_{\text{amb}}^4) \]  \hspace{1cm} (53)

where \( h_{\text{eff}} \) is the effective heat transfer coefficient including conduction through mat, steel and convection from steel to the environment \( h_{\text{eff}} \) can be calculated from the thermal circuit shown in Figure 76. Since the lack of mat properties, \( h_{\text{eff}} \) was chosen to be 10 W/m\(^2\) · K.

Figure 76 Schematic of the thermal circuit used to calculate \( h_{\text{eff}} \).

\[
\frac{1}{h_{\text{eff}} A_{\text{mat}}} = \frac{L_{\text{mat}}}{k_{\text{mat}} A_{\text{mat}}} + \frac{L_{\text{steel}}}{k_{\text{steel}} A_{\text{steel}}} + \frac{1}{h_{\text{convection}} A_{\text{convection}}} \]  \hspace{1cm} (54)
4.2 Data Structure and Transfer

A 10-layer 2D axisymmetric model is developed. In each layer, 1D channel model is used. However, 2D axisymmetric heat conduction is considered between adjacent layers. In addition, different inlet flow conditions (flow and temperature indices) can be specified for each layer.

For the input of the model, 14 lines signal including Emissions in and Exhaust in are employed for each layer, which is the same as the 1D channel model. Since there are 10 layers included in the 2D axisymmetric model, the total number of signal lines is 140.

Similarly, for the output of the model, the total number of signal lines for Emissions out and Exhaust out is 140. Besides the Emissions out and Exhaust out signals, the monolith temperature $T_{\text{mon}}$ is also included.

The detailed signals in the Emissions in and Emissions out buses are listed in Table 43.

<table>
<thead>
<tr>
<th>Line</th>
<th>Variable</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M_NO</td>
<td>Mass flow rate nitric oxide</td>
<td>kg/s</td>
</tr>
<tr>
<td>2</td>
<td>M_NO2</td>
<td>Mass flow rate nitrogen dioxide</td>
<td>kg/s</td>
</tr>
<tr>
<td>3</td>
<td>M_N2O</td>
<td>Mass flow rate nitrous oxide</td>
<td>kg/s</td>
</tr>
<tr>
<td>4</td>
<td>M_N2</td>
<td>Mass flow rate nitrogen</td>
<td>kg/s</td>
</tr>
<tr>
<td>5</td>
<td>M_CO</td>
<td>Mass flow rate carbon monoxide</td>
<td>kg/s</td>
</tr>
<tr>
<td>6</td>
<td>M_CO2</td>
<td>Mass flow rate carbon dioxide</td>
<td>kg/s</td>
</tr>
<tr>
<td>7</td>
<td>M_CH4</td>
<td>Mass flow rate methane (slow burn HC)</td>
<td>kg/s</td>
</tr>
<tr>
<td>8</td>
<td>M_C3H6</td>
<td>Mass flow rate propene (fast burn HC)</td>
<td>kg/s</td>
</tr>
<tr>
<td>9</td>
<td>M_H2</td>
<td>Mass flow rate hydrogen</td>
<td>kg/s</td>
</tr>
<tr>
<td>10</td>
<td>M_H2O</td>
<td>Mass flow rate water</td>
<td>kg/s</td>
</tr>
<tr>
<td>11</td>
<td>M_O2</td>
<td>Mass flow rate oxygen</td>
<td>kg/s</td>
</tr>
</tbody>
</table>
The detailed signals in the Exhaust in and Exhaust out buses are listed in Table 44.

<table>
<thead>
<tr>
<th>Line</th>
<th>Variable</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M_ExhGas</td>
<td>Mass flow rate of the exhaust</td>
<td>kg/s</td>
</tr>
<tr>
<td>2</td>
<td>T_ExhGas_in</td>
<td>Temperature of the exhaust</td>
<td>K</td>
</tr>
<tr>
<td>3</td>
<td>P_ExhGas</td>
<td>Pressure of the exhaust</td>
<td>Pa</td>
</tr>
</tbody>
</table>

The overall inputs and outputs of the 2D axisymmetric model are shown in Tables 45-47, where $n$ is the number of elements that a substrate is divided in the axial direction.
Table 45 Inputs of the 2D axisymmetric model

<table>
<thead>
<tr>
<th>No.</th>
<th>Variable</th>
<th>Bus Width</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Emissions in for layer 1</td>
<td>11×1</td>
<td>Model input of the exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>2</td>
<td>Exhaust in for layer 1</td>
<td>3×1</td>
<td>Model input of exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>3</td>
<td>Emissions in for layer 2</td>
<td>11×1</td>
<td>Model input of the exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>4</td>
<td>Exhaust in for layer 2</td>
<td>3×1</td>
<td>Model input of exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>5</td>
<td>Emissions in for layer 3</td>
<td>11×1</td>
<td>Model input of the exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>6</td>
<td>Exhaust in for layer 3</td>
<td>3×1</td>
<td>Model input of exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>7</td>
<td>Emissions in for layer 4</td>
<td>11×1</td>
<td>Model input of the exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>8</td>
<td>Exhaust in for layer 4</td>
<td>3×1</td>
<td>Model input of exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>9</td>
<td>Emissions in for layer 5</td>
<td>11×1</td>
<td>Model input of the exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>10</td>
<td>Exhaust in for layer 5</td>
<td>3×1</td>
<td>Model input of exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>11</td>
<td>Emissions in for layer 6</td>
<td>11×1</td>
<td>Model input of the exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>12</td>
<td>Exhaust in for layer 6</td>
<td>3×1</td>
<td>Model input of exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>13</td>
<td>Emissions in for layer 7</td>
<td>11×1</td>
<td>Model input of the exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>14</td>
<td>Exhaust in for layer 7</td>
<td>3×1</td>
<td>Model input of exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>15</td>
<td>Emissions in for layer 8</td>
<td>11×1</td>
<td>Model input of the exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>16</td>
<td>Exhaust in for layer 8</td>
<td>3×1</td>
<td>Model input of exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>17</td>
<td>Emissions in for layer 9</td>
<td>11×1</td>
<td>Model input of the exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>18</td>
<td>Exhaust in for layer 9</td>
<td>3×1</td>
<td>Model input of exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>19</td>
<td>Emissions in for layer 10</td>
<td>11×1</td>
<td>Model input of the exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>20</td>
<td>Exhaust in for layer 10</td>
<td>3×1</td>
<td>Model input of exhaust parameters</td>
<td>Various</td>
</tr>
</tbody>
</table>
Table 46 Emissions out and Exhaust out of the 2D axisymmetric model

<table>
<thead>
<tr>
<th>No.</th>
<th>Variable</th>
<th>Bus Width</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Emissions out for layer 1</td>
<td>11×1</td>
<td>Output of predicted exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>2</td>
<td>Exhaust out for layer 1</td>
<td>3×1</td>
<td>Output of predicted exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>3</td>
<td>Emissions out for layer 2</td>
<td>11×1</td>
<td>Output of predicted exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>4</td>
<td>Exhaust out for layer 2</td>
<td>3×1</td>
<td>Output of predicted exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>5</td>
<td>Emissions out for layer 3</td>
<td>11×1</td>
<td>Output of predicted exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>6</td>
<td>Exhaust out for layer 3</td>
<td>3×1</td>
<td>Output of predicted exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>7</td>
<td>Emissions out for layer 4</td>
<td>11×1</td>
<td>Output of predicted exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>8</td>
<td>Exhaust out for layer 4</td>
<td>3×1</td>
<td>Output of predicted exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>9</td>
<td>Emissions out for layer 5</td>
<td>11×1</td>
<td>Output of predicted exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>10</td>
<td>Exhaust out for layer 5</td>
<td>3×1</td>
<td>Output of predicted exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>11</td>
<td>Emissions out for layer 6</td>
<td>11×1</td>
<td>Output of predicted exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>12</td>
<td>Exhaust out for layer 6</td>
<td>3×1</td>
<td>Output of predicted exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>13</td>
<td>Emissions out for layer 7</td>
<td>11×1</td>
<td>Output of predicted exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>14</td>
<td>Exhaust out for layer 7</td>
<td>3×1</td>
<td>Output of predicted exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>15</td>
<td>Emissions out for layer 8</td>
<td>11×1</td>
<td>Output of predicted exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>16</td>
<td>Exhaust out for layer 8</td>
<td>3×1</td>
<td>Output of predicted exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>17</td>
<td>Emissions out for layer 9</td>
<td>11×1</td>
<td>Output of predicted exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>18</td>
<td>Exhaust out for layer 9</td>
<td>3×1</td>
<td>Output of predicted exhaust parameters</td>
<td>Various</td>
</tr>
<tr>
<td>19</td>
<td>Emissions out for layer 10</td>
<td>11×1</td>
<td>Output of predicted exhaust gas emissions</td>
<td>kg/s</td>
</tr>
<tr>
<td>20</td>
<td>Exhaust out for layer 10</td>
<td>3×1</td>
<td>Output of predicted exhaust parameters</td>
<td>Various</td>
</tr>
</tbody>
</table>

Table 47 T_mon of TWC the 2D axisymmetric model

<table>
<thead>
<tr>
<th>No.</th>
<th>Variable</th>
<th>Bus Width</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T_Mon for layer 1</td>
<td>n×1</td>
<td>Vector of monolith temperatures</td>
<td>K</td>
</tr>
<tr>
<td>2</td>
<td>T_Mon for layer 2</td>
<td>n×1</td>
<td>Vector of monolith temperatures</td>
<td>K</td>
</tr>
<tr>
<td>3</td>
<td>T_Mon for layer 3</td>
<td>n×1</td>
<td>Vector of monolith temperatures</td>
<td>K</td>
</tr>
<tr>
<td>4</td>
<td>T_Mon for layer 4</td>
<td>n×1</td>
<td>Vector of monolith temperatures</td>
<td>K</td>
</tr>
<tr>
<td>5</td>
<td>T_Mon for layer 5</td>
<td>n×1</td>
<td>Vector of monolith temperatures</td>
<td>K</td>
</tr>
<tr>
<td>6</td>
<td>T_Mon for layer 6</td>
<td>n×1</td>
<td>Vector of monolith temperatures</td>
<td>K</td>
</tr>
<tr>
<td>7</td>
<td>T_Mon for layer 7</td>
<td>n×1</td>
<td>Vector of monolith temperatures</td>
<td>K</td>
</tr>
<tr>
<td>8</td>
<td>T_Mon for layer 8</td>
<td>n×1</td>
<td>Vector of monolith temperatures</td>
<td>K</td>
</tr>
<tr>
<td>9</td>
<td>T_Mon for layer 9</td>
<td>n×1</td>
<td>Vector of monolith temperatures</td>
<td>K</td>
</tr>
<tr>
<td>10</td>
<td>T_Mon for layer 10</td>
<td>n×1</td>
<td>Vector of monolith temperatures</td>
<td>K</td>
</tr>
</tbody>
</table>
The inner structures of layer 1 and layer 10 are different from those of layers 2-9 because of the different boundary conditions. A Simulink coding technology “Mask” was employed. A mask hides the user interface of the block, and instead displays a custom dialog control for specific parameters of the masked block as shown in Figure 77 [37]. For the interior layers, layers 2-9, the code structures are the same except the layer number, which is used to reference the variables of the layer, for instance, the radius and the cross-section area are dependent variables of the layer number. Thus the 10-layer 2D axisymmetric model can be modified for any number of layers by copying the interior layer and specifying the designated layer number.

Figure 77 Mask for sub model layer 8
4.3 2D Axisymmetric Model Set Up

The input data file can be generated using “Input_Data_Generator.m” (see Appendix B-2) based on the 1D input data and Flow index, Temperature index and number of layers.

Table 48 lists all the input parameters needed for the 2D axisymmetric model (see Appendix B). These inputs need to be set according to the properties of the substrate and the exhaust gas.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>n_elements</td>
<td>Number of elements to simulate the monolith</td>
<td>-</td>
</tr>
<tr>
<td>Sh_inf</td>
<td>Asymptotic Sherwood number</td>
<td>-</td>
</tr>
<tr>
<td>Dens_ECT_mon</td>
<td>Monolith substrate density</td>
<td>kg/m³</td>
</tr>
<tr>
<td>L_ECT_mon</td>
<td>Total monolith length</td>
<td>m</td>
</tr>
<tr>
<td>hydraulic_radius</td>
<td>Cell hydraulic radius</td>
<td>m</td>
</tr>
<tr>
<td>N_ECT_CPSI</td>
<td>Cell density of monolith</td>
<td>Cells per square inch (CPSI)</td>
</tr>
<tr>
<td>E</td>
<td>Monolith void fraction</td>
<td>-</td>
</tr>
<tr>
<td>A_ECT_Mon</td>
<td>Monolith frontal area</td>
<td>m²</td>
</tr>
<tr>
<td>ox_storage_capacity</td>
<td>Oxygen storage capacity</td>
<td>kmol/m³</td>
</tr>
<tr>
<td>Noble_metal_Loading</td>
<td>Noble metal loading</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Dispersion</td>
<td>Noble metal dispersion</td>
<td>-</td>
</tr>
<tr>
<td>LBA_Monol</td>
<td>Substrate thermal conductivity along axial direction</td>
<td>J/(m·s·K)</td>
</tr>
<tr>
<td>LBA_Monol_r</td>
<td>Substrate thermal conductivity along radial direction</td>
<td>J/(m·s·K)</td>
</tr>
<tr>
<td>Nu_inf</td>
<td>Asymptotic Nusselt number</td>
<td>-</td>
</tr>
<tr>
<td>initial_mono_temp</td>
<td>initial monolith temperature</td>
<td>K</td>
</tr>
<tr>
<td>T_ambient</td>
<td>Ambient temperature</td>
<td>K</td>
</tr>
<tr>
<td>h_ambient</td>
<td>Convective heat transfer coefficient to ambient environment</td>
<td>W/m²·K</td>
</tr>
<tr>
<td>emissivity</td>
<td>Emissivity</td>
<td></td>
</tr>
<tr>
<td>cp_exhgas</td>
<td>Exhaust specific heat</td>
<td>J/(kg·K)</td>
</tr>
<tr>
<td>cp_monolith</td>
<td>Monolith specific heat</td>
<td>J/(kg·K)</td>
</tr>
</tbody>
</table>
4.4 Results Using GM FTP Data

Figure 78 shows the comparisons of conversion efficiencies using GM FTP cycle data [11] (uniform distribution of mass flow rate and temperature at inlet surface) among the 1D model, layer 1 (channel) and layer 10 (channel) in the 2D axisymmetric model. The layer 10 is the outer layer and is cooled by convection and radiation, thus the temperature is low which results in low conversion efficiencies. Since the layer 1 is the inner layer of the 2D axisymmetric model, the conversion efficiencies is therefore not affected much by the cooling of the convection and radiation at the boundary. For the 1D model, the adiabatic boundary condition was employed, as expected, the results on conversion efficiencies from the 1D model and the layer 1 in the 2D axisymmetric model are nearly the same. Figure 79 shows the contours of monolith temperature using GM FTP cycle data at different times for the 2D axisymmetric model. It can be seen from the figure that the temperature decreases as radial distance increases.
Figure 78 Comparisons of conversion efficiencies using GM FTP cycle data (uniform distribution of mass flow rate and temperature at inlet surface) among the 1D model, layer 1 and layer 10 in the 2D axisymmetric model.
Figure 79 Contours of monolith temperature using GM FTP cycle data at different times
4.5 Effects of Thermal Insulation of Catalytic Converters on Conversion Efficiencies

As shown in Equation (54) in section 4.1, the effective heat transfer coefficient $h_{eff}$ is affected by the thermal conductivity of the fibrous insulation mat $k_{mat}$. Since we are using GM FTP cycle data, the geometry of GM converter was used to calculate $h_{eff}$. The thermal conductivity of mat $k_{mat}$ was not mentioned in GM FTP cycle data, the thermal conductivity of Tenneco’s mat as shown in Equation (7) was used [15].

At temperature of 800K, $k_{mat}$ is about 0.15 $W/m \cdot K$. The thickness of steel $L_{steel}$ is 0.0015 m and the thickness of mat $L_{mat}$ is 0.007 m, both are small compared to the radius of the monolith (0.05285 m).

From Mr. Stephen Thomas’ suggestion, $h_{convection}$ is chosen to be 10 $W/m^2 \cdot K$ as it is a common value for the industry. $k_{steel}$ is chosen to be 50.2 $W/m \cdot K$ [38].

To compare the effects of thermal insulation to the catalyst converter performance, two other cases with $k_{mat}$ of ± 10% difference were chosen. The corresponding values of $h_{eff}$ are listed in Table 49.

<table>
<thead>
<tr>
<th>No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{mat}$, $W/m \cdot K$</td>
<td>0.135</td>
<td>0.15</td>
<td>0.165</td>
</tr>
<tr>
<td>$h_{eff}$, $W/m^2 \cdot K$</td>
<td>7.4148</td>
<td>7.6926</td>
<td>7.9358</td>
</tr>
</tbody>
</table>
\(k_{mat} = 0.135 \text{ W/m} \cdot \text{K}\)

\(h_{eff} = 7.41 \text{ W/m}^2 \cdot \text{K}\)

Average surface temperature at 300 seconds: 851.9 K

Average outlet temperature at 300 seconds: 884.1 K

\(k_{mat} = 0.15 \text{ W/m} \cdot \text{K}\)

\(h_{eff} = 7.69 \text{ W/m}^2 \cdot \text{K}\)

Average surface temperature at 300 seconds: 851.3 K

Average outlet temperature at 300 seconds: 883.8 K

\(k_{mat} = 0.165 \text{ W/m} \cdot \text{K}\)

\(h_{eff} = 7.94 \text{ W/m}^2 \cdot \text{K}\)

Average surface temperature at 300 seconds: 850.9 K

Average outlet temperature at 300 seconds: 883.6 K

Figure 80 Temperature Contours of the three cases at 300 seconds

120
From Figures 80 and 81, the temperature distributions of these three cases are very similar. The conversion efficiencies are nearly the same for the species $CO, CH_4, C_3H_6$ and $NO$. The 10% difference in the value of thermal conductivity $k_{mat}$ does not make much influence on the conversion performance.
4.6 Effects of Inlet Flow Non-uniformity on Conversion Efficiencies

In real situation, the flow and temperature distributions cannot be uniform at the inlet of substrates. The effects of flow and temperature non-uniformity need to be studied.

Figure 82 shows the comparison of overall conversion efficiencies with different inlet flow and temperature distributions (see Table 50). The respective monolith temperature distributions at 50 seconds are shown in Figure 83. The case with uniform flow and uniform temperature condition has the best performance. The temperature index plays a more prominent role and the conversion efficiencies decrease as the temperature index increases. With uniform inlet temperature distribution (temperature index = 0.25, red and green curves), the effect of flow non-uniformity is negligible. While with a large temperature index (such as 0.3, black and blue curves), the conversion efficiencies increases with a large flow index. A large temperature index means a higher temperature in the center layers, which will lead the conversion process to start at earlier time.

Table 50 Performance rank for cases with different flow index and temperature index

<table>
<thead>
<tr>
<th>Conversion efficiencies rank</th>
<th>Color</th>
<th>Flow index</th>
<th>Temperature index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>red</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>1</td>
<td>green</td>
<td>0.3</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>black</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>4</td>
<td>blue</td>
<td>0.25</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Figure 82 Comparisons of overall conversion efficiencies with different inlet flow and temperature distributions
Figure 83 Monolith temperature distributions of different 4 inlet conditions at 50 seconds
Chapter 5  Conclusions

The performance of a three-way catalytic converter has been investigated during the cold start. A cold flow simulation was performed to study the flow distribution in catalytic converters using ANSYS/Fluent. The kinetic model proposed by Holder et al’s was implemented in the 1D channel model. The 2D axisymmetric model that couples the 2D flow and heat transfer with the 1D channel model was developed. The conclusions are summarized here for each subject presented in chapters 2 – 4.

For the work stated in chapter 2, CFD simulations for cold flow and with the consideration of heat transfer were carried out on a relatively complex geometry, and the chemical kinetics was not included. A series of cold flow and light-off CFD simulations was performed to study the effects of the angle $\theta$, the L/D ratio, the inlet gas temperature, the mass flow rate and the cell density on the flow and temperature distributions, and the pressure drop. The results of the simulations suggest that a larger L/D ratio, smaller angle $\theta$, higher inlet gas temperature and smaller mass flow rate lead to a more uniform flow distribution (flow index $\sim 0.25$). A lower inlet gas temperature and larger mass flow rate result in a more uniform temperature distribution (temperature index $\sim 0.25$). A smaller L/D ratio, smaller angle $\theta$, smaller inlet gas temperature, and smaller mass flow rate result in a lower pressure drop that leads to a smaller power loss. The cell density does
not affect much the flow and temperature distribution without consideration of the chemical reactions. These findings can be used as a guide for a better design of catalytic converters.

Here are some guidelines for the mesh generation. Geometry cleanup is required before the mesh generation to delete or repair the dirty geometry features such as the unnecessary holes, small surfaces and rims as well as the crevices. DesignModeler, Solidworks and other similar software can be used. This step will improve the mesh quality. The mesh size should be fine enough to capture all the geometry features of the model but not too small to avoid huge computational cost. Usually the size should be finer than half of the smallest geometric feature. Prism layers should be generated on the fluid zone to capture the flow features in the near wall region. The orthogonal quality of the mesh should be larger than 0.05.

There are some principles to set up the model in Fluent. Firstly, the Reynolds number needs to be checked to determine whether the flow is laminar or turbulent. The user-defined function can be used to model the temperature-dependent material properties as well as the local heat transfer coefficient in porous media. Y+ values need to be checked to select the appropriate wall function. The CFD model should be constructed from simple to complex step by step. In this way it is easy to locate the errors in the model construction. The relaxation factors can be modified to solve the convergence issue. For example, if the energy residual drops fast and meets the convergent criteria while other residuals cannot, the relaxation factors can be set to smaller values to overcome the convergence issue.
For the work that involves chemical reactions (chapter 3 and chapter 4), MATLAB/Simulink programs were developed to model the heat and mass transfer with consideration of the chemical kinetics.

In chapter 3, the Holder et al’s chemical kinetics was implemented into the 1D channel model for catalytic converters in MATLAB/Simulink programs. The model includes the chemical kinetics as well as conductive and conduction heat transfer inside the monolith channel. A systematic study of the effects of the substrate properties was performed using the 1D channel model. The results suggested that a substrate with a larger cell density and more catalyst loaded in the front gave better conversion efficiencies. The kinetic parameters of 1D model were calibrated to match the Tenneco test data. Unfortunately the predicted conversion results do not match Tenneco’s experimental data well within the commonly used kinetic data ranges for the main oxidation reactions. Theoretically the kinetic data of the model could be tuned to match a given experimental data. However, the resulted kinetic data could be out of the accepted data ranges. In general a set of tuned kinetic data based on good experimental results of a given three-way catalytic converter can be used to predict the performance of the converter.

In chapter 4, the 2D axisymmetric model was developed by coupling the 2D axisymmetric flow and heat transfer with the 1D channel model. The 2D model can be used to predict the conversion efficiencies of converters with non-uniform flow and temperature distribution at the substrate inlet. The model also included the axisymmetric heat conduction. Studies of the effects of thermal insulation, the flow and temperature
non-uniformity at the substrate inlet were performed. The results indicate that a 10% difference in the value of thermal conductivity $k_{mat}$ does not have much influence on the converter’s performance. The case with uniform flow and uniform temperature condition has the best conversion efficiencies for a converter with a given flow condition. The temperature index plays a more prominent role. The conversion efficiencies decrease as the temperature distribution at the monolith inlet becomes more non-uniform. For a given temperature distribution at the monolith inlet, the effects of the flow distribution at the inlet on the conversions are negligible.

In the future, the works from chapters 2 and 4 can be combined to simulate the performance of the catalytic converter in a more accurate and realistic flow setting. The inlet flow and temperature distribution from CFD simulations can be used directly as the inlet conditions for the 2D axisymmetric model.
References


Appendix A: User Defined Function

UDF that simulates solidification by specifying a temperature-dependent air density property

#include "udf.h"
#include<math.h>

DEFINEPROPERTY(air_density, c, t)
{
    real rho_air; /* Density of Air */
    real temp = C_T(c, t); /* Temperature of Air */
    rho_air = 360.77819*pow(temp, (-1.00336));

    return rho_air;
}

/*****************************/
UDF that simulates solidification by specifying a temperature-dependent air viscosity property

DEFINEPROPERTY(air_viscosity, c, t)
{
    real rho_air;/* Density of Air */
    real kinematic_viscosity_air;/* Kinematic Viscosity of Air */
    real mu_air;/* Viscosity of Air */
    real temp = C_T(c, t);/* Temperature of Air */
    rho_air = 360.77819*pow(temp, (-1.00336));
    kinematic_viscosity_air = -1.1555*pow(10, -14)*pow(temp, 3) + 9.5728*pow(10, -11)*pow(temp, 2) + 3.7604*pow(10, -8)*temp - 3.4484*pow(10, -6);
    mu_air = rho_air*kinematic_viscosity_air;

    return mu_air;
}

/**********************************************************
**********************************************************/
UDF that simulates solidification by specifying a temperature-dependent air thermal conductivity property

******************************************************************************

DEFINE_PROPERTY(air_thermal_conductivity, c, t)
{
    real k_air; /* Thermal Conductivity of Air */
    real temp = C_T(c, t); /* Temperature of Air */
    k_air = 1.5207*pow(10, -11)*pow(temp, 3) - 4.8574*pow(10, -8)*pow(temp, 2) + 
           1.0184*pow(10, -4)*temp - 3.9333*pow(10, -4);

    return k_air;
}

******************************************************************************

UDF that simulates solidification by specifying a temperature-dependent substrate thermal conductivity property

******************************************************************************

DEFINE_PROPERTY(substrate_thermal_conductivity, c, t)
{ 
  real k_substrate;/* Thermal Conductivity of Substrate */
  real temp = C_T(c, t);/* Temperature of Substrate in Kelven */
  real tempc = temp - 273.15;/* Temperature of Substrate in Celius*/
  k_substrate = -2*pow(10, -9)*pow(tempc, 3) + 3*pow(10, -6)*pow(tempc, 2) - 
                   4*pow(10, -3)*tempc + 4.1;

  return k_substrate;
}

/***************************************************************************/
UDF that simulates solidification by specifying a temperature-dependent mat thermal conductivity property
/***************************************************************************/

DEFINEPROPERTY(mat_thermal_conductivity, c, t)
{
  real k_mat;/* Thermal Conductivity of Mat */
  real temp = C_T(c, t);/* Temperature of Mat */
  k_mat = 1*pow(10, -7)*pow(temp, 2) + 2.8*pow(10, -5)*temp + 6.7241*pow(10, -2);
return k_mat;
}

/***************************************************************************/

***************************************************************************/

This is a UDF to calculate the Heat Transfer Coefficient and Interfacial Area Density in a porous zone.

Here Porous medium is considered as a combination of SQUARE HOLES and heat transfer coefficient is calculated based on internal flow through these holes.

***************************************************************************/

DEFINE_PROFILE(Heat_trans_coeff, t, i)
{
    cell_t c;
    real Nu;
    real heat_tan_co;
    real dh; /*hydrolic diameter of side of each round hole*/
real dens; /* Fluid */
real visco; /* Fluid */
real cond; /* Fluid */
real W_vel;
real cp; /* Fluid */
real Re_local;

dh = 1.1557 * pow(10, -3); /* 'dh' indicates the diameter of sides of each round hole */

begin_c_loop(c, t)
{

dens = C_R(c, t); /* Density of Fluid */
visco = C_MU_L(c, t); /* Viscosity of Fluid */
cond = C_K_L(c, t); /* Conductivity of Fluid */
W_vel = C_W(c, t); /* Velocity of Fluid */
cp = C_CP(c, t); /* Specific Heat of Fluid */
Re_local = dens*dh*W_vel / visco;/* Local Reynolds Number; 'j' is used as length scale and local velocity is used */

if (Re_local < 2000)
{
    Nu = 2.98;/* For laminar flow */
}
else
{
    Nu = .023*pow(Re_local, 0.8)*pow((visco*cp / cond), 0.3); /* For Turbulent flow: Dittus-Boelter equation, if Ts<Tm, n = 0.3.....Ts>Tm, n = 0.4 */
}

F_PROFILE(c, t, i) = Nu*cond / dh;

end_c_loop(c, t)
Appendix B: Code for the MATLAB/Simulink Programs

Appendix B-1: MATLAB Code of Input Parameter for the 1D Channel Model

% Module name : Manifold_data_parameter_1D.m

% Wenbo Jia 02/22/16

% Description : Parameter file for manifold data.
% Modified for 1D model.

% There are 21 reactions in Holder et al's model, since we don't consider C3H8,
% Reaction 3 and 7 which are related to C3H8 are not modeled in the Simulink program. All other 19 reactions in Holder et al's model are considered.
% Reaction 6,8 and 9 are coded as reversible reactions.

% R1:  CO + 0.5O2 -> CO2
% R2:  H2 + 0.5O2 -> H2O
% R4:  C3H6 + 4.5O2 -> 3CO2 + 3H2O
% R5:  CH4 + 2O2 -> CO2 + 2H2O
% R6:  CO + H2O -> CO2 + H2
% R8:  C3H6 + 3H2O -> 3CO + 6H2
% R9:  CH4 + H2O -> CO + 3H2
% R10: CO + NO -> CO2 + 0.5N2
% R11: H2 + NO -> H2O + 0.5N2
% R12: C3H6 + 9NO -> 3H2O + 3CO2 + 4.5 N2
% R13: H2 + 2NO -> H2O + N2
% R14: N2O + H2 -> H2O + N2
% R15: CO + 2NO -> CO2 + N2
% R16: N2O + CO -> CO2 + N2
% R17: H2 + 2CeO2 -> H2O + Ce2O3
% R18: H2O + Ce2O3 -> H2 + 2CeO2
% R19: CO + 2CeO2 -> CO2 + Ce2O3
% R20: CO2 + Ce2O3 -> CO + 2CeO2
\[
\text{R21: } 0.5\text{O}_2 + \text{Ce}_2\text{O}_3 \rightarrow 2\text{CeO}_2
\]

\[
s1=1; \quad \% \text{ Switch for R1}
\]
\[
s2=1; \quad \% \text{ Switch for R2}
\]
\[
s4=1; \quad \% \text{ Switch for R4}
\]
\[
s5=1; \quad \% \text{ Switch for R5}
\]
\[
s6=1; \quad \% \text{ Switch for R6}
\]
\[
s8=1; \quad \% \text{ Switch for R8}
\]
\[
s9=1; \quad \% \text{ Switch for R9}
\]
\[
s10=1; \quad \% \text{ Switch for R10}
\]
\[
s11=1; \quad \% \text{ Switch for R11}
\]
\[
s12=1; \quad \% \text{ Switch for R12}
\]
\[
s13=1; \quad \% \text{ Switch for R13}
\]
\[
s14=1; \quad \% \text{ Switch for R14}
\]
\[
s15=1; \quad \% \text{ Switch for R15}
\]
\[
s16=1; \quad \% \text{ Switch for R16}
\]
\[
s17=1; \quad \% \text{ Switch for R17}
\]
\[
s18=1; \quad \% \text{ Switch for R18}
\]
\[
s19=1; \quad \% \text{ Switch for R19}
\]
\[
s20=1; \quad \% \text{ Switch for R20}
\]
\[
s21=1; \quad \% \text{ Switch for R21}
\]

\% Reaction Rate activation energies and pre-exponentials
\% Arrhenius Form: \( k = [A]\exp(-\text{activation\_energy}/(R*T\_mon)) \)
\% \([A] = \exp(A)\) in Simulink code,
\% \( R \) is universal gas constant, \( R = 8.3144621 \text{ J/(K\_mol)} \)
\% \text{activation\_energy} is in unit of J/mol, \( E = \text{activation\_energy}/R \)

\[
A1 = 35.60; \quad \% \text{ Holder}
\]
\%\(E1 = 105e3/8.3144621\)
\[
E1 = 12629; \quad \% \text{ Holder}
\]
\[
A2 = 36.00; \quad \% \text{ Holder}
\]
\[
E2 = 10223; \quad \% \text{ Holder}
\]
\[
A3 = 36.60; \quad \% \text{ Holder}
\]
\[
E3 = 13471; \quad \% \text{ Holder}
\]
\[
A4 = 35.30; \quad \% \text{ Holder}
\]
\[
E4 = 12629; \quad \% \text{ Holder}
\]
\[
A5 = 28.00; \quad \% \text{ Holder}
\]
\[
E5 = 14553; \quad \% \text{ Holder}
\]
\[
A6 = 6e5; \quad \% \text{ From reference [16-21] in report}
\]
\[
B6 = -12629; \quad \% \text{ From reference [16-21] in report}
\]
A7 = 27.70;  % Holder
E7 = 16357;  % Holder

A8 = 2.4e6;  % From reference [16-21] in report
B8 = -12629; % From reference [16-21] in report

A9 = 26.00;  % Holder
E9 = 16357;  % Holder

A10 = 28.60; % Holder
E10 = 9622;  % Holder

A11 = 25.28; % Holder
E11 = 8539;  % Holder

A12 = 24.00; % Holder
E12 = 9622;  % Holder

A13 = 29.80; % Holder
E13 = 8581;  % Holder

A14 = 31.00; % Holder
E14 = 9622;  % Holder

A15 = 27.20; % Holder
E15 = 9622;  % Holder

A16 = 25.80; % Holder
E16 = 8274;  % Holder

A17 = 7.35;  % Holder
E17 = 17115; % Holder

A18 = -6.28; % Holder
E18 = 12399; % Holder

A19 = 9.03;  % Holder
E19 = 17115; % Holder

A20 = 5.38;  % Holder
E20 = 16742; % Holder

A21 = -12.02; % Holder
E21 = 0;    % Holder
% Reaction Rate activation energies and pre-exponentials for inhibition terms

% Inhibition terms for reaction except 6 and 8
AI_1 = 2.00; % Holder
EI_1 = -1533; % Holder

AI_2 = 6.80; % Holder
EI_2 = -361; % Holder

AI_3 = 4.50; % Holder
EI_3 = -1191; % Holder

AI_4 = 5.77; % Holder
EI_4 = -1533; % Holder

AI_5 = 6.80; % Holder
EI_5 = -361; % Holder

AI_6 = 4.50; % Holder
EI_6 = -1191; % Holder

AI_7 = 11.00; % Holder
EI_7 = 0; % Holder

% Inhibition terms for reaction 6 and 8, from reference [16-21] in report
C1 = 65.6;
D1 = 961;
E1 = 2.08e3;
F1 = 361;
G1 = 3.98;
H1 = 11611;
I1 = 4.79e5;
J1 = -3733;

Aox = 35; % Aox,Box,Ared,Bred,Kpt are constants for the redox WGS sub model from reference [16-21] in report
Box = -11e3;
Ared = 20;
Bred = -11e3;
rh_gain = 1; % Value should be 1 or 0. Set to 1 if calculation of redox1 turned on and 0 if off

% Model Parameter
n_elements = 54; % Number of monolith segments coded
n_gas_species = 11; % Number of gas species
n_surface_species = 2; % Number of surface storage species not in gas (Cannot set to less than 1)
Relative Molar mass vector (NO NO2 N2O2 N2 CO CO2 CH4 C3H6 H2 H2O O2)
\[ \text{rmm} = (30 46 44 28 28 44 16 42 2 18 32); \]
\[ \text{rmm}\_\text{inv} = 1./\text{rmm}; \]

Mass transfer parameters
Diffusion coefficient
Fuller, 1966 to calculate for N2O N2 CO CO2 H2 H2O O2
Chapman-Enskog theory to calculate for NO CH4 C3H6
There's no need to calculate for N2O since N2O is not involved in all reactions

Fuller's expression = \( T^{1.75} \cdot \text{mol\_diff}/P \)
Diffusion volume = \[ 1 1 35.9 17.9 18.9 26.9 1 1 7.07 12.7 16.6; \]
Diffusion volumes of simple molecules, 1 for NO N2O CH4 C3H6
\[ \text{mol\_diff} = 100\cdot(\text{rmm}.^(-1) + 1/29).^{(1/3)} / (\text{diffusion\_volume}.^((1/3) + 20.1^((1/3))).^2); \]

Chapman-Enskog theory's expression = \( T^{1.5} \cdot \text{mol\_diff}/(P\cdot\Omega) \),
\( \Omega \): temperature-dependent collision integral
\[ \text{mol\_diff}(1) = 185.8\cdot\sqrt{1/\text{rmm}(1)/29}/((3.47 + 3.617)/2)^2; \]
\[ \text{mol\_diff}(7) = 185.8\cdot\sqrt{1/\text{rmm}(7)/29}/((3.78 + 3.617)/2)^2; \]
\[ \text{mol\_diff}(8) = 185.8\cdot\sqrt{1/\text{rmm}(8)/29}/((4.766 + 3.617)/2)^2; \]

\[ \text{mol\_diff} = \text{mol\_diff}/10000; \]
\[ \text{mol\_diff}(12) = 0; \]
\[ \text{mol\_diff}(13) = 0; \]

\[ \text{Sh}\_\text{inf} = 3.6; \]

ECT parameters
\[ \text{Dens\_ECT\_mon} = 920; \]
\[ \text{L\_ECT\_mon} = 0.0889; \]
\[ \text{hydraulic\_radius} = 0.000363; \]
\[ \text{N\_ECT\_cpsi} = 900; \]
\[ \text{e} = 0.7353; \]

\[ \text{A\_ECT\_mon} = 0.011; \]
\[ \text{ox\_storage\_capacity} = 60e-3; \]

\% Calculation of \( a(x) \): \( a(x) = \text{Noble metal loading} \cdot \text{Dispersion} \cdot \text{constant} \)
\% \[ \begin{bmatrix} [\text{m2/m3}] & [\text{kg/m3}] & [\text{m2/kg}] \end{bmatrix} \]
\[ \text{Noble\_metal\_Loading} = 5.76\cdot\text{ones}(1,n\_\text{elements}); \]
\[ \text{Dispersion} = 0.05\cdot\text{ones}(1,n\_\text{elements}); \]
ax = Noble_metal_Loading.*Dispersion*206.6e3; %catalytic surface area per unit reactor volume

% Assuming that of the 60mol/m3 O2 storage capacity, initial 50% O2 capacity stored -> 60 Ce2o3 & 120 CeO2

initial_Ce2O3 = ox_storage_capacity/n_elements; % initial surface concentration of Ce2O3 kmol/m3
initial_CeO2 = 2*ox_storage_capacity/n_elements; % initial surface concentration of CeO2 kmol/m3
bus_width=n_elements*(n_gas_species+n_surface_species);
initial_surface=zeros(1,bus_width);
initial_surface((bus_width-2*n_elements+1):(bus_width-n_elements))=initial_Ce2O3;
initial_surface((bus_width-n_elements+1):bus_width)=initial_CeO2;

% Calculated Parameters
Vol_ECT_mon = L_ECT_mon*A_ECT_mon; % monolith volume
N_ECT_cell = N_ECT_cpsi*(39.37^2)*A_ECT_mon; % Number of ECT cells
N_ECT_m = N_ECT_cpsi/(25.4e-3*25.4e-3); % ECT number of cells per square metre
Vol_ECT_seg = Vol_ECT_mon/n_elements; % volume of discrete monolith segment
M_ECT_mon = Vol_ECT_mon*Dens_ECT_mon*(1-e); % ECT Monolith mass (Kg)
M_ECT_seg = M_ECT_mon/n_elements; % Segment mass
L_ECT_seg = L_ECT_mon/n_elements; % segment length
GA = 2*e/hydraulic_radius; % Geometric catalyst surface to volume ratio (m^2/m^3)

%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Thermal model parameters %
%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Convection & Conduction Coefficients and specific heat
LBA_Monol =2.4; % [J/m.s.K] Substrate thermal conductivity
cy_exhgas =1089; % [J/kg.K] Exhust specific heat
Nu_inf =3.608; % Assyptotic Nusselt No. used to calculate h

% Monolith Cps = cp1 + (cp2)^cp3 + (cp4)^cp5

.cp1 = 500;
.cp2 = 0;
.cp3 = 1;
.cp4 = 0;
.cp5 = -2;

%%%%%%%%%%%%%%%%%%%%%%%%%%%
% %
% Lambda gas is set in Simulink %
% thermal model see thermal %

145
% model code block
%
% Surfaces & Dimensions
conductive_CSA = A_ECT_mon*(1-e); % cross sectional area of monolith solid
convection_surface_area = GA*Vol_ECT_seg; % [m2]

% Initial Temperatures for Thermal Model
initial_mono_temp = 295; % initial monolith temperature (K)
Appendix B-2: MATLAB Code of Input Data File Generator for the 2D Axisymmetric Model

% Module name : Input_Data_Generator.m
% 11/16/2015
% Wenbo Jia

% Description : Input data generator for GM FTP cycle data.
% Modified for 2D axisymmetric model.

% Input data generator based on the one-dimensional input data and Flow index, Temperature index and number of layers
clc; clear all;
m = dlmread('sample_data300s.txt'); % Read data from txt file
time = 301; % 0-300s
number_of_layers = 10; % Number of layers = 10
flow_index = 0.25; % Flow index = 27.744%
temperature_index = 0.25; % Temperature index = 25.5%

flow_proportion = zeros(1,number_of_layers); % Define size of flow proportion in each layer
for i = 1:number_of_layers
    flow_proportion(i) = (i^2-(i-1)^2)/number_of_layers^2;
end

data = zeros(time,(14*number_of_layers+1)); % Define new input data
data(:,1) = m(:,1); % Column for time
for i = 1:floor(number_of_layers/2);
    % Define inner 25% area layers
    data(:,((i-1)*14+2):(i*14-1)) = m(:,2:13)*flow_proportion(i)*flow_index*4; % Mass flow rate of 12 gas species
    data(:,(i*14)) = m(:,14)*temperature_index*4; % Temperature
end
for i = (floor(number_of_layers/2)+1):number_of_layers;
    % Define outer 75% area layers
    data(:,((i-1)*14+2):(i*14-1)) = m(:,2:13)*flow_proportion(i)*(1-flow_index)*4/3; % Mass flow rate of 12 gas species
    data(:,(i*14)) = m(:,14)*(1-temperature_index)*4/3; % Temperature
end
data(:,(i*14+1)) = m(:,15);  %
Pressure
end

fname = sprintf('Flow_index%f_Tem_index%f_%dL.txt',flow_index,temperature_index
,number_of_layers);
save(fname,'data','-ascii');
Appendix B-3: MATLAB Code of Input Parameter for the 2D Axisymmetric Model

% Module name : GM_FTP_cycle_data_parameter_2D_10_layers.m
% Wenbo Jia 02/22/16

% Description : Parameter file for GM FTP cycle data.
% Modified for 2D axisymmetric model.

% There are 21 reactions in Holder et al's model, since we don't consider C3H8,
% Reaction 3 and 7 which are related to C3H8 are not modeled in the Simulink program. All other 19 reactions in Holder et al's model are considered.
% Reaction 6,8 and 9 are coded as reversible reactions.

% R1:  CO + 0.5O2 -> CO2
% R2:  H2 + 0.5O2 -> H2O
% R4:  C3H6 + 4.5O2 -> 3CO2 + 3H2O
% R5:  CH4 + 2O2 -> CO2 + 2H2O
% R6:  CO + H2O -> CO2 + H2
% R8:  C3H6 + 3H2O -> 3CO + 6H2
% R9:  CH4 + H2O -> CO + 3H2
% R10: CO + NO -> CO2 + 0.5N2
% R11: H2 + NO -> H2O + 0.5N2
% R12: C3H6 + 9NO -> 3H2O + 3CO2 + 4.5 N2
% R13: H2 + 2NO -> H2O + N2O
% R14: N2O + H2 -> H2O + N2
% R15: CO + 2NO -> CO2 + N2
% R16: N2O + CO -> CO2 + N2
% R17: H2 + 2CeO2 -> H2O + Ce2O3
% R18: H2O + Ce2O3 -> H2 + 2CeO2
% R19: CO + 2CeO2 -> CO2 + Ce2O3
% R20: CO2 + Ce2O3 -> CO + 2CeO2
% R21: 0.5O2 + Ce2O3 -> 2CeO2

s1=1;  % Switch for R1
s2=1;  % Switch for R2
s4=1; % Switch for R4
s5=1; % Switch for R5
s6=1; % Switch for R6
s8=1; % Switch for R8
s9=1; % Switch for R9
s10=1; % Switch for R10
s11=1; % Switch for R11
s12=1; % Switch for R12
s13=1; % Switch for R13
s14=1; % Switch for R14
s15=1; % Switch for R15
s16=1; % Switch for R16
s17=1; % Switch for R17
s18=1; % Switch for R18
s19=1; % Switch for R19
s20=1; % Switch for R20
s21=1; % Switch for R21

% Reaction Rate activation energies and pre-exponentials
% Arrhenius Form: k = [A]exp(-activation_energy/(R*T_mon))
% [A] = exp(A) in Simulink code,
% R is universal gas constant, R = 8.3144621 J/(K*mol)
% activation_energy is in unit of J/mol, E = activation_energy/R

A1 = 35.60; % Holder
E1 = 12629; % Holder
A2 = 36.00; % Holder
E2 = 10223; % Holder
A3 = 36.60; % Holder
E3 = 13471; % Holder
A4 = 35.30; % Holder
E4 = 12629; % Holder
A5 = 28.00; % Holder
E5 = 14553; % Holder
A6 = 6e5; % From reference [16-21] in report
E6 = -12629; % From reference [16-21] in report
A7 = 27.70; % Holder
E7 = 16357; % Holder
A8 = 2.4e6; % From reference [16-21] in report
B8 =-12629;  % From reference [16-21] in report
A9 = 26.00;  % Holder
E9 = 16357;  % Holder
A10 = 28.60;  % Holder
E10 = 9622;  % Holder
A11 = 25.28;  % Holder
E11 = 8539;  % Holder
A12 = 24.00;  % Holder
E12 = 9622;  % Holder
A13 = 29.80;  % Holder
E13 = 8581;  % Holder
A14 = 31.00;  % Holder
E14 = 9622;  % Holder
A15 = 27.20;  % Holder
E15 = 9622;  % Holder
A16 = 25.80;  % Holder
E16 = 8274;  % Holder
A17 = 7.35;  % Holder
E17 = 17115;  % Holder
A18 = -6.28;  % Holder
E18 = 12399;  % Holder
A19 = 9.03;  % Holder
E19 = 17115;  % Holder
A20 = 5.38;  % Holder
E20 = 16742;  % Holder
A21 = -12.02;  % Holder
E21 = 0;  % Holder

% Reaction Rate activation energies and pre-exponentials for inhibition terms

% Inhibition terms for reaction except 6 and 8
AI_1 = 2.00;  % Holder
EI_1 = -1533;  % Holder
AI_2 = 6.80; % Holder
EI_2 = -361; % Holder

AI_3 = 4.50; % Holder
EI_3 = -1191; % Holder

AI_4 = 5.77; % Holder
EI_4 = -1533; % Holder

AI_5 = 6.80; % Holder
EI_5 = -361; % Holder

AI_6 = 4.50; % Holder
EI_6 = -1191; % Holder

AI_7 = 11.00; % Holder
EI_7 = 0; % Holder

% Inhibition terms for reaction 6 and 8, from reference [16-21] in report
C1 =65.6;
D1 =961;
E_1 =2.08e3;
F1 =361;
G1 =3.98;
H1 =11611;
I1 =4.79e5;
J1 =-3733;

Aox =35; % Aox,Box,Ared,Bred,Kpt are constants for the redox WGS sub model, from reference [16-21] in report
Box =-11e3;

Ared =20;
Bred =-11e3;

rh_gain=1; % Value should be 1 or 0. Set to 1 if calculation of redox1 turned on and 0 if off

% Model Parameter
n_elements = 54; % Number of monolith segments coded
n_gas_species = 11; % Number of gas species
n_surface_species = 2; % Number of surface storage species not in gas (Cannot set to less than 1)

% Relative Molar mass vector (NO NO2 N2O N2 CO CO2 CH4 C3H6 H2 H2O O2)
rmm =([30 46 44 28 28 44 16 42 2 18 32]);
rmm_inv = 1./rmm;

% %Mass transfer parameters
% Diffusion coefficient
% Fuller, 1966 to calculate for N2O N2 CO CO2 H2 H2O O2
% Chapman-Enskog theory to calculate for NO CH4 C3H6
% There's no need to calculate for N2O since N2O is not involved in all reactions

% Fuller's expression = T^1.75*mol_diff/P
% diffusion_volume = [11 35.9 17.9 18.9 26.9 11 7.07 12.7 16.6]; % Diffusion volumes of simple molecules, 1 for NO N2O CH4 C3H6
mol_diff = 100*(rmm.^(-1)+1/29).^(.5)./(diffusion_volume.^((1/3)+20.1^(1/3))).^2;

% Chapman-Enskog theory's expression = T^1.5*mol_diff/(P*Omega) ,
% Omega: temperature-dependent collision integral
mol_diff(1) = 185.8*sqrt(1/rmm(1)+1/29)/(((3.47+3.617)/2)^2); % NO
mol_diff(7) = 185.8*sqrt(1/rmm(7)+1/29)/(((3.78+3.617)/2)^2); % CH4
mol_diff(8) = 185.8*sqrt(1/rmm(8)+1/29)/(((4.766+3.617)/2)^2); % C3H6

mol_diff = mol_diff/10000; % Transfer from [cm2/s] to [m2/s]
mol_diff(12) = 0; % Cerium species bound on surface
mol_diff(13) = 0; % Cerium species bound on surface
Sh_inf = 3.6; % Assyptotic sherwood Number

%ECT parameters
Dens_ECT_mon            = 1720; % ECT Monolith density (kg/m3)
L_ECT_mon               = 0.2286; % ECT Monolith length (m)
hydraulic_radius        = 0.000524; % ECT cell hydraulic radius (m)
N_ECT_cpsi              = 400; % ECT number of cells per square inch
monolith                = 0.681; % ECT void fraction of the monolith
A_ECT_mon               = .008775; % monolith frontal area m2
ox_storage_capacity     = 60e-3; % Oxygen storage capacity in kmol/m3

% Calculation of a(x) : a(x) = Noble metal loading * Dispersion * constant
% [m2/m3] [kg/m3] [ ]
[m2/kg]
Noble_metal_Loading = 7.95*ones(1,n_elements); % Noble metal loading kg/m3
y=19:54;
Selector for 2nd brick
Noble_metal_Loading(y)=4.24; % Poisoned front inch
Noble_metal_Loading=Noble_metal_Loading;
Dispersion =0.05*ones(1,n_elements); % Dispersion (0.05 for unpoisoned 0.007 for poisoned)
Dispersion(1)=0.007; % Poisoned front inch
Dispersion(2)=0.007; % Poisoned front inch
Dispersion(3)=0.007; % Poisoned front inch

153
Dispersion(4)=0.007; % Poisoned front inch
Dispersion(5)=0.007; % Poisoned front inch
Dispersion(6)=0.007; % Poisoned front inch

ax = Noble_metal_Loading.*Dispersion*206.6e3; % Catalytic surface area per unit reactor volume

% Assuming that of the 60 mol/m³ O₂ storage capacity, initial 50% O₂
capacity stored -> 60 Ce₂O₃ & 120 CeO₂
initial_Ce2O3 = ox_storage_capacity/n_elements; % Initial surface concentration of Ce₂O₃ kmol/m³
initial_CeO2 = 2*ox_storage_capacity/n_elements; % Initial surface concentration of CeO₂ kmol/m³
bus_width=n_elements*(n_gas_species+n_surface_species);
initial_surface=zeros(1,bus_width);
initial_surface((bus_width-2*n_elements+1):(bus_width-n_elements))=initial_Ce2O3;
initial_surface((bus_width-n_elements+1):bus_width)=initial_CeO2;

% Calculated Parameters
Vol_ECT_mon = L_ECT_mon*A_ECT_mon; % Monolith volume
N_ECT_cell = N_ECT_cpsi*(39.37^2)*A_ECT_mon; % Number of ECT cells
N_ECT_m = N_ECT_cpsi/(25.4e-3*25.4e-3); % ECT number of cells per square metre
Vol_ECT_seg = Vol_ECT_mon/n_elements; % Volume of discrete monolith segment
M_ECT_mon = Vol_ECT_mon*Dens_ECT_mon*(1-e); % ECT Monolith mass (kg)
% M_ECT_seg = M_ECT_mon/n_elements; % Segment mass
L_ECT_seg = L_ECT_mon/n_elements; % Segment length
GA = 2*e/hydraulic_radius; % Geometric catalyst surface to volume ratio (m²/m³)

% New parameters for 2-D
m_elements = 10; % Number of monolith segments coded
R = 0.05285; % Radius of ECT (m)
R_ECT_seg = R/m_elements; % Radius for layer 1 [m]
R_ECT_seg = R/m_elements; % Number of layers coded

r(1) = l*R_ECT_seg; % Radius for layer 1 [m]
conductive_CSA(1) = pi*(r(1)^2)*(1-e); % Cross sectional area of monolith solid for layer 1 [m²]
CSA(1) = pi*(r(1)^2); % Cross sectional area of monolith for layer 1 [m²]
Vol_ECT_seg(1) = CSA(1)*L_ECT_seg; % Volume of discrete monolith segment in layer 1 [m³]
conductive_Vol_ECT_seg(1) = conductive_CSA(1)*L_ECT_seg; % Volume of discrete monolith segment in layer 1 [m³]
convection_surface_area(1) = GA*Vol_ECT_seg(1); % Convection surface area for layer 1 [m2]
M_ECT_seg(1) = Vol_ECT_seg(1)*Dens_ECT_mon*(1-e); % Segment mass for layer 1 [kg]

for i = 2:m_elements
    r(i) = i*R_ECT_seg; % Radius for layer i [m]
    conductive_CSA(i) = pi*(r(i)^2-r(i-1)^2)*(1-e); % Cross sectional area of monolith solid for layer i [m2]
    CSA(i) = pi*(r(i)^2-r(i-1)^2); % Cross sectional area of monolith for layer i [m2]
    Vol_ECT_seg(i) = CSA(i)*L_ECT_seg; % Volume of discrete monolith segment in layer i [m3]
    conduction_vol_ECT_seg(i) = conductive_CSA(i)*L_ECT_seg; % Volume of discrete monolith segment in layer i [m3]
    convection_surface_area(i) = GA*Vol_ECT_seg(i); % Convection surface area for layer i [m2]
    M_ECT_seg(i) = Vol_ECT_seg(i)*Dens_ECT_mon*(1-e); % Segment mass for layer i [kg]
end

T_ambient = 293; % Ambient temperature (K)
h_ambient = 10; % Convective heat transfer coefficient to ambient environment (W/m^2.K)
emissivity = 0.35; % Emissivity
Stefan_Boltzmann_constant = 5.670373e-8; % Stefan_Boltzmann_constant (W.m^-2.K^-4)

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Monolith Cps = cp1 + (cp2)T^cp3 + (cp4)T^cp5
cp1 = 1020;
cp2 = 0;
cp3 = 1;
cp4 = 0;
cp5 = -2;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Lambda gas is set in Simulink %
% thermal model see thermal %
% model code block %
% %
$\text{Initial Temperatures for Thermal Model}$

`initial_mono_temp = 293; % initial monolith temperature (K)`
Appendix C: Data for Calculating Diffusion Coefficients

Appendix C-1: Collision Diameters and Energy of Interaction [26]

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<th>Critical properties</th>
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**Other organic compounds:**

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Appendix C-2: Collision Integral [26]

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<th>$kT/\varepsilon$ (for viscosity and thermal conductivity)</th>
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<th>$\Omega_{\Sigma,AB}$ (for diffusivity)</th>
<th>$kT/\varepsilon$ (for viscosity and thermal conductivity)</th>
<th>$\Omega_\mu = \Omega_k$</th>
<th>$\Omega_{\Sigma,AB}$ (for diffusivity)</th>
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<td>1.107</td>
<td>1.013</td>
<td>50.0</td>
<td>0.6510</td>
<td>0.5763</td>
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<tr>
<td>2.50</td>
<td>1.0933</td>
<td>1.0006</td>
<td>75.0</td>
<td>0.6140</td>
<td>0.5415</td>
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<tr>
<td>2.60</td>
<td>1.0807</td>
<td>0.9890</td>
<td>100.0</td>
<td>0.5887</td>
<td>0.5180</td>
</tr>
</tbody>
</table>
Appendix C-3: Diffusion Volumes [27]

<table>
<thead>
<tr>
<th>Atomic and Structural Diffusion Volume Increments</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>(N)(^b)</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Diffusion Volumes of Simple Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
</tr>
<tr>
<td>D(_2)</td>
</tr>
<tr>
<td>He</td>
</tr>
<tr>
<td>N(_2)</td>
</tr>
<tr>
<td>O(_2)</td>
</tr>
<tr>
<td>Air</td>
</tr>
<tr>
<td>Ne</td>
</tr>
<tr>
<td>Ar</td>
</tr>
<tr>
<td>Kr</td>
</tr>
<tr>
<td>(Xe)</td>
</tr>
<tr>
<td>CO</td>
</tr>
</tbody>
</table>

\(^a\)\(^b\) = 1.75.
\(^b\) ( ) indicates that listed value is based on only a few data points.