

Ignition-Extinction Analysis of Coupled Homogeneous-Heterogeneous Reactions in Monolith Reactors

by
Bhaskar Sarkar

A dissertation submitted to the Department of Chemical and Biomolecular Engineering,
Cullen College of Engineering
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in Chemical Engineering

Chair of Committee: Vemuri Balakotaiah

Committee Member: Michael P. Harold

Committee Member: Praveen Bollini

Committee Member: Giles Auchmuty

Committee Member: Birol Dindoruk

University of Houston
August 2021

Copyright 2021, Bhaskar Sarkar

Acknowledgements

My deepest gratitude first goes to my advisor Professor Vemuri Balakotaiah for the continuous support and guidance. His enthusiasm, patience, and motivation kept me constantly engaged with my research and writing of this thesis. Without his advice and persistent help, this dissertation would not have been possible.

I would like to thank Prof. Michael Harold and Prof. Praveen Bollini for serving on my committee. Their invaluable comments and insightful feedback pushed me to improve my work. I am also thankful to Prof. Birol Dindoruk and Prof. Giles Auchmuty for taking the time off their busy schedule to read my thesis and serve on my committee. I would like to acknowledge SABIC Americas Inc. for the financial support.

I want to thank my friends and colleagues at the University of Houston for their help and support. I am grateful to Meet Shah for our many thought-provoking technical discussions. I want to thank Mingjie Tu and Zhe Sun for their friendship and help in a multitude of things. I am extremely thankful to Ramakrishna Dadi who taught me a lot of useful techniques when I was starting as a graduate student. I am grateful to Imran Alam for his invaluable suggestions during my job search. My special thanks goes to Ram Ratnakar for his motivation and wise insights which proved to be very useful in completing our joint papers.

I want to express my sincerest appreciation to Aarti Doshi who encouraged and supported me in all my endeavors. I am very thankful to Alex Suescun and his

family for making me feel belonged despite being far from home. I would also like to acknowledge my long-term roommate Abhishek Nair and my friends, Abhradeep Ghosh, Rangeet Pan, and Sayantrini Saha. Without them, my stay in Houston would never have been so enjoyable.

Finally, I would like to express my love and gratitude to my parents and brother for their support and encouragement.

Abstract

We use a multi-scale multi-mode reduced order model for coupled homogeneous-catalytic reaction systems to present a comprehensive ignition-extinction analysis of catalytically assisted propane and hydrogen combustion and oxidative coupling of methane (OCM) in monolith, gauze or wire-mesh type reactors. The reduced order models are expressed in terms of phase averaged multiple concentration (temperature) modes and interfacial fluxes which are related through various transfer coefficients that are local scale, flow and property dependent. Accurate expressions are provided for estimating the local transfer coefficient matrices in multi-component systems.

Using these reduced order models, the space of design and operating variables are explored to determine the different types of ignition-extinction behaviors occurring in the catalytically assisted combustion processes. Bifurcation theory is used to construct phase diagrams in the plane of equivalence ratio versus feed temperature and equivalence ratio versus space time to classify the behaviors occurring and the extent of coupling between the homogeneous and catalytic conversion of the fuel. We also examine the impact of channel hydraulic diameter, precious metal (Pt) loading/dispersion, Lewis number, heat loss effects, reactor length, and substrate thermal conductivity on the ignition-extinction behavior. The results of the comprehensive analysis are used to present guidelines on the design and scale-up of monolith reactors for carrying out the catalytically assisted combustion processes.

In OCM, we determine the impact of methane to oxygen ratio in the feed, space

time, channel hydraulic radius, washcoat properties, operating pressure and substrate thermal conductivity on the ignition-extinction behavior of the system as a function of the feed temperature. The computations show that for typical operating conditions, the methane conversion and C_2 product selectivity are non-monotonic on the ignited branch and there exists an optimum point of operation away from the extinction point. We also present the various species and temperature profiles along the length of the reactor and examine how these profiles are impacted by the substrate conductivity, space time and heat loss. The results obtained for monolith, gauze or wire-mesh reactors are compared to those in packed-beds and suggestions are provided for scale-up and optimization of these reactors for carrying out OCM.

Table of Contents

Acknowledgements	iii
Abstract	v
Table of Contents	vii
List of Tables	xi
List of Figures	xii
1 Introduction	1
1.1 Monolith reactors	1
1.2 Literature review	4
1.3 Objectives and outline	6
2 Mathematical Models	8
2.1 Introduction	8
2.2 Detailed models with multiple length and time scales:	10
2.3 Multi-mode reduced order models	14
2.3.1 Global and local equations	14
2.3.2 Generalization of local equations to arbitrary flow and washcoat geometries and finite gradients	21
2.4 Limiting models	24

2.4.1	Two-mode long channel model	25
2.4.2	Steady-state short monolith, gauze or wire-mesh reactor model	28
2.4.3	Interfacial flux and transfer coefficients	30
2.4.4	Construction of 2D/3D profiles from reduced order models . .	39
2.5	Numerical algorithms	40
2.5.1	Transient equations	41
2.5.2	Steady-state equations	41
2.5.3	Functions of matrices	47
3	Bifurcation analysis for oxidation of propane	49
3.1	Introduction	49
3.1.1	Short monolith or gauze reactor model	51
3.1.2	Transient simulations of multi-mode finite dispersion model . .	60
3.2	Summary	69
4	Bifurcation analysis of catalytically assisted hydrogen combustion	70
4.1	Introduction	70
4.2	Literature review	71
4.3	Kinetic model	73
4.4	Steady-state bifurcation analysis of short monolith model	75
4.4.1	Homogeneous or catalytic reaction only	76
4.4.2	Thermally coupled system under adiabatic conditions	81
4.4.3	Impact of channel hydraulic radius on thermal coupling	88
4.4.4	Impact of washcoat properties	92

4.4.5	Impact of heat loss	96
4.5	Bifurcation analysis of two-mode long channel model	101
4.6	Summary	114
5	Bifurcation analysis of oxidative coupling of methane	117
5.1	Introduction	117
5.2	Literature review	118
5.3	Kinetic model	121
5.4	Steady-state bifurcation analysis of short monolith or gauze or wire- mesh type reactors	126
5.4.1	Impact of inlet CH_4/O_2 mole ratio:	127
5.4.2	Impact of space time	130
5.4.3	Impact of channel hydraulic radius	133
5.4.4	Impact of pressure	137
5.4.5	Impact of heat loss from monolith to furnace or surroundings .	139
5.5	Bifurcation analysis of long channel model	142
5.5.1	Impact of reactor length and flow velocity	143
5.5.2	Impact of thermal conductivity of the substrate material . . .	148
5.5.3	Impact of heat loss	155
5.6	Summary	158
6	Microkinetic modeling of oxidative coupling of methane	161
6.1	Introduction	161
6.2	Mathematical model	164

6.3	Kinetic model	166
6.4	Isothermal simulations of short monolith model	170
6.4.1	Homogeneous contribution in the coupled homo-/hetero system	170
6.4.2	Impact of design and operating parameters	179
6.5	Summary	183
7	Conclusions and recommendations for future work	185
7.1	Conclusions	185
7.2	Recommendations for future work	188
	Bibliography	190

List of Tables

2.1	Constants used in external Sherwood number calculation for some common flow channel shapes	35
2.2	Effective washcoat diffusion lengths and constants used in internal Sherwood number calculation for some common washcoat shapes . . .	36
3.1	Kinetic, transport and physical parameters used in the calculation of propane oxidation	53
3.2	List of parameters for the transient two-phase model - propane	61
4.1	List of parameters for hydrogen combustion in short monolith model .	75
4.2	List of parameters for the two-mode long channel model - hydrogen .	102
5.1	Rate expressions for catalytic reactions	124
5.2	Kinetic parameters of catalytic reactions	125
5.3	Rate expressions for homogeneous reactions	125
5.4	List of parameters for the two-mode long channel model - OCM . . .	142
6.1	List of parameters for the transient, isothermal short monolith model	166
6.2	Elementary steps in gas phase OCM	167
6.3	Catalytic reaction mechanism of OCM	168

List of Figures

1.1	Ceramic monoliths with different cell densities (top) and a close-up view of channel geometry (bottom).	2
1.2	Metallic monolith (left) with close-up view of channel geometry (right).	3
2.1	Schematic diagram of a single monolith channel illustrating various domains (flow channel, washcoat layer and wall).	9
2.2	Schematic diagrams of monolith reactor with long channels (left) and short monolith/wiremesh or gauze type reactor (right).	24
2.3	Thiele modulus dependency of internal/external and cross-exchange Sherwood numbers for the case of negligible curvature (parallel plate geometry and thin washcoat layers).	33
2.4	Schematic diagram of pseduo-arc length continuation method	43
3.1	Computed phase diagram for lean combustion of propane with washcoat diffusion present (top) and without washcoat diffusional limitations (bottom).	54
3.2	Bifurcation diagrams of exit fluid (T_f) and solid temperature (T_w) against fluid inlet temperature ($T_{f,in}$) with washcoat diffusion (left column) and without washcoat diffusion (right column).	55
3.3	Computed phase diagram for lean combustion of propane in a monolith with and without washcoat diffusional limitations.	57

3.4	Bifurcation diagrams of exit fluid (T_f) and solid temperature (T_w) against fluid inlet temperature ($T_{f,in}$) with washcoat diffusion (left column) and without washcoat diffusion (right column).	58
3.5	Fluid and solid exit temperatures (top) and reactant conversion (bottom) during ramp up and ramp down.	62
3.6	Fluid and solid exit temperatures (top) and reactant conversion (bottom) during ramp up and ramp down.	64
3.7	Temperature profiles of fluid and solid at different fluid inlet temperatures during ramp up and ramp down.	65
3.8	Fluid and solid exit temperatures (top) and reactant conversion (bottom) during ramp up and ramp down.	67
3.9	Temperature profiles of fluid and solid at different fluid inlet temperatures during ramp up and ramp down.	68
4.1	Computed hysteresis loci for adiabatic lean combustion of hydrogen with either only catalytic (at 3 different catalyst activities) or only homogeneous reaction present.	77
4.2	Bifurcation diagrams of exit fluid and solid temperature vs. feed temperature for hydrogen combustion with only homogeneous reaction (left) and with only catalytic reaction (right).	78
4.3	Computed phase diagram for adiabatic lean combustion of hydrogen with both catalytic and homogeneous reactions present in equivalence ratio vs. space time plane.	81

4.4	Bifurcation diagrams of exit fluid (T_f) and solid temperature (T_w) vs. feed temperature ($T_{f,in}$) for adiabatic lean combustion of hydrogen.	82
4.5	Computed phase diagram for adiabatic lean combustion of hydrogen with both catalytic and homogeneous reactions present in equivalence ratio vs. feed temperature plane.	84
4.6	Bifurcation diagrams of exit fluid (T_f) and solid temperature (T_w) vs. space time (τ) for adiabatic lean combustion of hydrogen.	85
4.7	Bifurcation diagrams of exit fluid (T_f) and solid temperature (T_w) for adiabatic lean combustion of hydrogen with space time as bifurcation parameter.	89
4.8	Comparison of catalytic and thermally coupled hysteresis loci for adiabatic lean hydrogen combustion at two different channel hydraulic radii.	91
4.9	Computed catalytic (top) and thermally coupled hysteresis loci (bottom) for adiabatic lean combustion of hydrogen at different catalyst activities in equivalence ratio vs. space time plane.	93
4.10	Comparison of catalytic hysteresis loci for adiabatic lean hydrogen combustion at different washcoat diffusivities.	95
4.11	Computed phase diagram for non-adiabatic lean combustion of hydrogen in presence of washcoat diffusion.	96
4.12	Bifurcation diagrams of fluid and solid temperatures (left) and reactant conversions (right) for lean hydrogen combustion in presence of external heat loss.	97

4.13	Computed dynamic hysteresis plots of exit fluid temperature (top) and H_2 conversion (bottom) versus feed temperature at different reactor lengths.	103
4.14	Computed dynamic hysteresis plots of exit fluid temperature (top) and H_2 conversion (bottom) versus feed temperature at different substrate conductivities.	105
4.15	Temperature (top) and conversion (bottom) profiles along the reactor length in the ignited branch at different substrate conductivities for a feed temperature of 300 K.	106
4.16	Temperature and concentration contour plots in the flow channel and washcoat for $L = 2$ cm and substrate conductivity, $\kappa_w = 15$ W/m.K.	108
4.17	Temperature and concentration contour plots inside the reactor of length, $L = 2$ cm and substrate conductivity, $\kappa_w = 1.5$ W/m.K.	110
4.18	Computed dynamic hysteresis plots of exit fluid temperature (top) and H_2 conversion (bottom) versus feed temperature at two different channel hydraulic radii.	112
4.19	Temperature profiles along the reactor length on the ignited branch at two different feed temperatures for $R_{\Omega_f} = 250 \mu m$ (top) and $R_{\Omega_f} = 1 mm$ (bottom).	113
5.1	Computed bifurcation diagrams of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different inlet CH_4/O_2 mole ratio.	128

5.2	Computed bifurcation diagrams of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different space times, τ	131
5.3	Computed bifurcation diagrams of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature for different channel hydraulic radii.	133
5.4	Computed bifurcation diagrams of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different channel hydraulic radii and space time.	135
5.5	Computed bifurcation diagrams of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature for different total pressure, P_T	138
5.6	Computed bifurcation diagrams of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature in the presence of heat loss at different values of heat transfer coefficient, h_a	140
5.7	Computed dynamic hysteresis plots of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different reactor lengths.	143
5.8	Computed dynamic hysteresis plots of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different reactor lengths.	145

5.9	Computed dynamic hysteresis plots of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different solid conductivity.	147
5.10	Computed dynamic hysteresis plots of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different solid conductivity.	149
5.11	Concentration and selectivity profiles along the dimensionless reactor length on ignited branch (top) and at extinction (down).	151
5.12	Concentration and selectivity profiles along the dimensionless reactor length on ignited branch (top) and at extinction (down) points. . . .	153
5.13	Fluid and solid temperature profiles along the dimensionless reactor length for $L = 5 \text{ mm}$, $\kappa_w = 50 \text{ W/m.K}$ (top figure) and $L = 10 \text{ mm}$, $\kappa_w = 1.5 \text{ W/m.K}$ (bottom figure).	154
5.14	Computed dynamic hysteresis plots of exit fluid temperature (top), CH_4 conversion, O_2 conversion and C_2 selectivity (bottom) versus feed temperature in presence of heat loss.	156
5.15	Concentration (top) and temperature (bottom) profiles along the dimensionless reactor length for $L = 10 \text{ mm}$, $\kappa_w = 1.5 \text{ W/m.K}$ and $\tau = 50 \text{ ms}$ in presence of external heat loss.	157
6.1	Exit conversions (χ) of CH_4 & O_2 and selectivities (S) of C_2 products ($C_2H_6 + C_2H_4$) against fluid inlet temperatures using the kinetic parameters proposed by Karakaya et al. [98].	171

6.2	Homogeneous reaction pathways for carbon containing compounds at $T_{f,in} = 1100$ K and inlet mole ratio $CH_4/O_2 = 6$. The actual rate is scaled by a factor of 0.025.	172
6.3	Catalytic reaction pathways of carbon containing compounds at $T_{f,in} = 1100$ K and inlet mole ratio $CH_4/O_2 = 6$. The actual rate is scaled by a factor of 5.4×10^{-8}	173
6.4	Exit conversions (χ) of CH_4 & O_2 and selectivities (S) of C_2 products ($C_2H_6 + C_2H_4$) against fluid inlet temperatures using the kinetic parameters proposed by Kechagiopoulos et al [113].	175
6.5	Homogeneous reaction pathways of carbon containing compounds at $T_{f,in} = 1100$ K and inlet mole ratio $CH_4/O_2 = 6$. The actual rate is scaled by a factor of 0.018.	176
6.6	Catalytic reaction pathways of carbon containing compounds at $T_{f,in} = 1100$ K and inlet mole ratio $CH_4/O_2 = 6$. The actual rate is scaled by a factor of 3.6×10^{-8}	177
6.7	Exit conversions (χ) of CH_4 & O_2 and selectivities (S) of C_2 products ($C_2H_6 + C_2H_4$) against fluid inlet temperatures at different inlet CH_4/O_2 mole ratio.	179
6.8	Exit conversions (χ) of CH_4 & O_2 and selectivities (S) of C_2 products ($C_2H_6 + C_2H_4$) against fluid inlet temperatures at different space times.	181
6.9	Exit conversions (χ) of CH_4 & O_2 and selectivities (S) of C_2 products ($C_2H_6 + C_2H_4$) against fluid inlet temperatures at different total pressure.	182

Chapter 1

Introduction

1.1 Monolith reactors

Extruded monoliths are structured reactors consisting of many long and narrow parallel channels. A layer of high surface area material with catalytically active ingredients, known as washcoat, is deposited on these channel walls. Feed containing reactants and carrier gases flow through the channels and diffuse into the washcoat where they either react to form products or get trapped (adsorbed). Unlike conventional fixed bed reactors with catalyst pellets, monolith reactors provide homogeneous access to the catalytic surface and have higher void fraction (area open to flow). Because of these advantages, the associated pressure drop across the channels is low even at high throughputs. These reactors are widely used in the treatment of emissions from gasoline, diesel and natural gas powered vehicles. Typically, the substrate in the automotive converters are made of a ceramic material like cordierite. However, metallic substrates made of ferritic steels are also common in recent years. Fig. 1.1 shows ceramic monoliths with different channel densities (diameters). While the channel geometries in ceramic monoliths can come in several shapes like circular, triangular, and hexagonal, square is most common in commercial industries. Among metallic

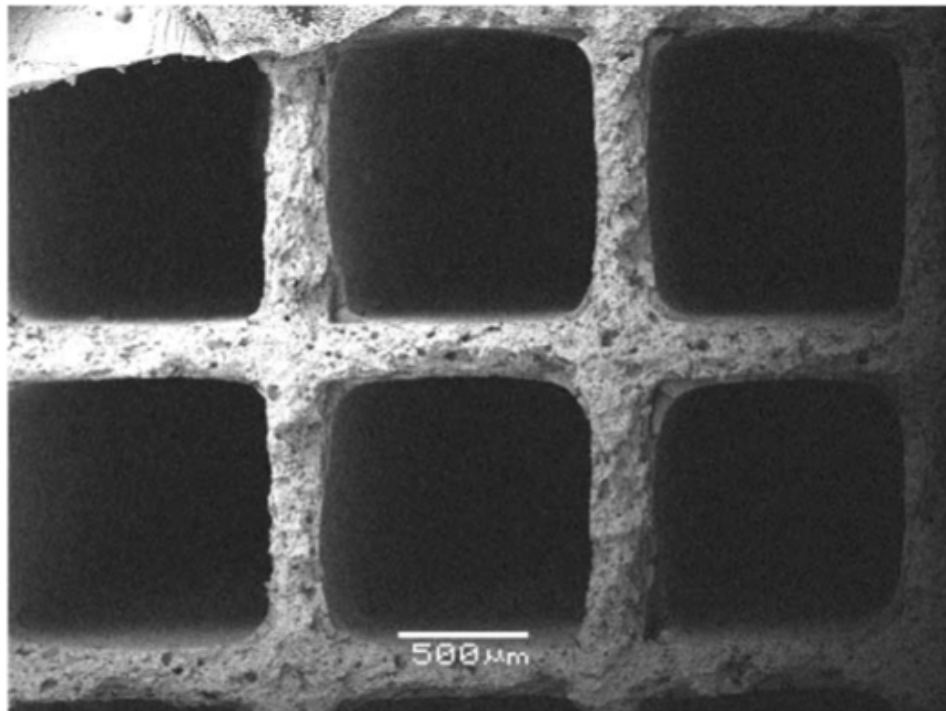
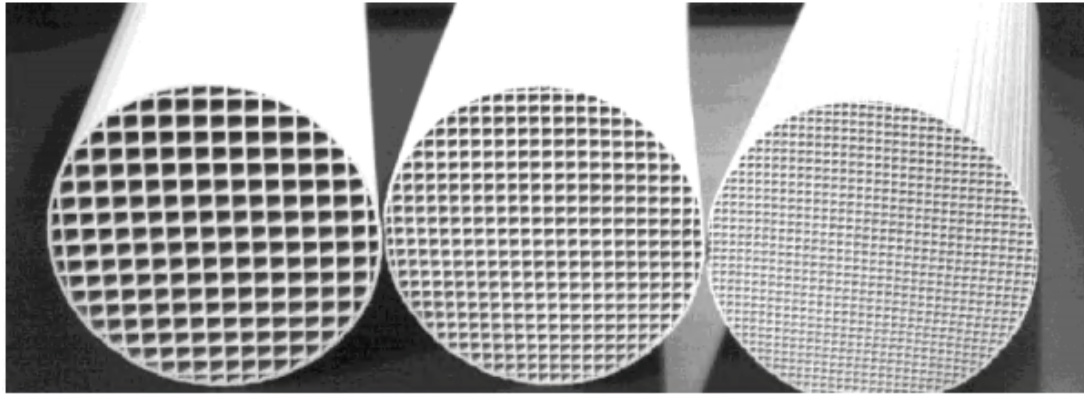


Figure 1.1: Ceramic monoliths with different cell densities (top) and a close-up view of channel geometry (bottom).

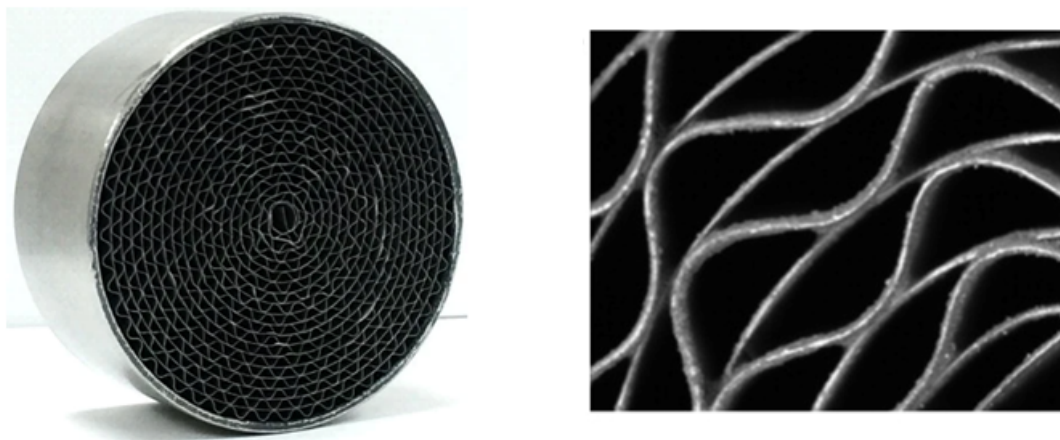


Figure 1.2: Metallic monolith (left) with close-up view of channel geometry (right).

monoliths, the channel shape is usually sinusoidal as shown in fig. 1.2. Both these substrates come with their respective advantages and disadvantages. Ceramic monoliths have higher porosity, thereby offering better adhesion of washcoat. Cordierite also has very low thermal expansion coefficient and hence can withstand high temperatures. On the other hand, metallic monoliths can provide better heat transfer properties and uniform temperature distributions owing to its high thermal conductivity and thin walls.

Other than automobile exhaust aftertreatment, monolith reactors are also used in chemical and power generation industries for selective reduction of NO_x , destruction of volatile organic compounds (VOCs), catalytically assisted combustion of fuels, and catalytic partial oxidation of hydrocarbons to syngas and chemicals. In some of these applications, homogeneous reactions between various gaseous species may also occur in the flow channel. Generally, the catalytic reactions have lower activation energies than the homogeneous counterparts. Ignition of the catalytic reactions can drive the reactor temperature to a high value at which the gas phase homogeneous

reactions may kick-in. The catalyst can also produce radical species by activating a reactant which may then combine in the gas phase to form products. Such thermal and species coupling in a homogeneous-heterogeneous (homo-hetero) reaction system adds another layer of complexity in the design and analysis of these reactors. Furthermore, due to the non-linear nature of reaction, convection and diffusion processes, these systems can exhibit complicated steady-state and transient behaviors like multiple steady-states, ignition-extinction and hysteresis phenomena, spatio-temporal patterns, and moving temperature/concentration fronts.

1.2 Literature review

Over the past two decades, there have been numerous studies in the area of homo-hetero reaction systems. Most of these studies have used detailed micro-kinetic reaction mechanisms or focused on the hydrodynamic aspects through the analysis of computational fluid dynamics (CFD) models. Such models are useful for predicting product distributions and conversions only in isothermal or small scale systems. Because of their mathematical complexity, detailed CFD type (system of partial differential equations) models are not amenable for determining the non-linear features of a scaled-up reactor (e.g., multiple steady state, ignition-extinction behavior). Therefore, the development of reduced order models becomes important. Using these reduced order models, we can perform a comprehensive bifurcation analysis of the homo-hetero reaction system and determine all the possible behaviors of the reactor in the space of multi-dimensional parameters. Since these relatively simpler models can speed-up computations by several orders of magnitude, they can also be utilized

to implement various control and real time optimization algorithms in automobile aftertreatment applications.

For a history of reduced order models of chemical reactors, we refer to the article by Chakraborty and Balakotaiah [1]. We review here only the literature relevant to coarse-graining of monolith reactor models. Because of their significant utility, several researchers have developed reduced order models for monolith reactors from the detailed models ([2]-[15]). Joshi et al. [3] demonstrated the accuracy and speed-up of transient simulations of monolith reactors using the low-dimensional models with asymptotic transfer coefficients. The values of the transfer coefficients for various channel geometries and flow conditions (fully developed as well as developing flow) were provided by Joshi et al. [4] and Gundlapally and Balakotaiah [5]. An asymptotic solution for washcoat pore diffusion was also presented by Bissett [6] which is valid only when the gradients in the washcoat are small. While the use of asymptotic transfer coefficients was adequate for many applications (especially those involving cold-start transient simulations of various after-treatment systems), it may lead to significant error for describing ignited branches due to strong washcoat diffusional limitations, which necessitates the use of kinetics and position dependent transfer coefficients ([7], [8]). Mozaffari et al. [9] and Rink et al. [10] utilized this approach for dual layered systems and illustrated their use with several applications. Their reduced order models are in the traditional form of the two-phase models that use binary transfer coefficients to describe the micro-scale local exchange. However, they may not be adequate for fast transients and/or reacting cases with non-uniform flow profiles. This was demonstrated by Ratnakar et al. [11] and Ratnakar and Balakotaiah ([12],

[13]). In these works, more accurate multi-mode reduced order models were derived using the Lyapunov-Schmidt (L-S) averaging technique, where it was shown that the Taylor dispersion, that arises due to velocity gradients and transverse diffusion in the channel, can be important when the inlet conditions vary rapidly (e.g., fast cycling of reactants). Only for the special case of steady-state or very slowly varying inlet conditions, the classical binary transfer coefficient concept remains valid. The L-S averaging technique has also been applied by Picardo and Pushpavanam [14] to develop reduced order models for two phase stratified flow in microchannels that involves mass transfer and reactions.

More recently, Ratnakar et al. [15] and Tu et al. [16] developed multi-scale reduced order models for monoliths with dual and multiple washcoat layers. It was shown that these models are more accurate than the traditional two-phase models and lead to exact solutions when position or local property dependent transfer coefficients are utilized. In this thesis, we extend their work by including homogeneous reactions in the fluid phase.

1.3 Objectives and outline

One of the main goals of this work is to first develop multi-mode reduced order models for monolith reactors with coupled homogeneous-heterogeneous chemistries and then illustrate their usefulness in performing comprehensive bifurcation analysis. We have taken three different reaction systems as our examples, namely, propane oxidation, hydrogen combustion and oxidative coupling of methane (OCM). A hierarchy of mathematical as well as chemistry models are used to study the ignition-extinction

phenomena. The second objective is to investigate how the various design and operating parameters such as feed conditions, residence time, reactor dimensions etc. influence the bifurcation behavior of those three reaction systems. The results of our analysis are used to present practical guidelines on the design and scale-up of monolith reactors with coupled homo-hetero chemistries.

The present thesis is structured as follows. We first present the relevant reduced order models for monolith reactors with coupled homo-hetero reactions. These reduced order models are expressed in terms of phase averaged multiple concentration (temperature) modes and interfacial fluxes which are related through various transfer coefficients that are local scale, flow and property dependent. Accurate expressions are provided for estimating the local transfer coefficient matrices for multi-component systems. In Chapter 3 we consider adiabatic propane oxidation and primarily show the impact of diffusional limitations on its ignition-extinction behavior. The case of catalytically assisted hydrogen combustion is demonstrated in Chapter 4. A wider range of parameters such as channel hydraulic radius, washcoat properties, reactor length and substrate conductivity are explored here. The case of OCM is presented in Chapter 5. A twelve step global reaction network comprising of seven catalytic reactions and five homogeneous reactions is considered here as the kinetic model. We present various species and temperature profiles along the reactor and examine how they are impacted by the substrate conductivity, space time and heat losses. In chapter 6 we extend our OCM analysis to microkinetic models and take a deeper look at the underlying reaction chemistry. Finally, in Chapter 7, the conclusions of this work and recommendations for future extensions are provided.

Chapter 2

Mathematical Models

2.1 Introduction

In this chapter we present the multi-scale reduced order models that are used in our study to simulate the reacting flow in a single channel of a monolith reactor. These reduced order models are derived using the Lyapunov-Schmidt (L-S) reduction technique of bifurcation theory, the mathematical methodology of which can be found in the recent work of Ratnakar et al. [15]. These models are useful in analyzing various non-linear features of scaled-up reacting systems, e.g., existence of multiple steady states, ignition-extinction and hysteresis behavior, spatial profiles, and so forth [17]. In addition, they also reduce the computational time significantly by implicitly considering the washcoat diffusional effects without actually solving the detailed diffusion-reaction problem, as shown by Joshi et al. [3] and Tu et al. [16].

A schematic diagram of a single channel of the reactor along with some common flow and washcoat geometries is shown in fig. 2.1. For ease of explanation and illustration, we first consider the simpler case, i.e., parallel plate geometry, single-component system, constant physical properties and a single reaction in the washcoat layer and the channel. Extension to the more general case of arbitrary washcoat and

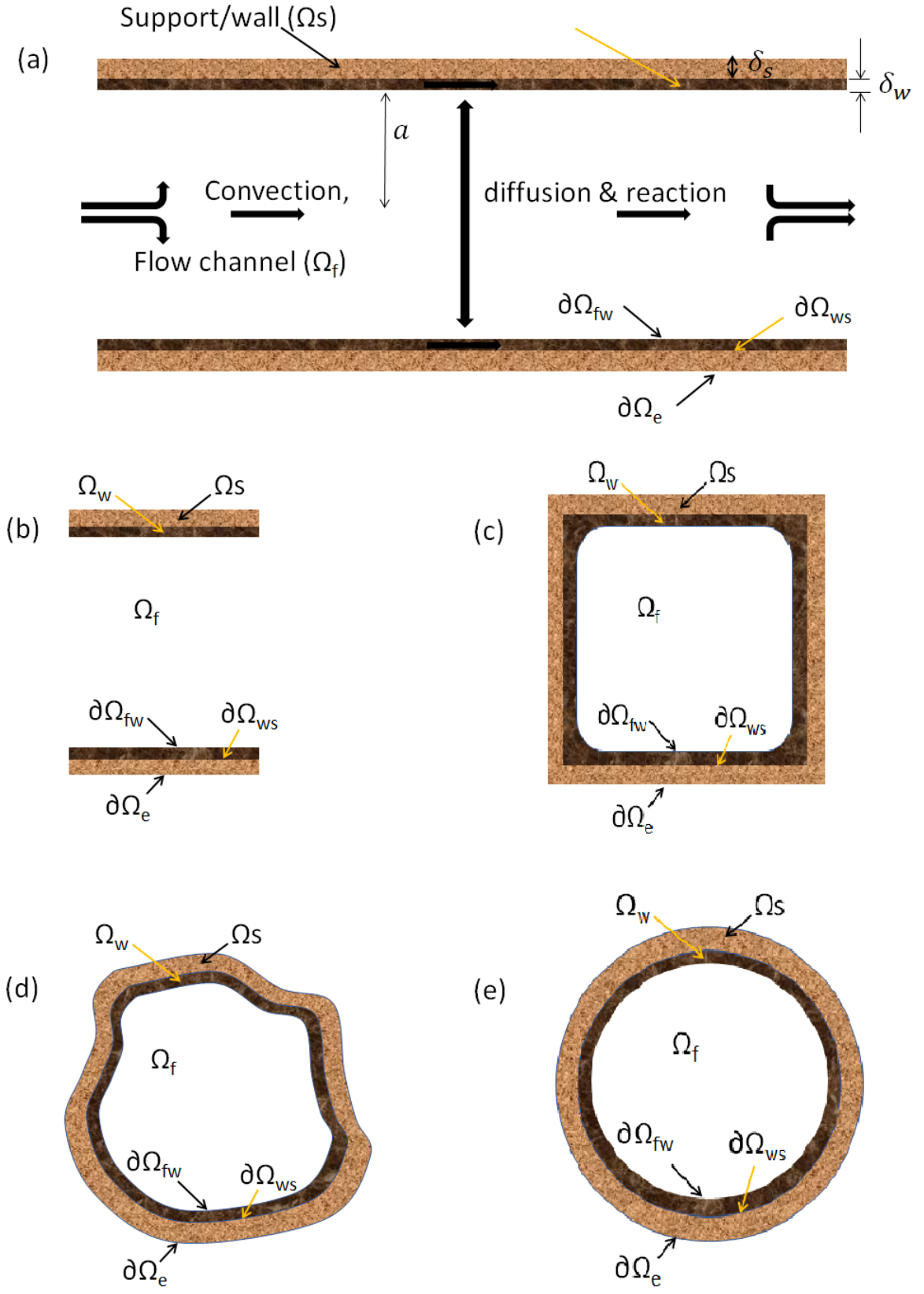


Figure 2.1: Schematic diagram of a single monolith channel illustrating various domains (flow channel, washcoat layer and wall).

flow geometries along with multicomponent reacting systems will be presented later.

2.2 Detailed models with multiple length and time scales:

The detailed mathematical model describing the transport and reaction ($A \rightarrow B$) for a single species in a catalytic monolith with a single washcoat layer is given by species and energy balance equations as follows:

$$\frac{\partial c_f}{\partial t} + u(y) \frac{\partial c_f}{\partial x} + r_f(x, t, c_f, T_f) = D_{mf} \frac{\partial^2 c_f}{\partial y^2} + D_{mf} \frac{\partial^2 c_f}{\partial x^2}, \quad (2.1)$$

$$\varepsilon_w \frac{\partial c_w}{\partial t} + r_w(x, t, c_w, T_w) = D_{ew} \frac{\partial^2 c_w}{\partial y^2} + D_{ew} \frac{\partial^2 c_w}{\partial x^2}, \quad (2.2)$$

$$\rho_f C_{pf} \left(\frac{\partial T_f}{\partial t} + u(y) \frac{\partial T_f}{\partial x} \right) = \kappa_f \frac{\partial^2 T_f}{\partial y^2} + \kappa_f \frac{\partial^2 T_f}{\partial x^2} + Q_f(x, t, c_f, T_f), \quad (2.3)$$

$$\rho_w C_{pw} \frac{\partial T_w}{\partial t} = \kappa_w \frac{\partial^2 T_w}{\partial y^2} + \kappa_w \frac{\partial^2 T_w}{\partial x^2} + Q_w(x, t, c_w, T_w), \quad (2.4)$$

$$\text{and } \rho_s C_{ps} \frac{\partial T_s}{\partial t} = \kappa_s \frac{\partial^2 T_s}{\partial y^2} + \kappa_s \frac{\partial^2 T_s}{\partial x^2}. \quad (2.5)$$

The initial and inlet (boundary) conditions are given by:

$$c_j|_{t=0} = c_j^0(y, x), \quad \left(u c_f - D_{mf} \frac{\partial c_f}{\partial x} \right) \Big|_{x=0} = u c_{f,in}(y, t), \quad (2.6)$$

$$T_j|_{t=0} = T_j^0(y, x), \quad \left(u T_f - \frac{\kappa_f}{\rho_f C_{pf}} \frac{\partial T_f}{\partial x} \right) \Big|_{x=0} = u T_{f,in}(y, t), \quad (2.7)$$

$$\frac{\partial T_f}{\partial x} \Big|_{x=L} = 0, \quad \frac{\partial c_f}{\partial x} \Big|_{x=L} = 0, \quad \frac{\partial T_w}{\partial x} \Big|_{x=0,L} = \frac{\partial T_s}{\partial x} \Big|_{x=0,L} = 0, \quad (2.8)$$

and transverse (or interfacial) boundary conditions as follows:

$$D_{mf} \frac{\partial c_f}{\partial y} = 0 = \kappa_f \frac{\partial T_f}{\partial y} \text{ at } y = 0, \quad (2.9)$$

$$c_f = c_w, \text{ and } D_{mf} \frac{\partial c_f}{\partial y} = D_{ew} \frac{\partial c_w}{\partial y} = -j_{fw} \text{ on } \partial\Omega_{fw} \equiv y = a, \quad (2.10)$$

$$D_{ew} \frac{\partial c_w}{\partial y} = -j_{ws} = 0 \text{ on } \partial\Omega_{ws} \equiv y = a + \delta_w, \quad (2.11)$$

$$T_f = T_w, \text{ and } \kappa_f \frac{\partial T_f}{\partial y} = \kappa_w \frac{\partial T_w}{\partial y} = -q_{fw} \text{ on } \partial\Omega_{fw} \equiv y = a, \quad (2.12)$$

$$T_w = T_s, \text{ and } \kappa_w \frac{\partial T_w}{\partial y} = \kappa_s \frac{\partial T_s}{\partial y} = -q_{ws} \text{ on } \partial\Omega_{ws} \equiv y = a + \delta_w, \quad (2.13)$$

$$\text{and } \kappa_s \frac{\partial T_s}{\partial y} = -q_e \text{ on } \partial\Omega_e \equiv y = a + \delta_w + \delta_s, \quad (2.14)$$

where the i^{th} phase (Ω_i) with $i = f, w$ and s represents the flow channel (f), washcoat layer (w) and support (s), respectively; a is the channel hydraulic radius (half the distance between parallel plates), δ_j is the effective thickness of the phase Ω_j ; c_i , T_i , ρ_i , C_{pi} and κ_i are concentration, temperature, density, specific heat capacity and thermal conductivity in the i^{th} phase; D_{mf} and D_{ew} are molecular (or effective) diffusivity in fluid and washcoat layer, respectively; ε_w is the porosity of washcoat layer; $u(y) = \frac{3}{2} \langle u \rangle \left(1 - \frac{y^2}{a^2}\right)$ is the velocity profile in the flow channel with $\langle u \rangle$ as average velocity in the flow channel. The sink terms $r_f(x, t, c)$ and $r_w(x, t, c)$ (or source if $r_i < 0, i = f, w$) represent reaction rates that may be functions of concentration, time and axial coordinate depending on the activity distribution; $Q_f = (-\Delta H_r)r_f$ and $Q_w = (-\Delta H_r)r_w$ are the heat generation terms, where ΔH_r being heat of reaction; j_{fw} and q_{fw} are the interfacial mass-flux and heat flux from fluid phase to the washcoat at the fluid-washcoat interface ($\partial\Omega_{fw}$); q_{ws} is the interfacial

heat-flux from washcoat layer to the wall at the interface $\partial\Omega_{ws}$. Here, the wall is considered non-porous (i.e., $j_{ws} = 0$); q_e is the heat-loss flux to the ambient that can be expressed in terms of the temperature difference between the outside wall temperature and the ambient temperature (T_a) as

$$q_e = h_a (T - T_a) \text{ on } \partial\Omega_e \equiv y = a + \delta_w + \delta_s \quad (2.15)$$

where h_a being the heat transfer coefficient. For an adiabatic channel, $q_e = 0$, i.e., no heat-loss to the ambient and this will be the case for the applications considered in this work. Also note that the transverse diffusion/conduction operator is expressed here as 1-D Laplacian operator $\frac{\partial^2}{\partial y^2}$ for parallel plate geometry. In the more general case of a channel with arbitrary flow and washcoat geometries, the transverse (local diffusion) operator is expressed as 2-D Laplacian $\nabla_{\perp}^2 = \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, and the state variables depend on 4 independent coordinates, i.e., x , y , z and t . We extend the procedure to this more general case later.

Note that in the species and energy balance for the flow channel (eqns. 2.1 and 2.3), the terms represent the accumulation, convection, transverse and axial diffusion/conduction and homogeneous reaction. Similarly, eqns. (2.6 - 2.8) denote the initial and (Danckwert's) inlet conditions while eqns. (2.9 - 2.14) denote the continuity in state variables and their fluxes at the interface boundaries $\partial\Omega_{fw}$ (fluid-washcoat interface), $\partial\Omega_{ws}$ (interface between the washcoat and the wall) and $\partial\Omega_e$ (outer boundary of the wall).

Note that if we neglect axial diffusion/conduction and heat-loss, there are eleven

time scales associated with the detailed model: one convection time in the flow channel (t_c), two transverse diffusion times (one in the flow channel and one in washcoat layer, t_{D_f} , t_{D_w}), three transverse heat conduction times in each domain (flow channel, washcoat and wall, t_{H_f} , t_{H_w} , t_{H_s}), two reaction times: one corresponding to the homogeneous reaction in the flow channel (t_{Rf}) and one in the washcoat (t_{Rw}), two heat generation times (t_{Q_f} , t_{Q_w}), and one real/physical time scale (t) that corresponds to the frequency in inlet conditions or experimental (observation) time. The first ten of these time scales are defined below:

$$t_c = \frac{L}{\langle u \rangle}, \quad t_{D_f} = \frac{a^2}{D_{mf}}, \quad t_{D_w} = \frac{\delta_w^2}{D_{ew}}, \quad (2.16)$$

$$t_{H_f} = \frac{a^2 \rho_f C_{pf}}{\kappa_f}, \quad t_{H_w} = \frac{\delta_w^2 \rho_w C_{pw}}{\kappa_w}, \quad t_{H_s} = \frac{\delta_s^2 \rho_s C_{ps}}{\kappa_s}, \quad (2.17)$$

$$t_{Rf} = \left(\frac{\partial r_f}{\partial c} \right)_{ref}^{-1}, \quad t_{Rw} = \left(\frac{\partial r_w}{\partial c} \right)_{ref}^{-1}, \quad (2.18)$$

$$t_{Qf} = \rho_f C_{pf} \left(\frac{\partial Q_f}{\partial T} \right)_{ref}^{-1}, \quad \text{and} \quad t_{Qw} = \rho_w C_{pw} \left(\frac{\partial Q_w}{\partial T} \right)_{ref}^{-1}. \quad (2.19)$$

The subscript '*ref*' represents some reference temperature (T_{ref}) and concentration (c_{ref}), which may be chosen as inlet/feed or local values. [Remark: The first six time scales defined above can also be expressed in terms of two heat capacity ratios and the four length scales, namely L , a (or $R_{\Omega f}$), δ_w , and δ_s , while the last 4 (reaction time scales) are independent of length scales.]

2.3 Multi-mode reduced order models

In this section, we explain the various temperature and concentration modes and the global and local equations of the multi-mode reduced order models.

2.3.1 Global and local equations

The methodology for developing multi-scale reduced order models of reacting systems (catalytic monoliths) was presented in a recent work by Ratnakar et al. [15], where transport and reaction of a multi-component system in a multi-layered monolith was considered. Even though the applications presented in that work did not include the homogeneous reaction in the flow channel, the methodology was presented for the general case where diffusion, convection and reaction may occur in any of the multiple layers. Applying the same approach, we derive the reduced order model from the detailed model presented above (eqns. 2.1 - 2.14), and express it in terms of the global equations as follows:

$$\frac{\partial \langle c_f \rangle}{\partial t} + \langle u \rangle \frac{\partial c_{fm}}{\partial x} - D_{mf} \frac{\partial^2 \langle c_f \rangle}{\partial x^2} + r_f(x, t, \langle c_f \rangle, \langle T_f \rangle) = -\frac{j_{fw}}{a}, \quad (2.20)$$

$$\varepsilon_w \frac{\partial \langle c_w \rangle}{\partial t} - D_{ew} \frac{\partial^2 \langle c_w \rangle}{\partial x^2} + r_w(x, t, \langle c_w \rangle, \langle T_w \rangle) = \frac{j_{fw}}{\delta_w}, \quad (2.21)$$

$$\rho_f C_{pf} \left(\frac{\partial \langle T_f \rangle}{\partial t} + \langle u \rangle \frac{\partial T_{fm}}{\partial x} \right) - k_f \frac{\partial^2 \langle T_f \rangle}{\partial x^2} - Q_f(x, t, \langle c_f \rangle, \langle T_f \rangle) = -\frac{q_{fw}}{a}, \quad (2.22)$$

$$\rho_w C_{pw} \frac{\partial \langle T_w \rangle}{\partial t} - k_w \frac{\partial^2 \langle T_w \rangle}{\partial x^2} - Q_w(x, t, \langle c_w \rangle, \langle T_w \rangle) = \frac{q_{fw} - q_{ws}}{\delta_w}, \quad (2.23)$$

$$\text{and } \rho_s C_{ps} \frac{\partial \langle T_s \rangle}{\partial t} - k_s \frac{\partial^2 \langle T_s \rangle}{\partial x^2} = \frac{q_{ws} - q_e}{\delta_s}, \quad (2.24)$$

where, $\langle c_j \rangle$ and $\langle T_j \rangle$ denote the cross-sectional (or phase) averaged concentration and temperature in j^{th} phase and subscript ‘ m ’ denotes the cup-mixing (velocity weighted averaged) quantities. The various phase-averaged concentration and temperature modes are defined below:

$$c_{fm}(x, t) = \frac{\langle uc \rangle_f}{\langle u \rangle} = \frac{1}{a} \int_0^a \frac{3}{2} \left(1 - \frac{y^2}{a^2} \right) c_f(x, t, y) dy, \quad (2.25)$$

$$\langle c_f \rangle(x, t) = \frac{1}{a} \int_0^a c_f(x, t, y) dy, \quad (2.26)$$

$$\langle c_w \rangle(x, t) = \frac{1}{\delta_w} \int_a^{a+\delta_w} c_w(x, t, y) dy, \quad (2.27)$$

$$\langle T_w \rangle(x, t) = \frac{1}{\delta_w} \int_a^{a+\delta_w} T_w(x, t, y) dy, \quad (2.28)$$

$$T_{fm}(x, t) = \frac{1}{a} \int_0^a \frac{3}{2} \left(1 - \frac{y^2}{a^2} \right) T_f(x, t, y) dy, \quad (2.29)$$

$$\text{and } \langle T_s \rangle(x, t) = \frac{1}{\delta_s} \int_{a+\delta_w}^{a+\delta_w+\delta_s} T_w(x, t, y) dy. \quad (2.30)$$

We note that the above equations (2.20 - 2.24) could be written down intuitively by volume averaging in each phase. It should also be noted that the global equations (eqns. 2.20 - 2.24) are not in closed form, i.e., they contain more number of unknown variables. They include seven concentration/temperature variables (two phase averaged concentration modes $\langle c_f \rangle$, $\langle c_w \rangle$, one velocity averaged concentration mode c_{fm} , three phase averaged temperature modes $\langle T_f \rangle$, $\langle T_w \rangle$, $\langle T_s \rangle$, one velocity averaged temperature mode T_{fm}) and the four fluxes (one interfacial mass-flux j_{fw} , two interfacial heat fluxes: q_{fw} and q_{ws} , and one external flux q_e due to heat loss), i.e.,

total of eleven variables with the number of equations being five. Therefore, six more equations are required to close the reduced order model. These local equations relate various concentration/temperature modes and the interfacial fluxes and, capture the physics at the small scales. Since the derivation of these local equations is discussed in prior work [15], we skip the details of obtaining these local equations, and simply present them. In the limit of small t_{Df} and t_{Hf} the difference between cup-mixing and average concentration/temperature in the flow channel can be expressed from as follows:

$$c_{fm} - \langle c_f \rangle = \frac{-2 \langle u \rangle t_{Df}}{105} \frac{\partial c_{fm}}{\partial x} + \frac{t_{Df}}{15a} j_{fw} \quad (2.31)$$

$$\text{and } T_{fm} - \langle T_f \rangle = \frac{-2 \langle u \rangle t_{Hf}}{105} \frac{\partial T_{fm}}{\partial x} + \frac{t_{Hf}}{15a\rho_f C_{pf}} q_{fw}. \quad (2.32)$$

Similarly, the difference between average concentrations/temperatures in the flow channel and washcoat layer can be expressed as follows:

$$\langle c_f \rangle - \langle c_w \rangle = \frac{-\langle u \rangle t_{Df}}{15} \frac{\partial c_{fm}}{\partial x} + \left(\frac{t_{Df}}{3a} + \frac{t_{Dw}}{3\delta_w} \right) j_{fw} \quad (2.33)$$

$$\begin{aligned} \text{and } \langle T_f \rangle - \langle T_w \rangle &= \frac{-\langle u \rangle t_{Hf}}{15} \frac{\partial T_{fm}}{\partial x} + \left(\frac{t_{Hf}}{3a\rho_f C_{pf}} + \frac{t_{Hw}}{3\delta_w\rho_w C_{pw}} \right) q_{fw} \\ &+ \frac{t_{Hw}}{6\delta_w\rho_w C_{pw}} q_{ws}. \end{aligned} \quad (2.34)$$

The difference between temperatures in the washcoat-layer and the support (wall) can be expressed as

$$\langle T_w \rangle - \langle T_s \rangle = \frac{t_{Hw}}{6\delta_w\rho_w C_{pw}} q_{fw} + \left(\frac{t_{Hw}}{3\delta_w\rho_w C_{pw}} + \frac{t_{Hs}}{3\delta_s\rho_s C_{ps}} \right) q_{ws} + \frac{t_{Hs}}{6\delta_s\rho_s C_{ps}} q_e. \quad (2.35)$$

In case of no heat loss to ambient (i.e., adiabatic channel or $q_e = 0$), the five global equations (2.20 - 2.24) and the five local equations (2.31 - 2.35) which are in closed and multi-mode form complete the reduced order model. However, in case of heat loss (i.e., flux $q_e \neq 0$), an additional local equation can be expressed in terms of the difference between average wall temperature and the ambient temperature as

$$\langle T_s \rangle - T_a = \frac{t_{Hs}}{6\delta_s \rho_s C_{ps}} q_{ws} + \left(\frac{t_{Hs}}{3\delta_s \rho_s C_{ps}} + \frac{1}{h_e} \right) q_e. \quad (2.36)$$

The inlet, initial and boundary conditions for the reduced order model can be obtained from eqns. (2.6- 2.8) as follows:

$$\langle c_j \rangle|_{t=0} = \langle c_j^0 \rangle(x), \quad c_{fm}|_{x=0} = c_{fm,in}(t), \quad (2.37)$$

$$\langle T_j \rangle|_{t=0} = \langle T_j^0 \rangle(x), \quad T_{fm}|_{x=0} = T_{fm,in}(t), \quad (2.38)$$

$$\left. \frac{\partial \langle T_f \rangle}{\partial x} \right|_{x=L} = 0, \quad \left. \frac{\partial \langle c_f \rangle}{\partial x} \right|_{x=L} = 0 \text{ and } \left. \frac{\partial T \langle w \rangle}{\partial x} \right|_{x=0,L} = \left. \frac{\partial \langle T_s \rangle}{\partial x} \right|_{x=0,L} = 0. \quad (2.39)$$

Thus, the global equations (2.20 - 2.24) and local equations (2.31 - 2.36) along with inlet, initial and boundary conditions (eqns. 2.37 - 2.39) complete the reduced order model. This multi-scale multi-mode model is expressed in terms of 11 unknowns (three concentration modes, four temperature modes, one mass flux and three heat fluxes including the heat loss to ambient) and consists of five global equations and six local equations. The five global equations are simply the volume averaged species and energy conservation equations in the respective domains. For example, eqns. (2.20 and 2.22) and eqns. (2.21 and 2.23) represent the volume averaged species and en-

ergy balances in the fluid phase and washcoat, respectively. The left hand side (LHS) represents the transient (accumulation), convection, axial diffusion/conduction and source/sink (corresponding to homogeneous reaction in channel and catalytic reaction in washcoat) terms while the right hand side (RHS) represents the net flux from the adjacent domains. Eqn. 2.24 represents the energy balance in the wall where LHS represents the transient accumulation and axial conduction terms while RHS represents the net flux from adjacent domain as well as heat loss to the ambient. Similarly, the six local equations represent the small scale gradients and are expressed in terms of the difference between various concentration/temperature modes and inter/intra phase fluxes.

As explained in the literature [11], for problems where separation in time (or length) scales exists, the L-S method can be used to derive the reduced order model to all orders (in local length/time scales) and is equivalent to the multi-scale expansion of the detailed model in powers of these time scales. The zeroth order model for which local gradients vanish, corresponds to the conservation equation volume-averaged over all the phases (i.e., pseudo-homogeneous model). In the current work, the expansion is truncated at first order in the transverse diffusion/conduction time scales, therefore the impact of the local gradients appears through the asymptotic inter and intra-phase transfer and dispersion coefficients in the local equations (2.31 - 2.36).

It should be noted that the local equations described in eqns. (2.31 - 2.36) in terms of the difference between various concentration/temperature modes are fundamentally different from the traditional (intuitively written with *a priori* assumption) models. In the latter, those differences are expressed using binary mass (or heat) transfer

coefficient using only one interfacial flux. However, as shown in previous work [15], the concentration (or temperature) gradient in any phase depends on the mass (or heat) influx from their adjacent domains (as can be expected intuitively) as well as the on intra-phase dispersion flux. Therefore, multiple transfer coefficients are required to express the concentration/temperature difference (or gradient) depending on various inter and intra-phase fluxes associated with phases involved.

We note that the detailed model given by eqns. (2.1 - 2.14) can also be formulated as a single transverse operator with self-adjoint formalism and a reduced order model can be obtained from overall transverse averaging with a single master mode (see previous works [11]-[13]). This single-zero eigenvalue approach is useful for determining the effective dispersion coefficients for non-reacting cases of transient heat and mass transfer. However, this approach with a single master mode has a smaller range of applicability and requires regularization to increase the range of validity for reacting cases and treatment of fast transients. Therefore, in the current work, we have utilized multi-phase and multi-scale formulation using multiple-zero eigenvalue approach as described by Ratnakar et al. [15], where the L-S procedure can be used to each phase separately to perform individual phase averaging for species and energy balances. This approach leads to reduced order models that have larger range of applicability and is preferable over the single master mode self-adjoint approach for many reasons: (i) it retains the cross-interaction between the phases through the continuity relations at phase boundaries; (ii) it automatically leads to the reduced order models in terms of more number of naturally appearing (phase averaged) concentration (and temperature) modes that retain more information and does not need

regularization. It also increases the range of validity of the reduced order models, especially for reacting systems where strong inter and intra-phase gradients can exist; (iii) it allows us to reduce the degrees of freedom only in domains where the gradients are expected to be small. For example, we can skip the averaging in phases where strong species/thermal gradients (that may be caused by fast reactions or fast transients) exist and average only the other phases where the local gradients are small. The so called 1+1D model for a monolith with reaction only in the washcoat is such an example where averaging is done in the flow channel but not in the washcoat; and (iv) it can treat a wider range of initial conditions (e.g., cases in which a species may be present only in one phase or layer initially), leading to more accurate solution of certain transient problems.

The above reduced order model can be simplified further for the common cases of adiabatic system (i.e., $q_e = 0$). In addition, in many applications of interest, the catalyst-layer and wall conductivities are sufficiently high (e.g., one to two orders of magnitude higher) compared to the same in the gas phase. Hence, in most applications, the temperature difference $T_w - T_s$ is much smaller compared to $T_f - T_w$, i.e., the temperature gradient in the transverse direction within the solid phase is negligible, and therefore the washcoat and wall temperatures can be assumed to be practically same. In such cases, the two global eqns. (2.23 and 2.24) corresponding to energy balances in the solid phases can be combined to one global equation as

$$(\delta_w \rho_w C_{pw} + \delta_s \rho_s C_{ps}) \frac{\partial \langle T_w \rangle}{\partial t} = (\delta_w k_w + \delta_s k_s) \frac{\partial^2 \langle T_w \rangle}{\partial x^2} + \delta_w Q_w(x, t, \langle c_w \rangle, \langle T_w \rangle) + q_{fw}. \quad (2.40)$$

Similarly, the three local eqns. (2.34 - 2.36) reduce to a single local equation as

$$\langle T_f \rangle - \langle T_w \rangle = \frac{-\langle u \rangle t_{Hf}}{15} \frac{\partial T_{fm}}{\partial x} + \left(\frac{t_{Hf}}{3a\rho_f C_{pf}} + \frac{t_{Hw}}{3\delta_w \rho_w C_{pw}} \right) q_{fw}. \quad (2.41)$$

Thus, in this special case of high solid to fluid conductivity ratio, the reduced order model can be expressed in terms of 8 variables (three concentration and three temperature modes, one mass and one heat flux at the interface) with 4 global equations and 4 local equations.

The presentation/derivation of the 11-mode and 8-mode reduced order models is one main contribution of this work.

2.3.2 Generalization of local equations to arbitrary flow and washcoat geometries and finite gradients

The reduced order model derived above for parallel plate geometry can be extended to the more general case of arbitrary flow and washcoat geometries. In this more general case, the 1-D transverse Laplacian operator $\frac{\partial^2}{\partial y^2}$ for parallel plate is replaced by the 2-D transverse Laplacian operator $\left(\nabla_{\perp}^2 = \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$. Some common geometries of interest in applications are shown in fig. 2.1 (c), (d) and (e). As shown in previous work [15], the structure of the reduced order model remains the same for arbitrary cross-section geometries/shapes of channel and washcoat. The global equations remain unchanged and the only difference being the numerical values of the various constants appearing in the local equations. For example, for the case of adiabatic channel and negligible transverse temperature gradient within the solid

phase, the four local equations (2.31 - 2.33, and 2.41) can be extended for arbitrary geometric shapes as follows:

$$c_{fm} - \langle c_f \rangle = -\Lambda_T \langle u \rangle t_{Df} \frac{\partial c_{fm}}{\partial x} + \Lambda_f \frac{t_{Df}}{R_{\Omega_f}} j_{fw}, \quad (2.42)$$

$$\langle c_f \rangle - \langle c_w \rangle = -\Lambda_f \langle u \rangle t_{Df} \frac{\partial c_{fm}}{\partial x} + \left(\frac{1}{Sh_e} \frac{t_{Df}}{R_{\Omega_f}} + \frac{1}{Sh_i} \frac{t_{Dw}}{R_{\Omega_w}} \right) j_{fw}, \quad (2.43)$$

$$T_{fm} - \langle T_f \rangle = -\Gamma_T \langle u \rangle t_{Hf} \frac{\partial T_{fm}}{\partial x} + \Gamma_f \frac{t_{Hf}}{R_{\Omega_f} \rho_f C_{pf}} q_{fw}, \quad (2.44)$$

$$\text{and } \langle T_f \rangle - \langle T_w \rangle = -\Gamma_f \langle u \rangle t_{Hf} \frac{\partial T_{fm}}{\partial x} + \left(\frac{1}{Nu_e} \frac{t_{Hf}}{R_{\Omega_f} \rho_f C_{pf}} + \frac{1}{Nu_i} \frac{t_{Hw}}{R_{\Omega_w} \rho_w C_{pw}} \right) q_{fw} \quad (2.45)$$

where Λ_T and Λ_f are the intra-phase dimensionless mass dispersion coefficients; Γ_T and Γ_f are the intra-phase dimensionless heat dispersion coefficients in the flow channel (Λ_T and Γ_T correspond to well known Taylor dispersion in the flow channel). Here, Sh_e and Nu_e represent the traditional external dimensionless mass-transfer coefficient (Sherwood number) and heat-transfer coefficient (Nusselt number), respectively in the flow channel, while Sh_i and Nu_i represent the traditional internal dimensionless mass-transfer coefficient (Sherwood number) and heat-transfer coefficient (Nusselt number), respectively in the washcoat. R_{Ω_f} and R_{Ω_w} are the hydraulic radii in the flow channel and washcoat-layer, respectively. Note that Sh_i (or Nu_i) describes the concentration (or temperature) gradient in the washcoat layer in terms of the difference between the fluid-washcoat interface concentration (or temperature) and the average washcoat concentration (or temperature). Similarly, intra-phase dispersion coefficients (Λ_T or Γ_T and Λ_f or Γ_f) imply that the transverse variation in

velocity (or other quantities such as reaction activity) can also lead to dispersion.

While the global equations for the general case of arbitrary flow and channel geometries remain the same as given by eqns. (2.20 - 2.22 and 2.40), the transverse (or effective local) length scales a and δ_w need to be replaced by hydraulic radius of the channel (R_{Ω_f}) and washcoat layer (R_{Ω_w}), respectively. Further, the ratio $\frac{\delta_s}{\delta_w}$ is replaced by the area ratio $\frac{A_s}{A_w}$ where A_s and A_w being cross-sectional area of wall (support) and washcoat layers, respectively. The global equations are simply the transverse averaged versions of the detailed model but contain the local scales that appear in the weighted average concentration/temperature modes. For example, the transient accumulation, axial diffusion/conduction and source/sink due to reactions occurring over each phase-domain are represented in terms of phase averaged modes. Similarly, the convection terms are represented in terms of velocity weighted averaged (cup-mixing) mode due to transverse variation in the velocity profile. These modes naturally appear in the global equations due to transverse variation of various quantities such as velocity, reaction activity or due to the transverse boundary conditions.

It can be seen that the general structure of local equations (2.42 - 2.45) reduces to the local equations (2.31 - 2.33 and 2.41) when asymptotic values of transfer and dispersion coefficients (corresponding to parallel channels) are used. However, using the general structure of the local equations with the exact expressions for these coefficients can significantly improve the accuracy of the reduced order model as shown in the previous works ([15], [16]). The expressions for these transfer coefficients (or Sherwood/Nusselt numbers) can be determined by solving the local diffusion-reaction

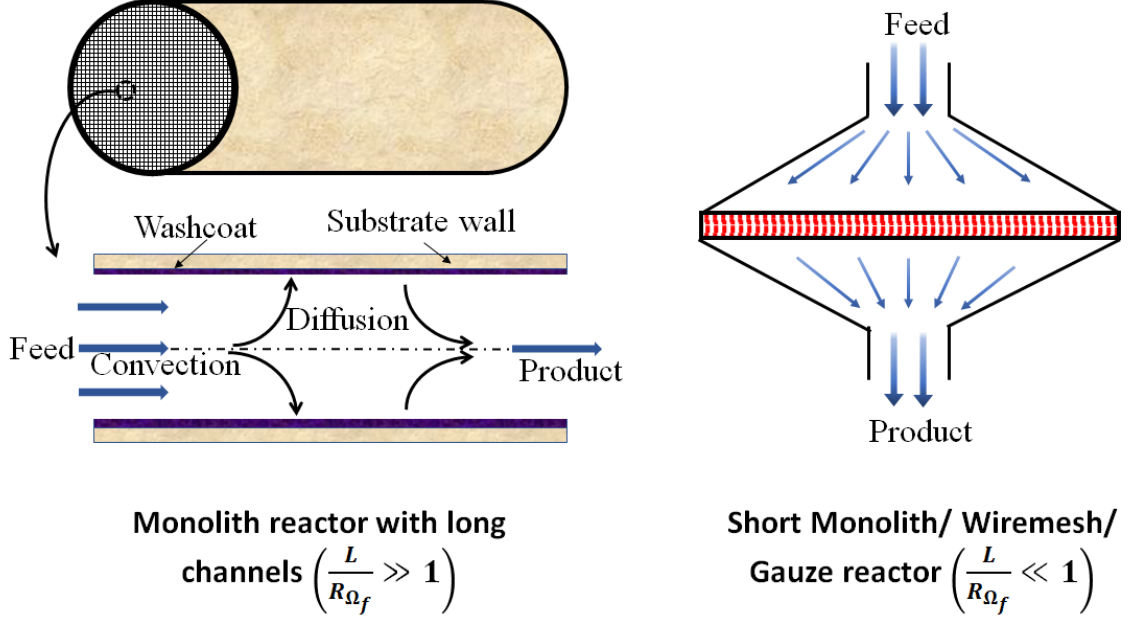


Figure 2.2: Schematic diagrams of monolith reactor with long channels (left) and short monolith/wiremesh or gauze type reactor (right).

problem for any phase for the special case of linear kinetics. We present the exact expressions of these mass-and heat transfer coefficients that are derived by considering the steady-state problems with linear kinetics in the subsequent sections.

2.4 Limiting models

Here, we discuss the two most important limiting cases of the reduced order multi-mode models presented above, namely, (i) two-mode long channel limit, and (ii) short-monolith or gauze or wire-mesh type reactor limit. A schematic diagram illustrating these two type of reactor limits is shown in fig. 2.2. For simplicity in notation, we remove the angular bracket and denote the phase averaged quantities such as $\langle c_j \rangle$ and $\langle T_j \rangle$ by c_j and T_j , respectively. In addition, we assume the reaction activity profile to be uniform in x and independent of time.

It is important to note that discretization of the long channel model using upwind first-order differencing scheme, leads to a sequence of short monolith models, similar to the classical cell or tanks-in-series model for the homogeneous case. Thus, these two models cover the extreme cases of zero and complete species and thermal backmixing in the fluid phase.

The main assumptions, that apply for both short and long channel models, are the following: (i) laminar flow, (ii) negligible pressure drop across the channel and weak coupling between momentum balance and species or energy balances, (iii) developing flow with low Schmidt, Sc and Prandtl, Pr numbers (flat velocity profile) or negligible dispersion due to velocity gradients, and (iv) uniform washcoat thickness and catalyst activity. [The Schmidt number, Sc is the ratio of the hydrodynamic boundary layer thickness to the concentration boundary layer thickness. Analogously, Prandtl number, Pr is the ratio between the hydrodynamic and thermal boundary layer thicknesses. Lower values of Sc and Pr suggest that the hydrodynamic boundary layer thickness is considerably smaller than the widths of concentration and thermal boundary layers, thereby signifying developing flow or flat velocity profile.]

2.4.1 Two-mode long channel model

In addition to the assumptions mentioned above, for the case of long channel model, the ratio of the reactor length to hydraulic diameter is considered to be large ($L/d_h \gg 1$). As a result, the axial dispersion terms are negligible when compared to the convective terms in fluid phase species and energy balance equations. The conduction term in the solid phase energy balance is however significant and is taken

into account. With these considerations, the governing equations of the two-mode long channel model are given as follows:

$$\frac{\partial c_{f,j}}{\partial t} + \langle u \rangle \frac{\partial c_{f,j}}{\partial x} = -\frac{j_{fwc,j}^*}{R_{\Omega_f}} + \sum_{i=1}^{Nh} \nu_{ij}^h r_i^h(\mathbf{c}_f, T_f), \quad (2.46)$$

$$\varepsilon_{wc} \frac{\partial c_{wc,j}}{\partial t} = \frac{j_{fwc,j}^*}{R_{\Omega_{wc}}} + \sum_{i=1}^{Nc} \nu_{ij}^c r_i^c(\mathbf{c}_{wc}, T_w), \quad (2.47)$$

$$\widetilde{C_{pf}} \left(\frac{\partial T_f}{\partial t} + \langle u \rangle \frac{\partial T_f}{\partial x} \right) = -\frac{h_o}{R_{\Omega_f}} (T_f - T_w) + \sum_{i=1}^{Nh} [-\Delta H_{R,i}^h(T_f)] r_i^h(\mathbf{c}_f, T_f), \quad (2.48)$$

$$\begin{aligned} \text{and } \rho_w C_{pw} \frac{\partial T_w}{\partial t} &= \kappa_w \frac{\partial^2 T_w}{\partial x^2} + \frac{h_o}{R_{\Omega_w}} (T_f - T_w) - \frac{h_a}{R_{\Omega_w}} (T_w - T_a) \\ &+ \frac{R_{\Omega_{wc}}}{R_{\Omega_w}} \sum_{i=1}^{Nc} [-\Delta H_{R,i}^c(T_w)] r_i^c(\mathbf{c}_{wc}, T_w). \end{aligned} \quad (2.49)$$

The initial conditions of the above model are,

$$c_{f,j}(x, t = 0) = c_{f,j}^0(x), \quad c_{wc,j}(x, t = 0) = c_{wc,j}^0(x), \quad (2.50)$$

$$T_f(x, t = 0) = T_f^0(x) \text{ and } T_w(x, t = 0) = T_w^0(x), \quad (2.51)$$

and the inlet/boundary conditions are given by,

$$c_{f,j}(x = 0, t) = c_{f,j}^{in}(t), \quad T_f(x = 0, t) = T_f^{in}(t), \quad (2.52)$$

$$\frac{\partial T_w}{\partial x}(x = 0, t) = 0 \text{ and } \frac{\partial T_w}{\partial x}(x = L, t) = 0. \quad (2.53)$$

Here, $c_{f,j}$ and $c_{wc,j}$ are the volume averaged concentration of j^{th} species in fluid phase and washcoat, respectively, whereas, T_f and T_w are the respective gas and solid (washcoat + wall/support) temperatures; ν_{ij}^k with $k = h$ and c denotes the

stoichiometric coefficient of j^{th} species in i^{th} reaction, the volumetric rate and enthalpy of which are given by r_i^k and $[\Delta H_{R,i}^k]$, respectively. The superscript ‘ h ’ is used to represent the homogeneous reactions and ‘ c ’ represents the catalytic reactions. It is to be noted that for uniform washcoat distribution and catalyst activity the reaction rates are only functions of corresponding concentration vector, $\mathbf{c}_m$ ($m = f$ and wc), and temperature, T_n ($n = f$ and w). Nh and Nc are the total number of homogeneous and catalytic reactions, respectively; $j_{f_{wc},j}^*$ is the interfacial mass flux of species j from fluid phase to washcoat whereas h_o is the overall heat transfer coefficient at the fluid-washcoat interface. R_{Ω_f} is the channel hydraulic radius which is defined as the ratio of cross-sectional area open to flow to the wetted perimeter and is related to the hydraulic diameter, d_h as $R_{\Omega_f} = d_h/4$. For parallel plate geometry, the hydraulic diameter, d_h , is twice the spacing between the plates, and for circular flow geometry, d_h is the actual diameter of the channel. The effective washcoat thickness is given by $R_{\Omega_{wc}}$ and the effective solid thickness, which is the combined width of the washcoat and the wall (support), is taken as R_{Ω_w} ; ρ_w , C_{pw} and κ_w are the effective density, heat capacity and thermal conductivity of the solid respectively, and are estimated as the weighted mean of the corresponding properties of washcoat and support, i.e., $R_{\Omega_w}\rho_w C_{pw} = R_{\Omega_{wc}}\rho_{wc} C_{pwc} + R_{\Omega_s}\rho_s C_{ps}$ and $R_{\Omega_w}\kappa_w = R_{\Omega_{wc}}\kappa_{wc} + R_{\Omega_s}\kappa_s$. The subscripts ‘ wc ’ and ‘ s ’ refer to washcoat and support respectively. ε_{wc} is the washcoat porosity, $\widetilde{C_{pf}}$ is the volumetric heat capacity of the gas mixture and $\langle u \rangle$ is the axial velocity. Both $\widetilde{C_{pf}}$ and $\langle u \rangle$ may be taken as functions of the fluid temperature, and hence are axial position dependent variables [In most of our calculations, we take average values]. In eqn. 2.49, h_a denotes the heat transfer coefficient for external

heat loss, and T_a represents the ambient temperature (or inlet/furnace temperature for laboratory reactors). The value of h_a depends on the combined effect of convective and radiative heat losses from the monolith reactor to the surrounding (or furnace), the mathematical details of which can be found in Sarsani et al. [18]. It is well understood that, in absence of any heat loss or symmetric or zero flux boundary conditions when considering a single channel of monolith, $h_a = 0$ corresponds to the adiabatic limit.

2.4.2 Steady-state short monolith, gauze or wire-mesh reactor model

The short monolith model averages over the axial direction retaining the transverse gradients, and is ideal for systems where the axial diffusion time scale is much smaller compared to the transverse diffusion, convection and reaction time scales (or the longitudinal length scale is smaller compared to the transverse length scale) [19]. This simple model can capture all the underlying physics of reactor systems such as short-monoliths, gauze reactors (used in ammonia oxidation in Ostwald’s process [20] and HCN synthesis by Andrussov process [21]), shallow packed bed reactors (used for OCM [22]), and stacked wire-mesh reactors (used in VOC combustion [23]). In the context of assumptions, it should be noted that, unlike the long channel model, here the channel length is much smaller relative to the hydraulic diameter, i.e., L/d_h

$\ll 1$. The steady state version of the SM model are given as follows:

$$\frac{c_{f,j}^{in} - c_{f,j}}{\tau} - \frac{j_{fwc,j}^*}{R_{\Omega_f}} + \sum_{i=1}^{Nh} \nu_{ij}^h r_i^h(\mathbf{c}_f, T_f) = 0, \quad (2.54)$$

$$\frac{j_{fwc,j}^*}{R_{\Omega_{wc}}} + \sum_{i=1}^{Nc} \nu_{ij}^c r_i^c(\mathbf{c}_{wc}, T_w) = 0, \quad (2.55)$$

$$\widetilde{C_{pf}} \frac{T_f^{in} - T_f}{\tau} - \frac{h_o}{R_{\Omega_f}} (T_f - T_w) + \sum_{i=1}^{Nh} [-\Delta H_{R,i}^h(T_f)] r_i^h(\mathbf{c}_f, T_f) = 0, \quad (2.56)$$

$$\text{and } \frac{h_o}{R_{\Omega_{wc}}} (T_f - T_w) + \sum_{i=1}^{Nc} [-\Delta H_{R,i}^c(T_w)] r_i^c(\mathbf{c}_{wc}, T_w) - h_a(T_w - T_a) = 0, \quad (2.57)$$

where, $c_{f,j}^{in}$ and T_f^{in} are the respective inlet concentration of species j and feed temperature, and $\tau = L/\langle u \rangle$ is the space or convection time.

In order to account for the changes in gas density and total number of moles due to both homogeneous and catalytic reactions, we can also present the short monolith model in terms of molar flow rates. In that case, the governing equations of the steady-state version of the model are:

$$\frac{F_j^{in} - F_j}{V_R} - a_v j_{fwc,j}^* + \epsilon_f \sum_{i=1}^{Nh} \nu_{ij}^h r_i^h(\mathbf{c}_f, T_f) = 0, \quad (2.58)$$

$$\frac{j_{fwc,j}^*}{R_{\Omega_{wc}}} + \sum_{i=1}^{Nc} \nu_{ij}^c r_i^c(\mathbf{c}_{wc}, T_w) = 0, \quad (2.59)$$

$$-\frac{1}{V_R} \sum F_j^{in} \int_{T_f^{in}}^{T_f} C_{p,j}(T') dT' - h_o a_v (T_f - T_w) + \epsilon_f \sum_{i=1}^{Nh} [-\Delta H_{R,i}^h(T_f)] r_i^h(\mathbf{c}_f, T_f) = 0, \quad (2.60)$$

$$\text{and } \frac{h_o}{R_{\Omega_{wc}}} (T_f - T_w) + \sum_{i=1}^{Nc} [-\Delta H_{R,i}^c(T_w)] r_i^c(\mathbf{c}_{wc}, T_w) - h_a(T_w - T_a) = 0. \quad (2.61)$$

Here, F_j^{in} and F_j are the inlet and exit molar flow rates of species j , respectively; a_v is the solid-fluid interfacial area per unit reactor volume, and is related to the hydraulic radius of the flow channel by $a_v = \epsilon_f/R_{\Omega_f}$, where ϵ_f is the fluid volume fraction of the reactor. For example, for the case of a circular flow channel with a uniform washcoat thickness, ϵ_f is related to the monolith channel dimensions by, $\epsilon_f = 4R_{\Omega_f}^2/(2R_{\Omega_f} + R_{\Omega_w})^2$, which can be further simplified to $\epsilon_f = R_{\Omega_f}/(R_{\Omega_f} + R_{\Omega_w})$ in the limit of thin washcoat and support thickness, i.e., $(R_{\Omega_w} + R_{\Omega_s})/R_{\Omega_f} \ll 1$. [Here, $R_{\Omega_w} = R_{\Omega_{wc}} + R_{\Omega_s}$, where $R_{\Omega_{wc}}$ is the washcoat thickness and R_{Ω_s} is the half-wall/support thickness]. Similarly, for parallel plates of half-wall thickness R_{Ω_s} with a washcoat of thickness $R_{\Omega_{wc}}$ separated by a distance $2a$ (with $R_{\Omega_f} = a$), $\epsilon_f = R_{\Omega_f}/(R_{\Omega_f} + R_{\Omega_w})$. The space time here is defined based on the gas inlet conditions and is related to the reactor (or catalyst) volume, V_R , through the following equation,

$$V_R = \tau q^{in} = \frac{\tau F_T^{in}}{C_0^{in}} \quad (2.62)$$

where, q^{in} is the volumetric flow rate, F_T^{in} is the total molar flow rate and C_0^{in} is the total concentration at the inlet of the reactor.

2.4.3 Interfacial flux and transfer coefficients

The interfacial species flux vector $\mathbf{j}_{fw}^*$, where each element $j_{fw,j}^*$ represents the mass flux of the j^{th} species, can be calculated from the overall mass transfer coefficient matrix $\mathbf{K}_o$ and the concentration difference between fluid and washcoat using the

following equations [24]:

$$\mathbf{j}_{f_{wc}}^* = \mathbf{K}_o(\mathbf{c}_f - \mathbf{c}_{wc}), \quad (2.63)$$

$$\mathbf{K}_o^{-1} = \mathbf{K}_i^{-1} + \mathbf{K}_e^{-1}, \quad (2.64)$$

$$\mathbf{D}_{wc}^{-1} \mathbf{K}_i R_{\Omega_{wc}} = \mathbf{Sh}_i = \mathbf{Sh}_i(\Phi_{wc}), \quad (2.65)$$

$$\mathbf{D}_f^{-1} \mathbf{K}_e d_h = \mathbf{Sh}_e = \mathbf{Sh}_e(\widehat{\Phi}_f), \quad (2.66)$$

$$\mathbf{Sh}_i(\Phi_{wc}) = Sh_{i,\infty} \mathbf{I} + \Phi_{wc} \tanh(\lambda_{wc}^* \Phi_{wc}), \quad (2.67)$$

$$\text{and } \mathbf{Sh}_e(\widehat{\Phi}_f) = Sh_{e,\infty} \mathbf{I} + \widehat{\Phi}_f \tanh(\lambda_f^* \widehat{\Phi}_f) \quad (2.68)$$

where, $\mathbf{D}_f$ is a diagonal matrix with diagonal elements representing the bulk diffusivities of the species in fluid phase and $\mathbf{D}_{wc}$ is the effective diffusivity matrix in the washcoat, which is also a diagonal matrix and is related to $\mathbf{D}_f$ through washcoat porosity ε_{wc} and tortuosity τ_c by the following correlation,

$$\mathbf{D}_{wc} = \frac{\varepsilon_{wc}}{\tau_c} \mathbf{D}_f. \quad (2.69)$$

The respective internal (in the washcoat) and external (in the fluid phase) mass transfer coefficient matrices $\mathbf{K}_i$ and $\mathbf{K}_e$ are calculated from the corresponding Sherwood matrices, $\mathbf{Sh}_i$ and $\mathbf{Sh}_e$, which in turn are functions of Φ_{wc} and $\widehat{\Phi}_f$, where Φ_{wc}^2 is the species Thiele matrix in the washcoat and $\widehat{\Phi}_f^2$ is the effective species Thiele matrix in the fluid phase. The $M \times M$ Thiele (modulus squared) matrices for multi-component

system, with M being the total number of species, are defined as follows:

$$\Phi_{\mathbf{wc}}^2 = R_{\Omega_{wc}}^2 \mathbf{D}_{wc}^{-1} \left(-\frac{\partial \mathbf{R}^c(\mathbf{c}, T)}{\partial \mathbf{c}} \right) \Big|_{\mathbf{c}=\mathbf{c}_s, T=T_s}, \quad (2.70)$$

$$\Phi_{\mathbf{f}}^2 = R_{\Omega_f}^2 \mathbf{D}_f^{-1} \left(-\frac{\partial \mathbf{R}^h(\mathbf{c}, T)}{\partial \mathbf{c}} \right) \Big|_{\mathbf{c}=\mathbf{c}_f, T=T_f}, \quad (2.71)$$

$$\widehat{\Phi}_{\mathbf{f}}^2 = \Phi_{\mathbf{f}}^2 + \mathbf{P}(x), \quad (2.72)$$

$$\text{and } \mathbf{P}(x) = \frac{\langle u \rangle R_{\Omega_f}^2}{x} \mathbf{D}_f^{-1}. \quad (2.73)$$

Here, $\mathbf{R}^c(\mathbf{c}, T) = (\boldsymbol{\nu}^c)^t \mathbf{r}^c(\mathbf{c}, T)$ and $\mathbf{R}^h(\mathbf{c}, T) = (\boldsymbol{\nu}^h)^t \mathbf{r}^h(\mathbf{c}, T)$ are the respective net catalytic and homogeneous species formation (or consumption) rate vectors, and $\boldsymbol{\nu}^k$ ($k = h$ and c) is the corresponding stoichiometric coefficient matrix. [Remark: $\mathbf{r}^c(\mathbf{c}, T)$ and $\mathbf{r}^h(\mathbf{c}, T)$ are the reaction rate vectors with all positive components]. Here, the superscript ‘ t ’ is used to denote transpose of a vector/matrix. It is important to point out that the Jacobian of homogeneous species formation rate vector is evaluated at the fluid phase concentration and temperature $\mathbf{c}_f$ and T_f , and that of catalytic species formation rate vector is evaluated at the interfacial conditions, $\mathbf{c}_s$ and T_s . The effect of boundary layer formation, especially near the reactor entrance, is accommodated through the use of axial position dependent transverse Peclet number $\mathbf{P}(x)$ in the calculation of fluid phase effective Thiele matrix, $\widehat{\Phi}_{\mathbf{f}}^2$. Note that $\mathbf{P}(x)$ is a diagonal matrix where each diagonal elements refer to the ratio of transverse diffusion time of species j to the convection time.

The constants $Sh_{i,\infty}(Sh_{e,\infty})$ and $\lambda_{wc}^*(\lambda_f^*)$ in the expression of $\mathbf{Sh}_i(\mathbf{Sh}_e)$ matrix depend solely on the shape and geometry of the washcoat (flow channel). The values of

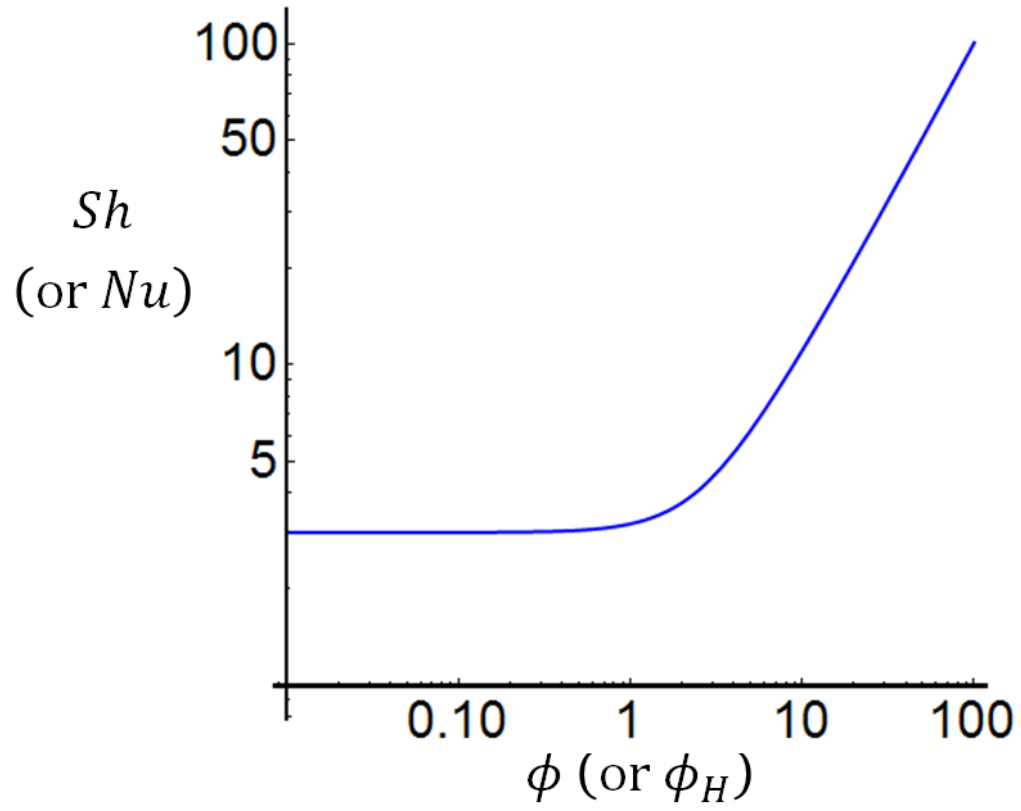


Figure 2.3: Thiele modulus dependency of internal/external and cross-exchange Sherwood numbers for the case of negligible curvature (parallel plate geometry and thin washcoat layers).

$Sh_{e,\infty}$ and λ_f^* for various flow channel geometries are listed in Table 2.1, whereas, the respective values for the internal Sherwood number matrix calculation can be found in Table 2.2. [Remark: Unless specified otherwise, all the calculations presented in this work are for parallel plate geometry with $Sh_{i,\infty} = Sh_{e,\infty} = 3.0$ and $\lambda_{wc}^* = \lambda_f^* = 0.2$]. $Sh_{i,\infty}$ signifies the asymptotic value of internal Sherwood number in the limit of slow catalytic reaction ($\phi_{wc}^2 \rightarrow 0$) [16], whereas $Sh_{e,\infty}$ is the asymptotic value of the external Sherwood number, achieved in the limit of slow homogeneous reaction at infinite channel length ($\widehat{\phi}_f^2 \rightarrow 0$) [25]. Note that the Sherwood numbers have two asymptotes in the limit of very small and very large Thiele moduli as shown in fig. 2.3 which plots the internal/external Sherwood/Nusselt number as a function of the mass and heat Thiele moduli for negligible curvature.

In absence of any dilution in feed, the bulk diffusivities of each species $D_{f,j}$ are calculated from the binary diffusion coefficients $D_{i,j}$ using Wilke-Fairbank's equations whereas, $D_{i,j}$ are calculated using the Fuller-Schettler-Giddings correlation [26] which are given as:

$$D_{i,j} = \frac{10^{-7} T_f^{1.75} \left(\frac{1}{Mw_i} + \frac{1}{Mw_j} \right)^{0.5}}{P_T \left[(\sum \vartheta_i)^{\frac{1}{3}} + (\sum \vartheta_j)^{\frac{1}{3}} \right]^2}, \quad (2.74)$$

$$D_{f,j} = \frac{1 - y_{f,j}}{\sum_{i=1(j \neq i)}^M \frac{y_{f,i}}{D_{i,j}}}, \quad (2.75)$$

$$\text{and } y_{f,j} = \frac{c_{f,j}}{C_o} \quad (2.76)$$

where, Mw_i and Mw_j are the respective molecular weights of species i and j , $\sum \vartheta_i$

Table 2.1: Constants used in external Sherwood number calculation for some common flow channel shapes

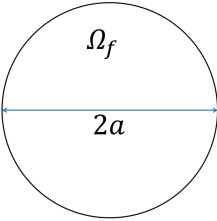
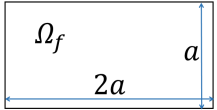
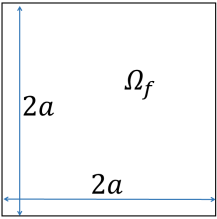
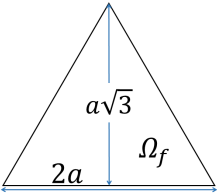
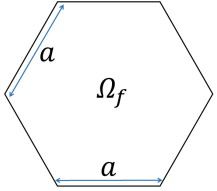
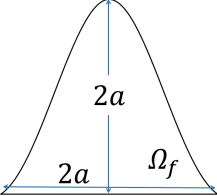
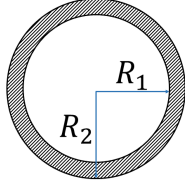
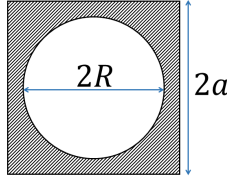
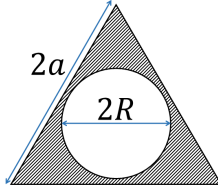
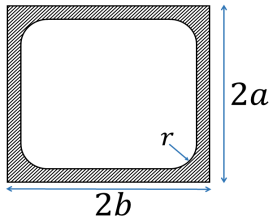
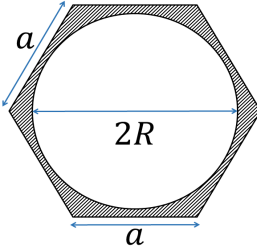
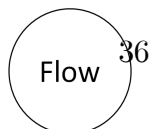
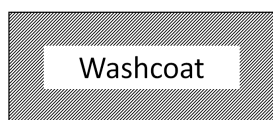
Flow Channel Shape	$\frac{R_{\Omega_f}}{a}$	$Sh_{e,\infty}$	λ_f^*
	0.5	2.0	0.2879
	0.3333	1.9435	0.2946
	0.5	1.7784	0.3267
	0.2887	1.6667	0.3615
	0.4330	1.8821	0.3033
	0.3026	1.6279	0.3455

Table 2.2: Effective washcoat diffusion lengths and constants used in internal Sherwood number calculation for some common washcoat shapes

Channel Shape	R_{Ω_w}	$Sh_{i,\infty}$ and λ_w^*												
	b-a	$Sh_{i,\infty} = 3$ and $\lambda_w^* = 0.18$												
	$(R_2^2 - R_1^2)/(2R_1)$	<table><tr><th>R_2/R_1</th><th>$Sh_{i,\infty}$</th><th>λ_w^*</th></tr><tr><td>1.01</td><td>3.0125</td><td>0.20</td></tr><tr><td>1.1</td><td>3.153</td><td>0.19</td></tr><tr><td>1.2</td><td>3.311</td><td>0.18</td></tr></table>	R_2/R_1	$Sh_{i,\infty}$	λ_w^*	1.01	3.0125	0.20	1.1	3.153	0.19	1.2	3.311	0.18
R_2/R_1	$Sh_{i,\infty}$	λ_w^*												
1.01	3.0125	0.20												
1.1	3.153	0.19												
1.2	3.311	0.18												
	$(4a^2 - \pi R^2)/(2\pi R)$	<table><tr><th>a/R</th><th>$Sh_{i,\infty}$</th><th>λ_w^*</th></tr><tr><td>1</td><td>0.826</td><td>0.45</td></tr><tr><td>1.1</td><td>1.836</td><td>0.46</td></tr><tr><td>1.2</td><td>2.533</td><td>0.31</td></tr></table>	a/R	$Sh_{i,\infty}$	λ_w^*	1	0.826	0.45	1.1	1.836	0.46	1.2	2.533	0.31
a/R	$Sh_{i,\infty}$	λ_w^*												
1	0.826	0.45												
1.1	1.836	0.46												
1.2	2.533	0.31												
	$(\sqrt{3}a^2 - \pi R^2)/(2\pi R)$	<table><tr><th>a/R</th><th>$Sh_{i,\infty}$</th><th>λ_w^*</th></tr><tr><td>1.7321</td><td>0.84</td><td>0.42</td></tr><tr><td>1.9245</td><td>1.45</td><td>0.53</td></tr><tr><td>2.4744</td><td>2.92</td><td>0.31</td></tr></table>	a/R	$Sh_{i,\infty}$	λ_w^*	1.7321	0.84	0.42	1.9245	1.45	0.53	2.4744	2.92	0.31
a/R	$Sh_{i,\infty}$	λ_w^*												
1.7321	0.84	0.42												
1.9245	1.45	0.53												
2.4744	2.92	0.31												
	$\frac{(4b^2 - 4a^2 + 4r^2 - \pi r^2)}{(2\pi r + 8a - 8r)}$	<table><tr><th>b/a</th><th>b/r</th><th>$Sh_{i,\infty}$</th><th>λ_w^*</th></tr><tr><td>1.11</td><td>5</td><td>2.645</td><td>0.21</td></tr><tr><td>1.25</td><td>10</td><td>3.088</td><td>0.20</td></tr></table>	b/a	b/r	$Sh_{i,\infty}$	λ_w^*	1.11	5	2.645	0.21	1.25	10	3.088	0.20
b/a	b/r	$Sh_{i,\infty}$	λ_w^*											
1.11	5	2.645	0.21											
1.25	10	3.088	0.20											
	$(3\sqrt{3}a^2 - 2\pi R^2)/(4\pi R)$	<table><tr><th>a/R</th><th>$Sh_{i,\infty}$</th><th>λ_w^*</th></tr><tr><td>1.155</td><td>0.814</td><td>0.50</td></tr><tr><td>1.17</td><td>1.16</td><td>0.76</td></tr><tr><td>1.2</td><td>1.74</td><td>0.54</td></tr></table>	a/R	$Sh_{i,\infty}$	λ_w^*	1.155	0.814	0.50	1.17	1.16	0.76	1.2	1.74	0.54
a/R	$Sh_{i,\infty}$	λ_w^*												
1.155	0.814	0.50												
1.17	1.16	0.76												
1.2	1.74	0.54												

Where washcoat and flow area are designated as shown below:



and $\sum \vartheta_j$ are their diffusion volumes. $y_{f,j}$ is the mole fraction of j^{th} species in fluid phase and is related to the bulk concentration $c_{f,j}$ through the total gas concentration $C_o = \frac{P_T}{R_g T_f}$. P_T is the total pressure and R_g is the universal gas constant.

Similar to the calculation of mass transfer coefficients, the interfacial heat flux between the fluid and solid (washcoat + support) phases, q_{fw}^* , and the overall heat transfer coefficient h_o can be evaluated from the internal and external Nusselt numbers as follows:

$$q_{fw}^* = h_o(T_f - T_w), \quad (2.77)$$

$$\frac{1}{h_o} = \frac{1}{h_i} + \frac{1}{h_e}, \quad (2.78)$$

$$h_i = \frac{R_{\Omega_w}}{Nu_i(\phi_{hw})\kappa_w}, \quad h_e = \frac{d_h}{Nu_e(\widehat{\phi_{hf}})\kappa_f}, \quad (2.79)$$

$$Nu_i(\phi_{hw}) = Nu_{i,\infty} + \phi_{hw} \tanh(\lambda_{wc}^* \phi_{hw}), \quad (2.80)$$

$$\text{and } Nu_e(\phi_{hf}) = Nu_{e,\infty} + \phi_{hf} \tanh(\lambda_f^* \phi_{hf}) \quad (2.81)$$

where, ϕ_{hw}^2 and $\widehat{\phi_{hf}}^2$ are the heat Thiele modulus in the solid (washcoat + support) and fluid, respectively. The expressions of ϕ_{hw}^2 and $\widehat{\phi_{hf}}^2$ in terms of the heat generated through catalytic reactions, $Q_{wc} = [-\Delta \mathbf{H}_R^c]^t \mathbf{r}^c(\mathbf{c}, T)$ and homogeneous reactions,

$Q_f = [-\Delta \mathbf{H}_R^h]^t \mathbf{r}^h(\mathbf{c}, T)$ are given by:

$$\phi_{hw}^2 = \frac{R_{\Omega_w}^2}{\kappa_w} \left(\frac{\partial Q_{wc}}{\partial T} \right)_{\mathbf{c}=\mathbf{c}_s, T=T_s}, \quad (2.82)$$

$$\phi_{hf}^2 = \frac{R_{\Omega_f}^2}{\kappa_f} \left(\frac{\partial Q_f}{\partial T} \right)_{\mathbf{c}=\mathbf{c}_f, T=T_f}, \quad (2.83)$$

$$\widehat{\phi_{hf}}^2 = \phi_{hf}^2 + P_h(x), \quad (2.84)$$

$$\text{and } P_h(x) = \frac{\langle u \rangle R_{\Omega_f}^2}{x \alpha_f}. \quad (2.85)$$

Again, the partial derivative of Q_{wc} with respect to temperature is evaluated at the interfacial concentrations $\mathbf{c}_s$ and temperature, T_s , and that of Q_f is evaluated at the bulk conditions, $\mathbf{c}_f$ and T_f . $P_h(x)$ is the position dependent transverse heat Peclet number, κ_f is the gas thermal conductivity and $\alpha_f = \kappa_f / \widehat{C_{pf}}$ is the thermal diffusivity of the gas mixture. The volumetric heat capacity $\widehat{C_{pf}}$ can be equated to the average molar heat capacity $\widehat{C_{pf}}$ through total concentration C_0 , i.e., $\widehat{C_{pf}} = C_0 \widehat{C_{pf}}$ and $\widehat{C_{pf}} = \sum_{i=1}^M y_{f,i} \langle C_{p,i} \rangle$, where $\langle C_{p,i} \rangle$ is the molar specific heat of i^{th} species averaged over the temperature range of 300K - 1500K. The heat capacities and the enthalpies of formation for each species are calculated as functions of temperature using GRI thermodynamic database [27]. [Again, all the calculations presented in this work are for parallel plate geometry with $Nu_{i\infty} = Nu_{e\infty} = 3.0$ and $\lambda_{wc}^* = \lambda_f^* = 0.2$].

The methodology to calculate the interfacial mass and heat fluxes in short monolith model is equivalent to that of the long channel model with the only difference residing in the definitions of the transverse mass and heat Peclet numbers. For the case of short monolith model, the convection time is same as the space time and the

species transverse Peclet number matrix and the transverse heat Peclet number can be expressed as

$$\mathbf{P} = \frac{R_{\Omega_f}^2}{\tau} \mathbf{D}_f^{-1} \text{ and } P_h = \frac{R_{\Omega_f}^2}{\tau \alpha_f}. \quad (2.86)$$

2.4.4 Construction of 2D/3D profiles from reduced order models

Generally, the reduced order models expressed in terms of phase-averaged quantities are convenient as they enable real-time simulations and bifurcation analysis in the entire parameter space. While they should be used with caution as they are only qualitatively valid when the local gradients are large. However, when the local gradients are small and within the range of applicability of these models, they can be used to reconstruct back the 2D spatial variations in the concentration and temperature profiles ([15],[25],[28]). For example, for the case of flat velocity profile and parallel plate geometry, the 2D transient profile of concentration vectors and temperature in the monolith can be expressed by using the transverse functions (explained and tabulated in Supplementary Material of Ratnakar et al. [15]) to the first order correction as follows:

$$\mathbf{c}(x, y, t) = \begin{cases} \langle \mathbf{c}_f \rangle(x, t) + \frac{1}{2} \mathbf{K}_e^{-1} \mathbf{j}_{f_{wc}}^*(x, t) \cdot \left(1 - 3 \frac{y^2}{R_{\Omega_f}^2} \right), \\ \langle \mathbf{c}_w \rangle(x, t) + \frac{1}{2} \mathbf{K}_i^{-1} \mathbf{j}_{f_{wc}}^*(x, t) \cdot \left(2 - 6 \left(\frac{y - R_{\Omega_f}}{R_{\Omega_{wc}}} \right) + 3 \left(\frac{y - R_{\Omega_f}}{R_{\Omega_{wc}}} \right)^2 \right), \end{cases} \quad (2.87)$$

and

$$T(x, y, t) = \begin{cases} \langle T_f \rangle(x, t) + \frac{1}{2} h_e^{-1} q_{fw}^*(x, t) \cdot \left(1 - 3 \frac{y^2}{R_{\Omega_f}^2} \right), \\ \langle T_w \rangle(x, t) + \frac{1}{2} h_i^{-1} q_{fw}^* \cdot \left(2 - 6 \left(\frac{y - R_{\Omega_f}}{R_{\Omega_{wc}}} \right) + 3 \left(\frac{y - R_{\Omega_f}}{R_{\Omega_{wc}}} \right)^2 \right). \end{cases} \quad (2.88)$$

In the above expressions, the phase-averaged concentrations, $\langle \mathbf{c}_f \rangle(x, t)$ and $\langle \mathbf{c}_w \rangle(x, t)$ and temperatures, $\langle T_f \rangle(x, t)$ and $\langle T_w \rangle(x, t)$, are same as the quantities used without the angular brackets in the model equations described by eqns. (2.46 - 2.49). It is only to distinguish between the 2D concentration $\mathbf{c}(x, y, t)$ and the phase-averaged concentration $\mathbf{c}(x, t)$, we have added the angular brackets in eqn. 2.87. In what follows, $\mathbf{c}_f$ or $\mathbf{c}_{wc}$ should be assumed to be phase-averaged quantities unless otherwise mentioned. This holds true for the temperature notations as well. Within the curly bracket, the top expression is for the fluid phase, i.e., $0 < y < R_{\Omega_f}$, whereas the bottom one is for the appropriate solid phase. For concentration profiles, the appropriate solid phase only consists of washcoat layer, i.e., $R_{\Omega_f} < y < R_{\Omega_f} + R_{\Omega_{wc}}$ and for temperature profiles, the solid phase consists of both washcoat and the support (half-wall thickness), i.e., $R_{\Omega_f} < y < R_{\Omega_f} + R_{\Omega_w}$.

2.5 Numerical algorithms

In this section, we discuss the different numerical algorithms employed to solve the transient and steady-state model equations described above. Also, a brief discussion on the Cayley Hamilton Theorem used to compute the functions of matrices given by eqns. (2.67 - 2.68) is provided.

2.5.1 Transient equations

The transient equations denoted by eqns. (2.46 - 2.49) are a set of partial differential equations (PDEs). In these set of PDEs, the first-order spatial derivative $\partial/\partial x$ terms are discretized using the first-order upwind scheme (backward difference), whereas the second-order term, $\partial^2/\partial x^2$, is discretized following the central-difference method. Spatial discretization converts these original set of PDEs into ordinary differential equations (ODEs) which are now integrated in time using solver packages like LSODA and VODE (<https://www.netlib.org>). This entire approach of solving PDEs is called Method of Lines.

2.5.2 Steady-state equations

The steady-state equations described by eqns. (2.54 - 2.57) form a set of non-linear algebraic equations. Since these set of equations can have multiple roots for a fixed parameter, the common root-finding algorithms like Newton-Raphson, hybrid, etc. may not work well because of the difficulty in providing good initial guesses to reach each of those multiple solutions. Also, the total number of roots possible at a fixed parameter may not be known a priori. On top of that, for certain choices of parameters, the Jacobian of these equations can become singular, in which case those common methods will completely fail. For these reasons, we use continuation algorithms to trace out all the roots as the value of a parameter is varied. Two of the continuation algorithms used in our calculation are described below.

Pseudo-arc length continuation method

The parameter dependent solution to a set of non-linear equations can be generalized as

$$\mathbf{f}(\mathbf{x}, \lambda, \mathbf{p}^*) = \mathbf{0} \quad (2.89)$$

where, $\mathbf{x}$ is the vector of unknown and $\mathbf{f}$ is the function vector, both of dimension n . λ is the independent parameter of interest (to be varied) and $\mathbf{p}^*$ represents the vector of all the fixed parameters. Since λ is varied, eqn. 2.89 can be seen as n equations with $(n + 1)$ unknowns and hence can be rewritten as

$$\mathbf{f}(\mathbf{y}(s), \mathbf{p}^*) = \mathbf{0}. \quad (2.90)$$

Here, s is the pseudo-arc length along the solution curve and $\mathbf{y}(s) = \begin{pmatrix} \mathbf{x}(s) \\ \lambda(s) \end{pmatrix}$. An additional equation to define s is given as,

$$\sum_{i=1}^{n+1} (y_i - y_i^0)^2 - (s - s^0)^2 = 0. \quad (2.91)$$

When x is scalar, the above equation defines a circle in (x, λ) plane as shown in fig. 2.4. The center of the circle, $O(y_0, \lambda_0)$, represents the current solution point. The circle radius is $\Delta s = \|A - O\|$, where $A(y_{-1}, \lambda_{-1})$ is the previous solution point. If Δs is of proper value, the solution curve crosses the circle at one and only one point different from $A(y_{-1}, \lambda_{-1})$. In order to guarantee the next calculated solution

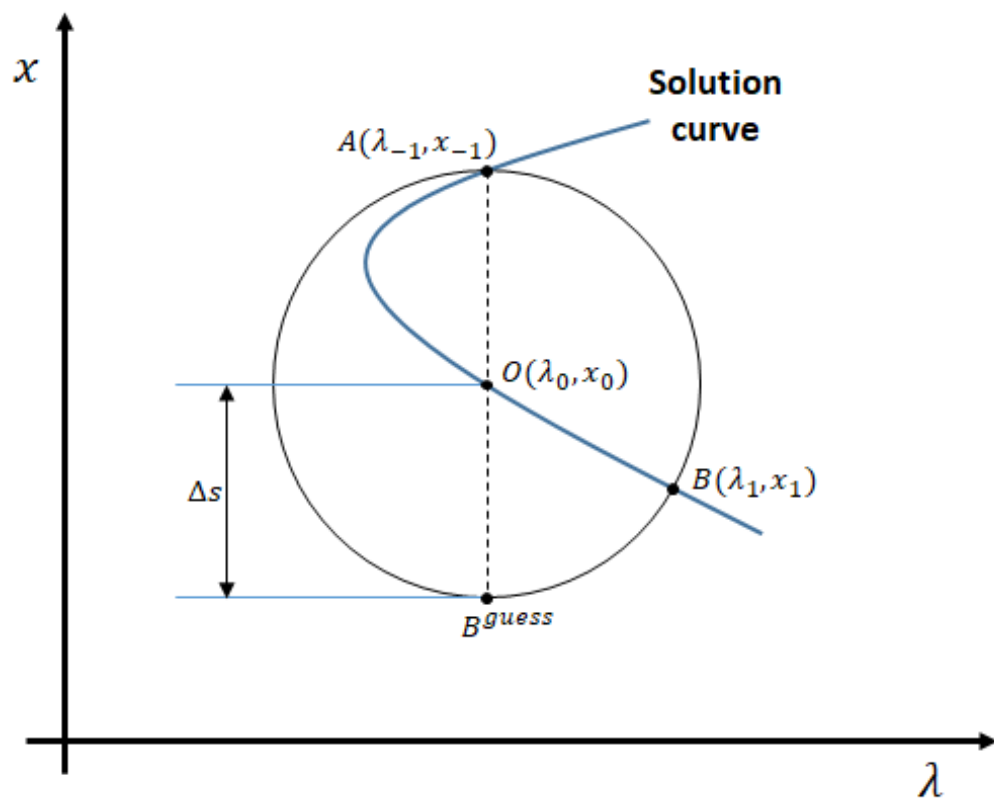


Figure 2.4: Schematic diagram of pseudo-arc length continuation method

to be different from $A(y_{-1}, \lambda_{-1})$, the initial guess for solving the non-linear equations is chosen to be point B^{guess} , which is located on the circle (hence satisfies eqn. 2.91) and has the longest distance from $A(y_{-1}, \lambda_{-1})$, i.e.,

$$x_1^{guess} = 2x_0 - x_{-1} \quad (2.92)$$

$$\text{and } \lambda_1^{guess} = 2\lambda_0 - \lambda_{-1}, \quad (2.93)$$

or in the vector form, $\mathbf{y}_1^{guess} = 2\mathbf{y}_0 - \mathbf{y}_{-1}$.

It is understood from the above description that two initial solution points (A and O) are required to start the continuation of the solution curve. The distance between these two initial points is Δs , which is fixed within the course of continuation. It should be mentioned here that, when $\mathbf{x}$ is an n dimensional unknown vector, the circle in fig. 2.4 becomes an $(n+1)$ -dimensional sphere. In a nutshell, the pseudo arc-length method converts the parameter dependent solution of n non-linear equations to solution of $(n+1)$ non-linear equations. Carefully chosen step size is crucial for the proper progress of the solution curve.

Arc-length continuation method

In the limit of Δs approaching 0, eqn. 2.91 becomes

$$\sum_{i=1}^{n+1} \left(\frac{dy}{ds} \right)^2 - 1 = 0. \quad (2.94)$$

Now if we take the derivative of eqn. 2.90 with respect to s , we get

$$\frac{\partial \mathbf{f}}{\partial \mathbf{y}} \cdot \frac{d\mathbf{y}}{ds} = 0 \quad (2.95)$$

where, $d\mathbf{f}/d\mathbf{y}$ is the Jacobian matrix with dimensions $n \times (n+1)$. The above equation can be further rearranged by taking column k out from the Jacobian matrix and written as

$$\mathbf{J}_k \boldsymbol{\beta}_k = -\frac{\partial \mathbf{f}}{\partial y_k}. \quad (2.96)$$

Here, $\mathbf{J}_k = \left(\frac{\partial \mathbf{f}}{\partial y_1} \dots \frac{\partial \mathbf{f}}{\partial y_{k-1}} \frac{\partial \mathbf{f}}{\partial y_{k+1}} \dots \frac{\partial \mathbf{f}}{\partial y_{n+1}} \right)$ is an $n \times n$ matrix and $\boldsymbol{\beta}_k = \left(\frac{dy_1}{dy_k} \dots \frac{dy_{k-1}}{dy_k} \frac{dy_{k+1}}{dy_k} \dots \frac{dy_{n+1}}{dy_k} \right)^T$ is n dimensional vector of unknowns. In practice k is chosen such that $\frac{dy_k}{ds}$ has the maximum value to ensure $\mathbf{J}_k$ is not singular and $\frac{\partial \mathbf{f}}{\partial y_k}$ is a non-zero vector. $\boldsymbol{\beta}_k$ may then be obtained by solving the system of non-singular linear equations given by eqn. 2.96.

Finally, substituting $\boldsymbol{\beta}_k$ into eqn. 2.94 gives

$$\left(\frac{dy_k}{ds} \right)^2 \sum_{i=1}^{n+1} \beta_i^2 = 1. \quad (2.97)$$

Eqns. 2.96 and 2.97 are used to solve all $\frac{dy_i}{ds}$ values. The original problem of parameter dependent solution of non-linear equations is now converted to an initial value problem (IVP) with s being the independent variable. Integration of these IVPs result in an unique solution.

The well established DERPARG subroutine [29] is used in our study to implement this algorithm. In this subroutine, Gaussian elimination with complete pivoting is

used to solve the linear system of equations given by eqn. 2.96. Afterwards, the IVPs are integrated using fourth-order explicit Adams-Bashforth method. The integration provides a good approximate solution for eqn. 2.90 which is then used as an initial guess in Newton-Raphson algorithm to get a more polished solution.

Bifurcation diagram, sets and hysteresis locus

By employing any of these continuation algorithms, both the state variables and the bifurcation parameter can be varied along the arc-length, thereby making the bifurcation parameter another unknown in the system. The bifurcation diagrams are generated by solving the model equations with feed temperature or space time as the bifurcation parameter. Following the ignition/extinction points in the bifurcation diagram while another extra parameter (τ if $T_{f,in}$ is bifurcation parameter and vice versa) is varied leads to the computation of bifurcation sets (ignition-extinction locus). The coalescence of ignition and extinction points occurs at the hysteresis point. A locus of all such points is called hysteresis locus, which can be calculated by varying one more parameter (i.e., fuel composition in the current work). The hysteresis locus demarcates the region of multiplicity in the parameter space from the region where only a single-valued solution as a function of the bifurcation parameter (τ or $T_{f,in}$) is

possible, and can be evaluated using the following equations [30]:

$$\mathbf{f}(\mathbf{x}, \lambda, \mathbf{p}^*) = \mathbf{0}, \quad (2.98)$$

$$\mathbf{J} \cdot \mathbf{y}_0 = \mathbf{0}, \quad (2.99)$$

$$\mathbf{J}^T \cdot \mathbf{v}_0 = \mathbf{0}, \quad (2.100)$$

$$\langle D_{xx}^2 \mathbf{f}(\mathbf{y}_0, \mathbf{y}_0), \mathbf{v}_0 \rangle = 0, \quad (2.101)$$

$$\text{and } \langle \mathbf{y}_0, \mathbf{v}_0 \rangle = 1. \quad (2.102)$$

Here, $\mathbf{J}$ is the Jacobian matrix, where $\mathbf{J}^T$ represents its transpose. $\mathbf{y}_0$ and $\mathbf{v}_0$ are the respective eigenvector and adjoint eigenvector, $D_{xx}^2 \mathbf{f}$ denotes the second Fréchet derivative of the function $\mathbf{f}$.

2.5.3 Functions of matrices

For a square matrix $\mathbf{A}$ of $n \times n$ dimension, the characteristic equation is given by

$$\begin{aligned} P_n(\lambda) &= (-\lambda)^n + a_1 (-\lambda)^{n-1} + \dots + a_{n-1} (-\lambda) + a_n = 0, \\ &= (\lambda_1 - \lambda)(\lambda_2 - \lambda) \dots (\lambda_n - \lambda), \end{aligned} \quad (2.103)$$

where, $\{\lambda_1, \lambda_2, \dots, \lambda_n\}$ are its eigenvalues. According to Cayley Hamilton theorem, every such square matrix $\mathbf{A}$ satisfies its own characteristic equation, i.e., $P_n(\mathbf{A}) = 0$. Rearranging the terms, the theorem can be explicitly rewritten as

$$\mathbf{A}^n = c_1 \mathbf{A}^{n-1} + c_2 \mathbf{A}^{n-2} + \dots + c_{n-1} \mathbf{A} + c_n \mathbf{I} \quad (2.104)$$

where $c_i = (-1)^{1-i} a_i$. It can be further shown that not only just $\mathbf{A}^n$ but any analytical function of $\mathbf{A}$ can be expressed as a polynomial of degree $(n - 1)$ in $\mathbf{A}$, i.e.,

$$f(\mathbf{A}) = c_1 \mathbf{A}^{n-1} + c_2 \mathbf{A}^{n-2} + \dots + c_{n-1} \mathbf{A} + c_n \mathbf{I}. \quad (2.105)$$

By plugging in the n eigenvalues in the above equation in place of $\mathbf{A}$, one can form a system of n linear equations which can be solved to obtain the coefficients $\{c_1, c_2, \dots, c_n\}$. Using those coefficients, the function of $\mathbf{A}$ can then be computed. If instead of distinct values, any of the eigenvalues is repeated r times, those many coefficients can directly be obtained by differentiating eqn. 2.105 r times with respect to that repeated eigenvalue.

In our applications, the eigenvalues of the Thiele matrices ($\Phi_{\mathbf{w}\mathbf{c}}^2$ and $\widehat{\Phi}_{\mathbf{f}}^2$) can be positive, negative and even complex. However, the final form of the $\mathbf{Sh}$ matrices, which are expressed as functions of the Thiele module matrix, will always be real [16].

Chapter 3

Bifurcation analysis for oxidation of propane

3.1 Introduction

Catalytically stabilized thermal combustion (CSTC) is a growing technology for developing next generation gas turbines and has huge potential in reducing NO_x emissions. In such catalytic burners, premixed fuel and air are passed through honeycomb monoliths which are washcoated with catalyst. The role of the catalyst is to ignite the lean reacting mixture and generate enough heat to initiate the gas phase homogeneous reactions in the reactor downstream. Typically, the composition of the incoming fuel mixture is kept lower than the lean flammability limit. Thereby, contrary to the conventional flame burners, the maximum temperature attained in these catalytic combustors can be maintained well below the thermal NO_x formation threshold ([31], [32]). Although, the original idea of CSTC by Pfefferle [33] conceived of complete fuel conversion through both heterogeneous and homogeneous routes over the catalyst, the high temperature requirements of a modern heavy-duty turbine may delimit the fuel conversion in the catalytic reactor and include a post-

catalytic homogeneous combustion zone [34]. The principles of coupled homo-/hetero combustion are also exploited in microburners (reactor gap size < 1 mm) for portable or decentralized power generation. Due to the channel confinement and large surface to volume ratio, the catalytic reaction is usually more dominant in a microreactor than the homogeneous counterpart. However, the onset of gas phase reactions cannot always be ignored and may be desirable for some specific applications [35].

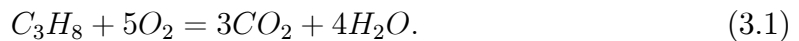
For obvious reasons, the design and analysis of such reactors require a comprehensive understanding of both homogeneous-heterogeneous chemistry and their coupling with the transport effects. Advances in non-intrusive experimental techniques like Raman spectroscopy and planar laser induced fluorescence (PLIF) of radical species, combined with detailed numerical simulations have provided invaluable insights on these complex processes, as reviewed in a recent article by Mantzaras et al. [36]. Furthermore, the coupling between diffusion, convection and homo-/hetero reactions can lead to complicated steady state and transient behaviors (e.g., ignition-extinction and hysteresis, multiple steady-states, spatio-temporal patterns, etc.) ([31], [35]), study and analysis of which may not be practical through traditional numerical computations. In this regard, bifurcation analysis is a very important mathematical tool, which can aid in analyzing the multiple steady states and different possible behaviors of the system for various choices of physical parameters [37].

In this chapter (and the next), we demonstrate the use of our reduced order models in performing the bifurcation and transient analysis of such catalytically assisted combustion in monolith reactors. As a specific example, here we consider the case of propane combustion in a monolith reactor with washcoat. While there have

been many literature studies on the modeling of catalytically assisted combustion of propane in parallel plate channels, most of these studies do not consider the impact of washcoat diffusional effects on the ignition and extinction behavior ([38]-[41]). Our objective here is to illustrate the impact of washcoat diffusion on the bifurcation behavior for the case of propane combustion in a monolith reactor. We start with the short monolith model and compare the results obtained by Alam et al. [17] using wall reaction instead of washcoat diffusion-reaction. Though the generic bifurcation features (S and double S-shaped bifurcation diagrams) are found to be similar in both cases, the extinction temperature of catalytic reaction and the hysteresis loci of catalytic and thermally coupled homogeneous-catalytic case are found to be notably different when washcoat diffusion-reaction is taken into consideration. Next, we analyze the transient model with a flat velocity profile (or negligible dispersion in fluid phase) and calculate the dynamic hysteresis plots by slowly varying the inlet temperature to illustrate the impact of heat Peclet number on the bifurcation behavior.

3.1.1 Short monolith or gauze reactor model

The complete combustion of propane in air using global kinetics is given by



The homogeneous rate expression for this global reaction is taken from Westbrook and Dryer [42] as

$$r_h = k_{0h} \exp \left[-\frac{E_h}{RT_f} \right] y_{fA}^n y_{fB}^m C_0 \quad (3.2)$$

and the volumetric rate of heterogeneous reaction in the washcoat can be obtained from Hiam et al. [43] as

$$r_c = k_{0c} \exp \left[-\frac{E_c}{RT_w} \right] y_{wA}^{n'} y_{wB}^{m'} C_0 \quad (3.3)$$

where, y_{fA} and y_{fB} are cup-mixing mole fractions of A (C_3H_8) and B (O_2) in the fluid phase respectively, and y_{wA} and y_{wB} are the averaged mole fractions in the washcoat, defined in eqn. 5.1. The kinetic parameters along with physical and transport quantities are taken from Alam et. al. [17] and listed in Table 3.1. The reader is referred to the cited references for further details regarding the calculation of these constants and parameters.

Using the above global kinetic model, the steady state multi-component short monolith model as given by eqns. (2.54 - 2.57) is numerically solved using the arc-length continuation algorithm to generate the bifurcation diagrams of state variables versus feed temperature. The hysteresis locus is computed using the approach outlined by eqns. (2.98 - 2.102). Fig. 3.1 shows the hysteresis locus of propane oxidation in a monolith reactor with channel hydraulic radius $R_{\Omega_f} = 1.32 \text{ mm}$ and washcoat thickness $R_{\Omega_{wc}} = 100 \text{ }\mu\text{m}$. To illustrate the contrast between the case of washcoat diffusion and wall (surface) reaction, we have provided the hysteresis locus of the

Table 3.1: Kinetic, transport and physical parameters used in the calculation of propane oxidation

Quantities	Unit	Value
$\alpha_f = \frac{k_f}{C_{pf}}$	m ² /s	$9.8 \times 10^{-10} \frac{T^{1.75}}{P}$
D_{mf,C_3H_8}	m ² /s	$5.25 \times 10^{-10} \frac{T^{1.75}}{P}$
D_{mf,O_2}	m ² /s	$9.24 \times 10^{-10} \frac{T^{1.75}}{P}$
P_T	bar	1
$\widetilde{C_{pf}}$	J/m ³ -K	875
k_{0h}	s ⁻¹	2.67×10^8
k_{0c}	s ⁻¹	5.06×10^8
E_h/R	K	15097
E_c/R	K	8555
n		0.1
m		1.65
n'		1
m'		0.5
ΔH_R	kJ/mol	-2044
ν		5
ε_w		0.4
τ_c		4
$Sh_{e,\infty}, Sh_{i,\infty}$		3.0
$Nu_{e,\infty}, Nu_{i,\infty}$		3.0
λ_f^*, λ_w^*		0.2

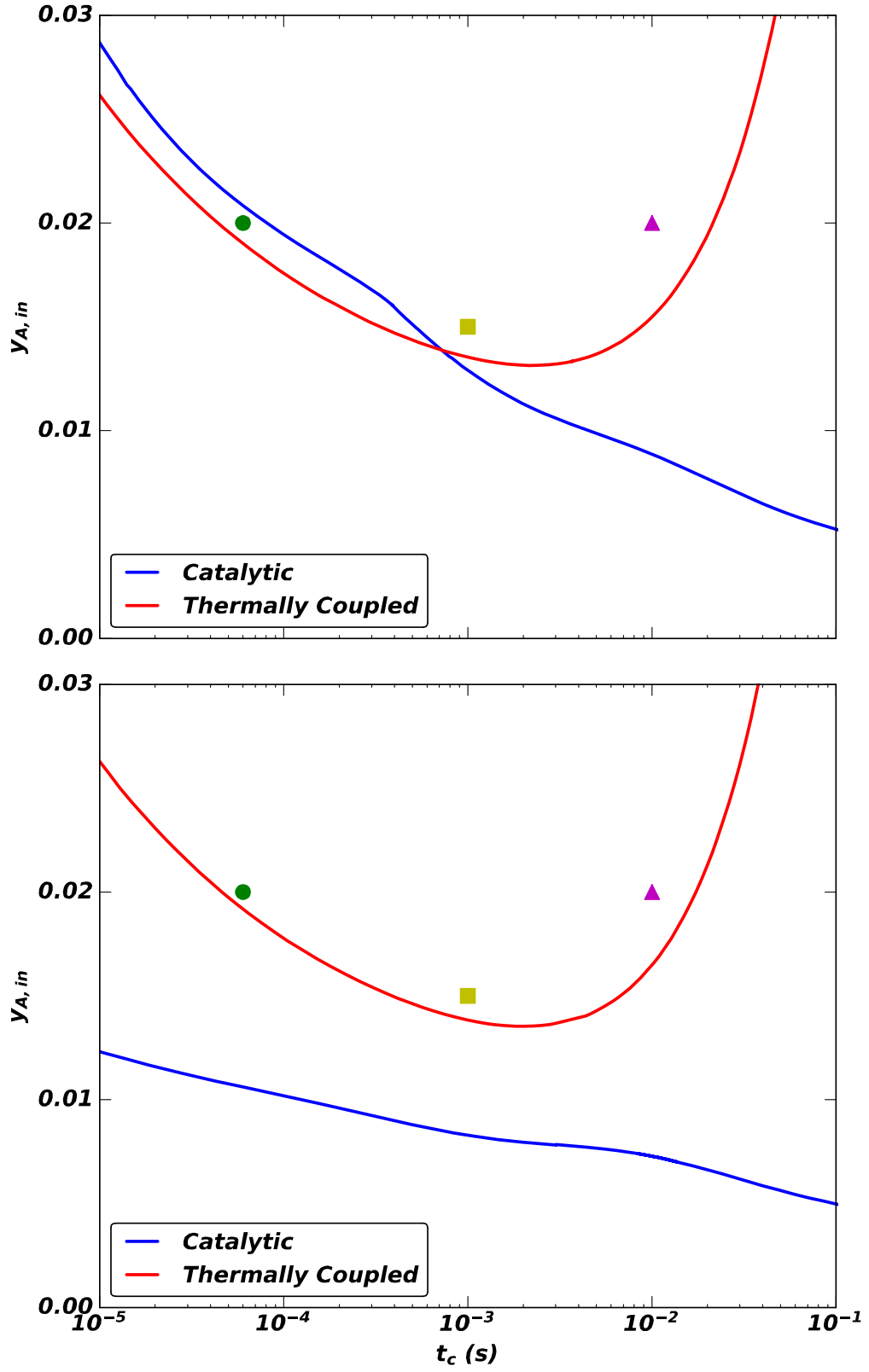


Figure 3.1: Computed phase diagram for lean combustion of propane with washcoat diffusion present (top) and without washcoat diffusional limitations (bottom).

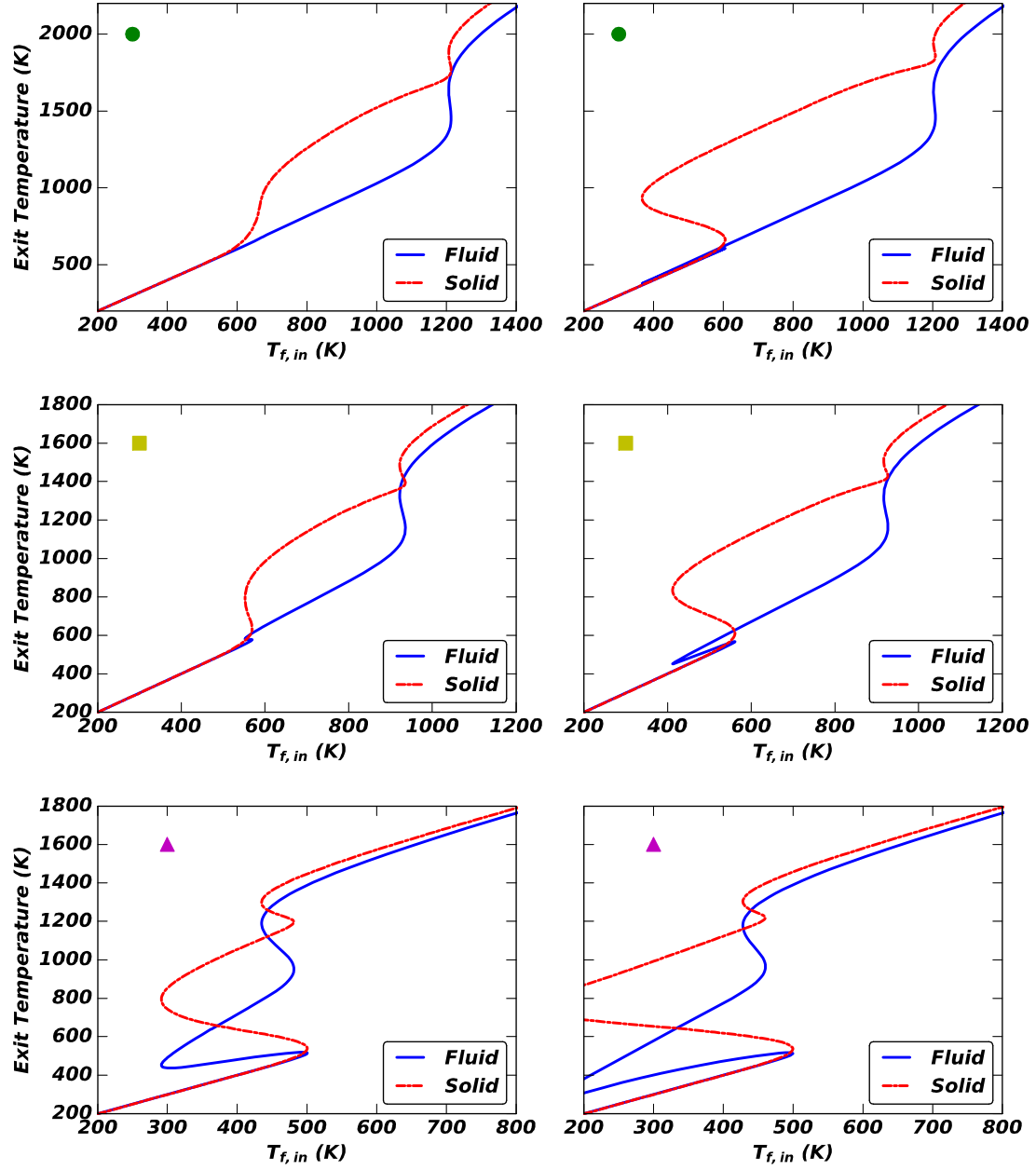


Figure 3.2: Bifurcation diagrams of exit fluid (T_f) and solid temperature (T_w) against fluid inlet temperature ($T_{f,in}$) with washcoat diffusion (left column) and without washcoat diffusion (right column).

same system in the limit of infinite diffusivity in the washcoat so that there is practically no internal diffusional limitations (and all catalytic sites are on the wall). Alam et al. [17] calculated this same hysteresis plot using short monolith model with wall reaction present. It can be noted from the figure that for low space times ($t_c < 10^{-3}$ s) when the washcoat internal diffusional limitation is significant, the region of multiplicity of the catalytic reaction shrinks and moves towards higher inlet mole fractions. Fig. 3.2 illustrates the bifurcation diagrams (of fluid and solid temperatures versus inlet temperature) for three different choices of inlet C_3H_8 mole fraction, $y_{A,in}$ and space time t_c , as marked in fig. 3.1. For the choice of parameters studied here, the first ignition-extinction pair in fig. 3.2 corresponds to the catalytic reaction and the second one corresponds to thermally coupled homogeneous-catalytic system. Because of internal diffusional resistance, the extinction temperature of the catalytic reaction for the case where washcoat diffusion is present (shown in the left column of fig. 3.2) is found to be considerably higher than that in the case of wall reaction (shown in the right column). Since the case corresponding to $y_{A,in} = 0.02$ and $t_c = 0.06$ ms lies outside the region of multiplicity of catalytic reaction when washcoat diffusion is considered, unlike the wall reaction case, only one pair of ignition-extinction is observed in this bifurcation diagram (shown in the top row).

For a fixed ratio of catalyst to fluid volume fraction, if the hydraulic radius of the monolith is decreased by 5 times from $R_{\Omega_f} = 1.32$ mm to 264 μ m, the hysteresis region of thermally coupled reaction shrinks and the system becomes catalytic reaction dominant for a wider range of inlet mole fractions and space times, as show in fig. 3.3. Similar to the previous case, at lower space times the region of multiplicity of

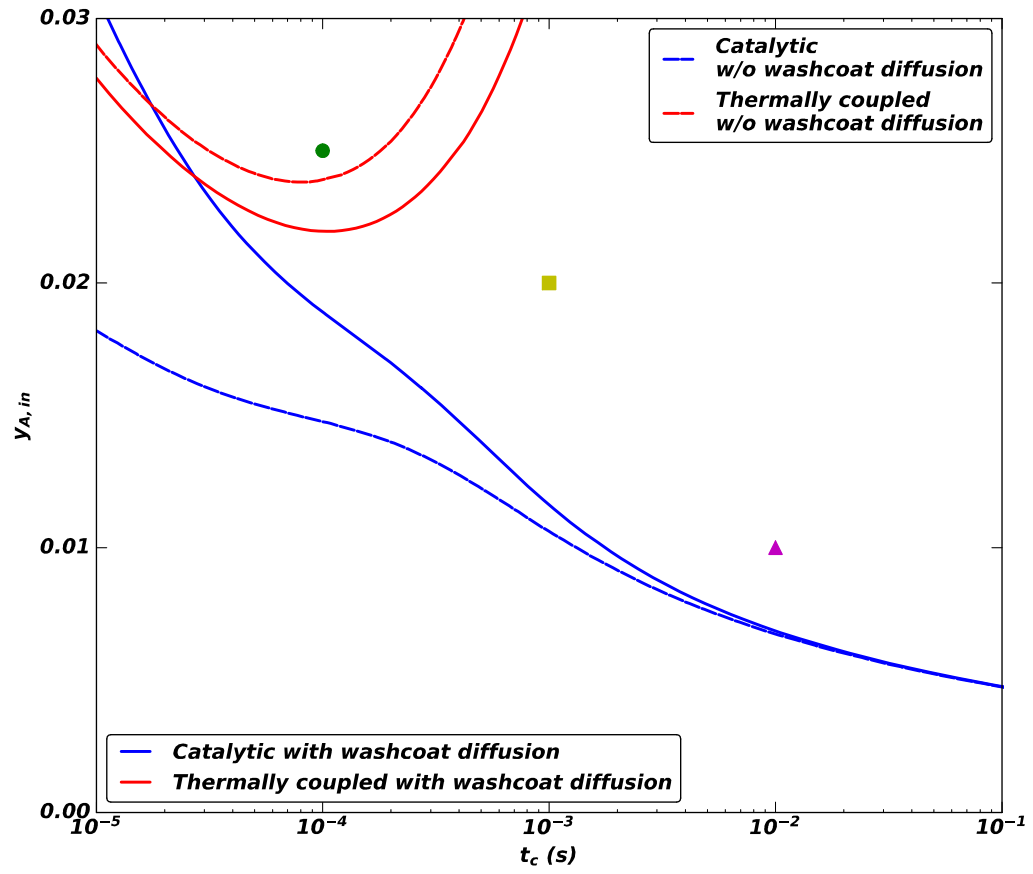


Figure 3.3: Computed phase diagram for lean combustion of propane in a monolith with and without washcoat diffusional limitations.

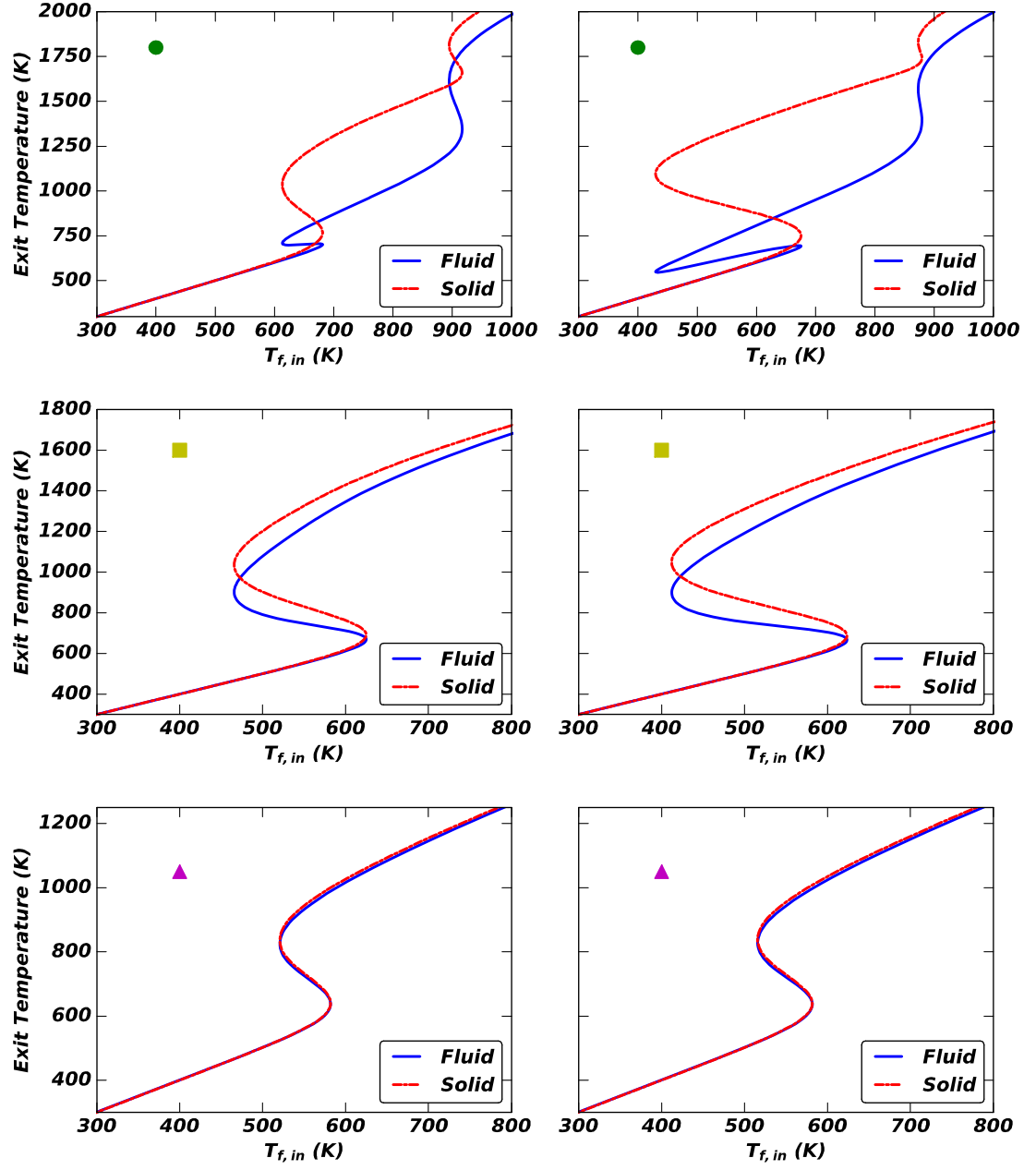


Figure 3.4: Bifurcation diagrams of exit fluid (T_f) and solid temperature (T_w) against fluid inlet temperature ($T_{f,in}$) with washcoat diffusion (left column) and without washcoat diffusion (right column).

the catalytic reaction shrinks and moves upwards in presence of washcoat diffusional limitations. It is also interesting to note here that, the hysteresis region of thermally coupled homogeneous reaction expands when washcoat diffusion is taken into account. As the overall activity of the catalytic reaction is reduced due to significant internal diffusional resistance, it is the thermally coupled homogeneous reaction that assists more in the conversion of fuel, resulting in the slight expansion of its region of multiplicity. Fig. 3.4 shows the bifurcation diagrams of the points marked in fig. 3.3. At higher space times, the reactants get enough time to diffuse and react inside the washcoat. Thereby, the extinction temperatures of catalytic reaction for both the cases (with and without washcoat diffusion) are found to be very close. Whereas at lower space times, the internal diffusional resistance becomes more significant, resulting in higher extinction temperature of catalytic reaction when washcoat diffusion is taken into account (shown in the top row in fig. 3.4).

The phase diagrams shown in figs. 3.1 and 3.3 give a complete global (or the big) picture of how the ignition and extinction phenomenon change (or can be controlled) in coupled homo-cat systems by varying the space time, inlet mole fraction, channel hydraulic diameter or washcoat properties. The lower curve (marked catalytic hysteresis) is the boundary between unique and multiple solutions in the absence of homogeneous reaction (or when the homo rate is negligible). The thermally coupled hysteresis boundary is U-shaped because at higher space times, most of the limiting reactant (e.g., propane in lean combustion) is consumed by the catalytic reaction and hence not much reactant is left to cause homogeneous ignition/extinction. This is not the case at low space times where catalytic reaction is ignited and is in the

mass transfer controlled regime but the (bulk) reactant concentration in the channel is still high, leading to homogeneous ignition/extinction. As can be expected intuitively, this boundary moves to higher reactant inlet mole fractions as the channel hydraulic radius is reduced (or higher surface area to volume ratio favoring catalytic reaction) and in the opposite direction when washcoat diffusional effects are present (suppressing the catalytic reaction rate).

3.1.2 Transient simulations of multi-mode finite dispersion model

Finally, we consider the multicomponent version of transient two phase model described by eqns. (2.46 - 2.53) with position and reaction parameters dependent transfer coefficients for propane oxidation at three different choices of axial velocity $\langle u \rangle$ and reactor length L but at the same space time. In case (a) $\langle u \rangle = 0.1 \text{ m/s}$ and $L = 1 \text{ mm}$, case (b) $L = 5 \text{ mm}$, $\langle u \rangle = 0.5 \text{ m/s}$ and in case (c) $\langle u \rangle = 2 \text{ m/s}$ and $L = 20 \text{ mm}$. To calculate the dynamic hysteresis of the system, the feed temperature is increased from 300 K to 600 K at a ramp rate of 1 K/min and then decreased to 300 K at the same ramp rate. Such a low ramp rate is chosen so that the hysteresis observed is due to steady state multiplicity and not because of any combined effect of steady state multiplicity and ramp rate [44]. The reactants are found to reach full conversion within this range of inlet temperatures for both the cases studied here. In this context, it is important to introduce effective axial heat Peclet number, $Pe_{h,eff}$ which is defined as the ratio of convective heat flow in fluid to conductive heat flow

in solid and can be expressed for the current system as

$$Pe_{h,eff} = \frac{\langle u \rangle \widetilde{C_{pf}} R_{\Omega_f} L}{R_{\Omega_{wc}} \left(\kappa_{wc} + \frac{A_s}{A_{wc}} \kappa_s \right)}.$$

Since in cases (b) [(c)], both $\langle u \rangle$ and L are chosen to be 5[4] times of the values in case (a)[(b)], the convection time t_c and the transverse Peclet number p is same in both the cases, whereas $Pe_{h,eff}$ in case (b) is 25 [16] times of that in case (a)[(b)]. The calculated values of these dimensionless numbers (for a fixed average temperature) along with other additional parameters used in this model are listed in Table 3.2.

Table 3.2: List of parameters for the transient two-phase model - propane

Quantities	Unit	Value
L	mm	1.0, 5.0 or 20.0
$\langle u \rangle$	m/s	0.1, 0.5 or 2
R_{Ω_f}	mm	1.32
$R_{\Omega_{wc}}$	μm	100
$\frac{A_s}{A_{wc}}$	-	0.9
$y_{A,in}$	-	0.02
C_{pwc}, C_{ps}	J/kg-K	1000
ρ_{wc}	kg/m ³	1550
ρ_s	kg/m ³	2500
κ_{wc}, κ_s	W/m-K	1.5
$Pe_{h,eff}$	-	0.4, 10 or 160
p	-	1.7

Fig. 3.5 shows the computed dynamic hysteresis plots of fluid exit temperature, solid exit temperature and reactant conversion against feed inlet temperature for

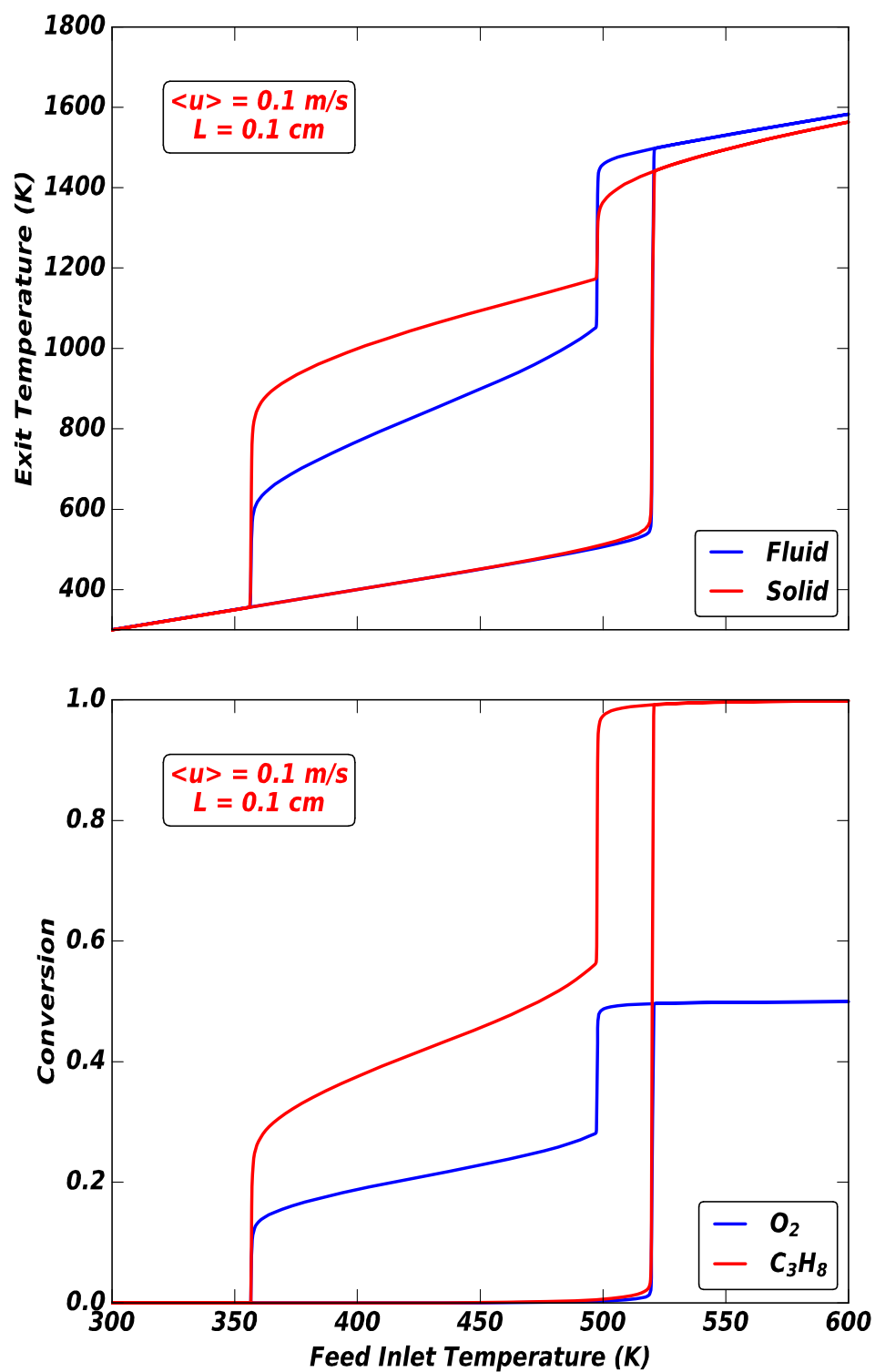


Figure 3.5: Fluid and solid exit temperatures (top) and reactant conversion (bottom) during ramp up and ramp down.

case (a). This diagram should be compared with the bottom left diagram of fig. 3.2 computed using the short monolith limit. Since the heat Peclet number for this case is small, we expect very little impact of the axial gradients on the location of the ignition and extinction points. We note that the bifurcation diagram is qualitatively the same and even the quantitative differences are small. Further, because of the strong coupling between the catalytic and homogeneous reactions (due to short length and/or low axial heat Peclet number), upon ignition of the catalytic reaction, the system jumps directly to the high temperature branch where fuel conversion is very high (and this case is an example of catalytically assisted homogeneous ignition). When the inlet temperature is varied slowly, we do not notice the second ignition (of the homogeneous reaction) as this point lies to the left of the first ignition. However, when the inlet temperature is reduced slowly, we do notice two extinctions, first that of the homogeneous and later that of the catalytic at lower temperatures. This strong coupling case is fundamentally different from the next two cases discussed below, though the space time is the same in all cases.

Fig. 3.6 shows the dynamic hysteresis plots of fluid exit temperature, solid exit temperature and reactant conversion against feed inlet temperature for case (b). Upon ignition of the catalytic reaction at 520 K, though the system goes to a high temperature branch (fluid at 1100 K and solid at 1200 K), the fuel conversion only reaches about 60%. The thermally coupled homogeneous reaction does not exhibit another ignition but assists in later part of the fuel conversion. Although the phase diagram in fig. 3.1 (for short monolith model) suggests the presence of hysteresis in both catalytic and homogeneous reaction at $y_{A,in} = 0.02$ and $t_c = 10 \text{ ms}$, ignition-extinction can be

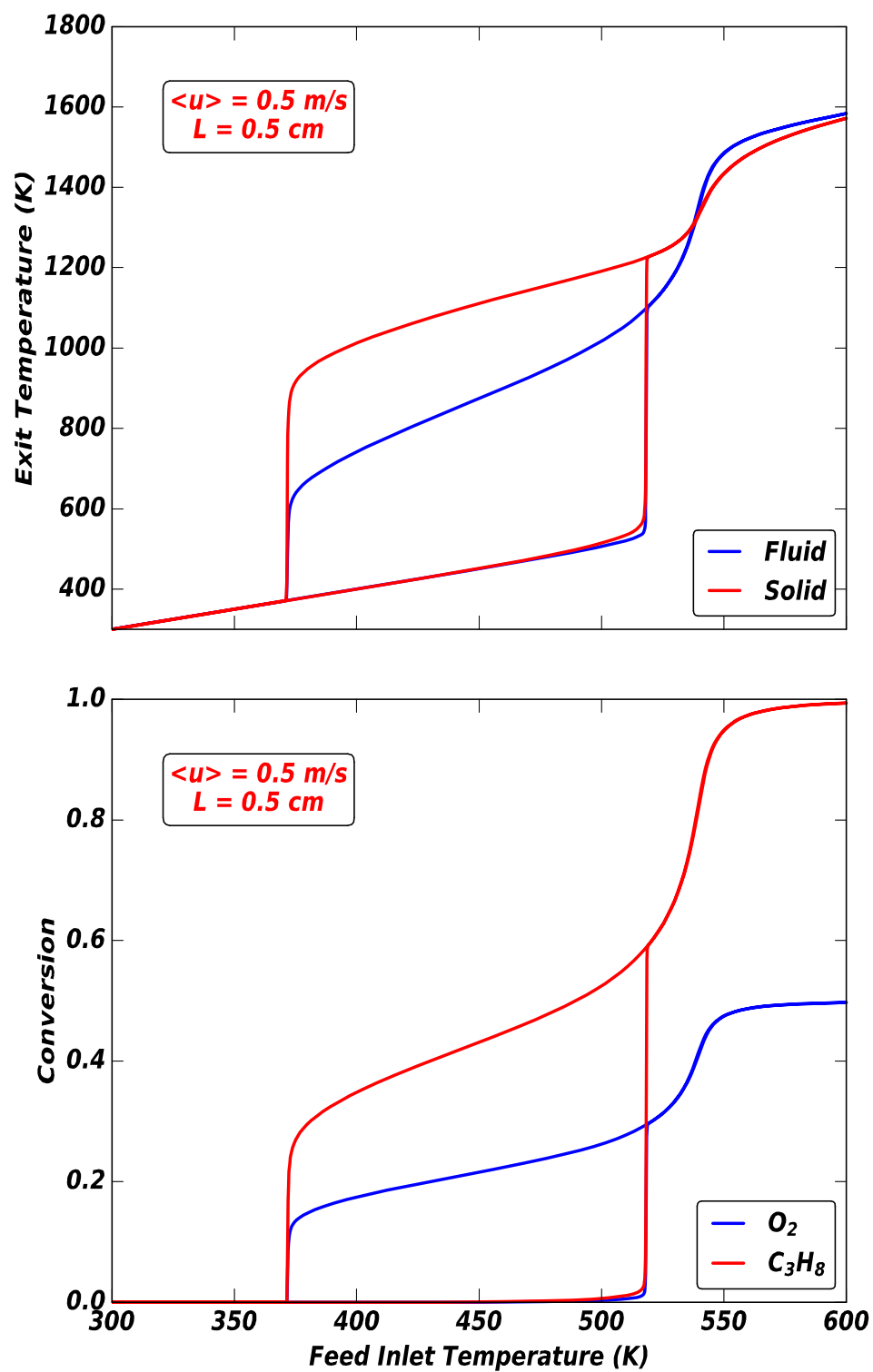


Figure 3.6: Fluid and solid exit temperatures (top) and reactant conversion (bottom) during ramp up and ramp down.

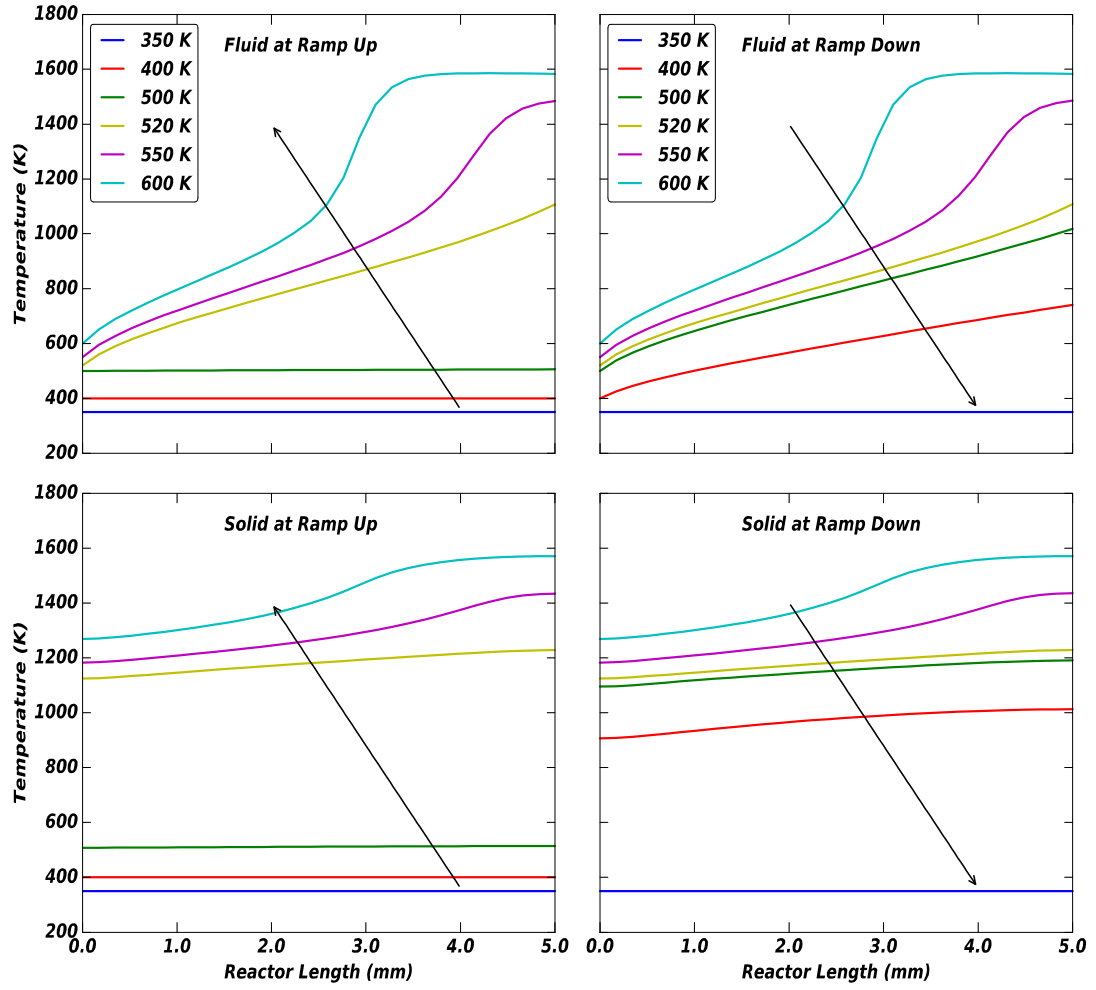


Figure 3.7: Temperature profiles of fluid and solid at different fluid inlet temperatures during ramp up and ramp down.

only observed in catalytic reaction in this case. This is due to the axial gradients and the effect of mass and heat Peclet numbers ($Pe_{h,eff} > 1$) on the region of hysteresis. Longer channel (high Peclet number) reduces the extent of reactor level thermal and species backmixing, thereby resulting in a decrease of the width of hysteresis, while exhibiting stronger gradients inside the reactor. This can be also confirmed from the spatial temperature profiles shown in fig. 3.7. In spite of the higher conductivity, there is a gradual gradient in the solid temperatures along the length of reactor. This effect is more amplified as the length of the channel and Peclet numbers are increased. As shown in fig. 3.8, when the $Pe_{h,eff}$ is increased further by 16 times (by increasing both the length of the reactor and inlet velocity by 4 times and keeping all other parameters fixed), the extinction temperature of the catalytic reaction increases by 50 K, while further shrinking the region of hysteresis. Also, the amount of fuel converted through the initial catalytic ignition (52%) is lower than the prior case. At such high value of Peclet numbers, the solid phase exhibits significantly pronounced gradients as shown in fig. 3.9.

In this context, it is relevant to note that the velocity $\langle u \rangle$, is taken as an average value over temperature and the space time along with Peclet numbers are calculated accordingly. However, the reduced order model can be extended to include the variation of velocity with state variables as well. In that case, it is necessary to pay attention while comparing the qualitative features of the dynamic hysteresis curve against the phase diagram, since the latter is constructed using average values. For example, if we take a linear dependence of velocity with temperature $\left(\langle u \rangle = \langle u \rangle_{in} \frac{T_f}{T_{in}} \right)$ and define space time based on inlet conditions ($t_{c,in}$), the average space time will be

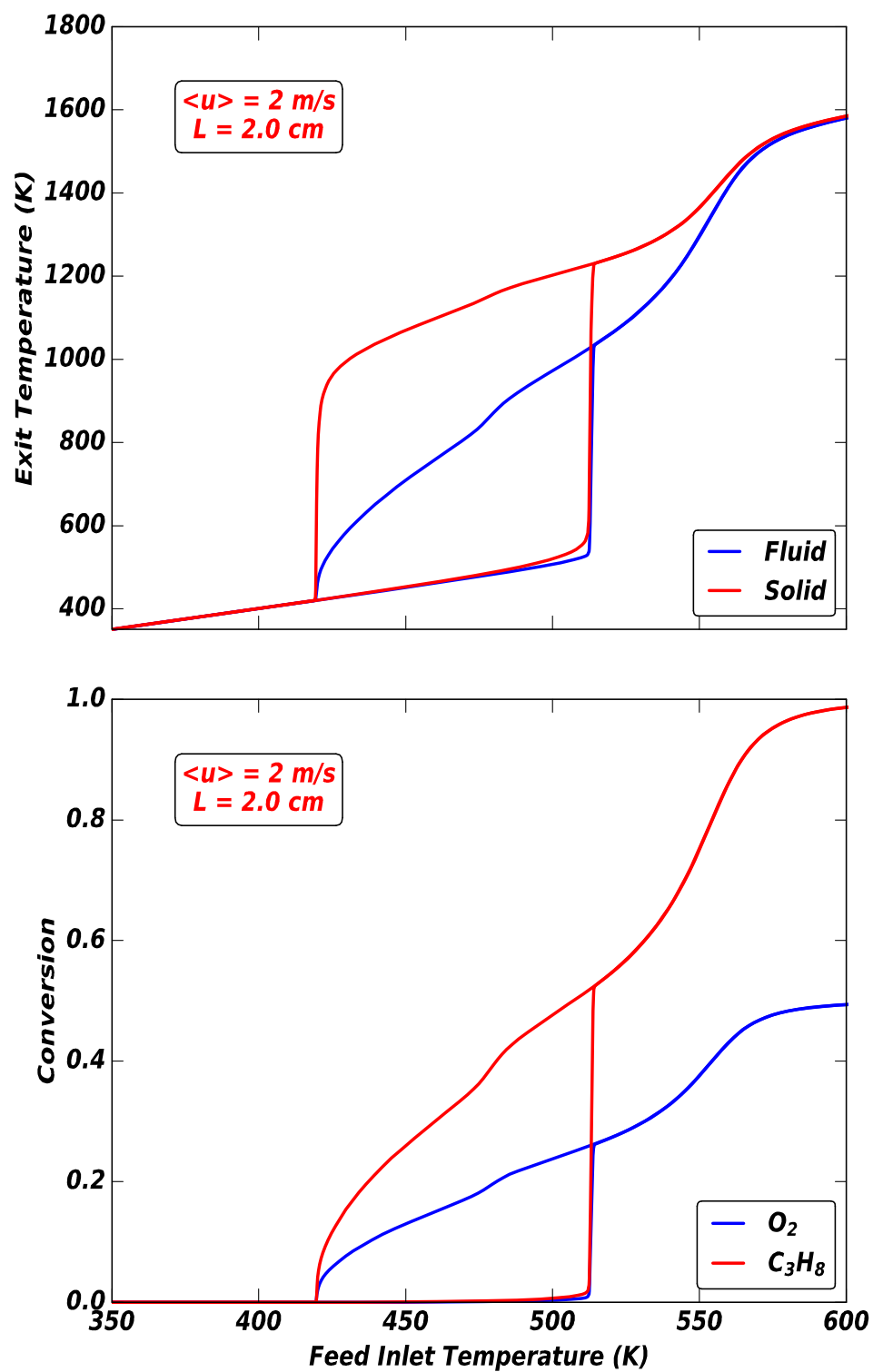


Figure 3.8: Fluid and solid exit temperatures (top) and reactant conversion (bottom) during ramp up and ramp down.

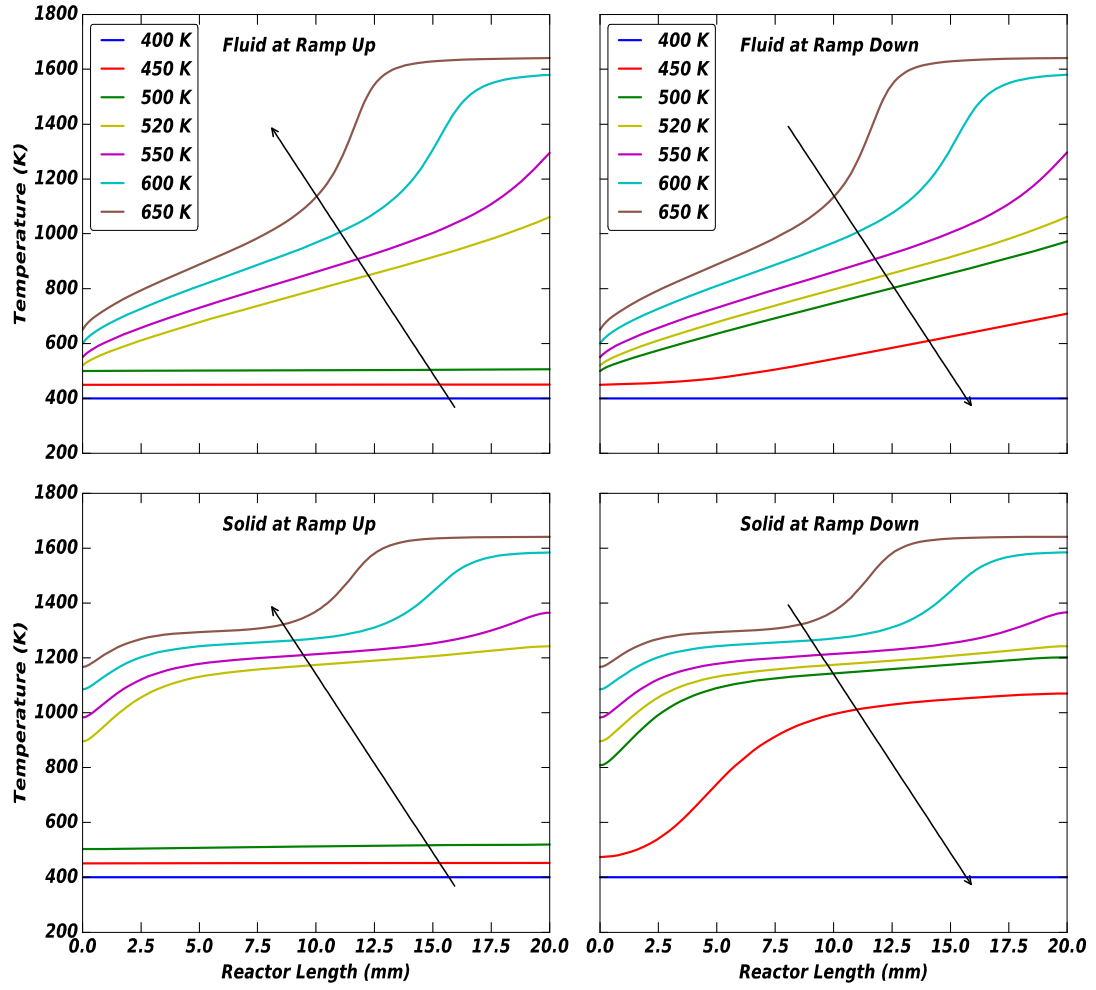


Figure 3.9: Temperature profiles of fluid and solid at different fluid inlet temperatures during ramp up and ramp down.

2-3 times lower than $t_{c,in}$. The bifurcation features of this result will actually map to that of the average space time in the phase diagram.

3.2 Summary

To conclude, we have compared the phase diagrams of catalytic and thermally coupled homogeneous reactions of propane oxidation against two cases - one in presence of washcoat diffusion and the other with just wall reaction without any diffusional barrier. Our results show that the presence of washcoat diffusion shrinks the region of multiplicity for the catalytic reaction and expands the same for the homogeneous reaction. At lower channel hydraulic radius (higher surface to volume ratio) the catalytic reaction dominates over the homogeneous counterpart. As a result the hysteresis region of the latter shrinks and moves further up towards higher inlet mole ratios and lower space times.

We also showed that the width of the hysteresis in the bifurcation diagram depends on the extent of thermal backmixing. At a fixed space time, increasing the length and axial velocity decreases the extents of heat and mass backflow which eventually reduces the overall width of hysteresis. Also, under such conditions, hysteresis is primarily observed in the catalytic reaction only. The homogeneous reaction just lights-off to assist in later stages of fuel conversion without exhibiting any multiplicity. Therefore, one way to ensure simultaneous ignition of the catalytic and homogeneous reaction is through the use of shorter channels with high conductivity substrates so that there is strong backmixing of both heat and mass in the reactor.

Chapter 4

Bifurcation analysis of catalytically assisted hydrogen combustion

4.1 Introduction

In the last chapter, we primarily focused on the aspects of washcoat diffusion and reactor length and studied how they impact the bifurcation features of adiabatic propane combustion. Here, we take a deeper look and investigate a gamut of various design and operating parameters such as inlet fuel composition, hydraulic diameter of the monolith channel, catalyst loading, washcoat pore diffusion, reactor length, substrate conductivity and external heat losses to surroundings. Also, the role of Lewis number, which is defined as the ratio of thermal diffusivity to mass diffusivity, is highlighted here. For this purpose we have chosen hydrogen as the fuel in this study. Unlike propane, hydrogen has a Lewis number less than unity, because of which it exhibits interesting features of major importance within the context of reactor design.

The main objective of this work is to explore the space of design and operating variables to determine the best monolith reactor configuration(s) for carrying out catalytically assisted combustion of hydrogen. To achieve this, we use bifurcation theory

to construct phase diagrams in the plane of feed composition vs. feed temperature (and feed composition vs. space time) that classify the different types of ignition and extinction behaviors occurring in the catalytically assisted combustion of hydrogen.

4.2 Literature review

Experimentally, Williams et al. [45] studied bifurcation behavior of various fuels over platinum foils and observed two ignitions, one extinction and one autothermal steady-state with propane. Using a stagnation-point flow model, Song et al. [46] matched these experimental results with simplified global kinetics. Vlachos and co-workers ([47] - [49]) investigated the ignition-extinction features in homo/-hetero combustion of hydrogen over platinum surface using stagnation flow. Using bifurcation theory, Russo et al. [50] investigated both steady state and dynamic stability features of lean combustion of propane-hydrogen mixtures in presence of heat losses. Only homogeneous reactions were considered in their work. Norton et al. [51] observed self-ignition of hydrogen and hydrogen assisted propane/air mixtures in catalytic platinum based micro-devices. It was concluded that small fractions of hydrogen in feed can result in self-ignition of propane, whereas higher hydrogen concentrations can lead to faster startup of the system. More recently, Pan et al. [52] showed hysteresis phenomena of H_2 /Air mixtures experimentally in a micro-catalytic combustor and studied the effects of various operating conditions on the bifurcation behavior. They also performed numerical simulation to compare the axial temperature profiles against their experimental results, however modeling of the particular hysteresis phenomena observed was not pursued.

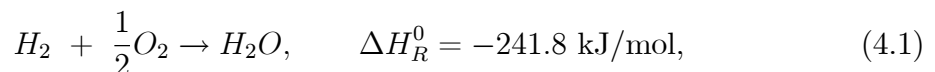
There has also been a large volume of work published using computational fluid dynamics (CFD). Appel et al. [53] performed both experimental and numerical studies on catalytically stabilized hydrogen combustion using a hierarchy of chemistry models and found the best predictions of homogeneous ignition distances with elementary reaction mechanisms. Stefanidis et al. [54] analyzed the impact of reactor gap size, feed composition, inlet velocity and heat loss on the extinction and blowout limits of propane combustion using a two-dimensional CFD model with global chemistry. Both these CFD studies considered wall type reactions with negligible washcoat diffusional limitations. Also, higher values of axial Peclet number, which is defined as the ratio of convective to diffusive rates, were chosen. Kaisare and co-workers ([40],[55]) studied steady state ignition and transient start-up behavior in a microreactor with catalyst segmentation. Karaginniadis et al. [56] demonstrated the effect of pressure, channel confinement and wall conductivity on the stability maps, drawn in the plane of heat transfer coefficient and inlet velocity, for both propane/air and methane/air combustion in a microreactor. The effect of wall conductivity on the interaction of homo-/hetero hydrogen combustion and flame stability are also elucidated by Chen et al. [57] through CFD simulations. Similar numerical and experimental studies are performed with methane and hydrogen assisted methane fuels as well ([58]-[60]).

Though, these studies provide useful mechanistic details on the synergy between thermal effects and homo-/hetero reaction chemistry, a comprehensive analysis of the various bifurcation features in the multi-dimensional parameter space in presence of washcoat diffusion is missing. CFD models coupled with detailed micro-kinetic reaction mechanism are powerful to study single, specific solutions in great detail.

However, due to their mathematical complexity, they are not amenable for bifurcation analysis and hence not useful in determining the non-linear features of scaled-up systems. Additionally, the studies on ignition-extinction behavior addressed by Song et al. [46] and Vlachos and co-workers ([47] - [49]) used simplified stagnation-point flow model, which is not realistic for relevant industrial applications. Earlier studies of Alam et al. and Sarkar et al. ([17], [24]) have examined bifurcation phenomena for the case of propane oxidation in a monolith reactor under adiabatic conditions using reduced order models. In this chapter, we extend our earlier work and analyze the case of catalytically assisted lean hydrogen combustion. Also, the impact of external heat losses is examined to explore the possible existence of additional bifurcation features (e.g., isola and mushroom type bifurcation diagrams).

4.3 Kinetic model

We used a global kinetic model for hydrogen combustion with a single step mechanism for both catalytic and homogeneous phases. The overall reaction for complete combustion of hydrogen in air is given by



where, the volumetric rate of the homogeneous reaction in the flow channel is taken from Marinov et al. [61] as

$$r_h = k_{0h} \exp \left[-\frac{E_h}{RT_f} \right] c_{H_2} c_{O_2}^{0.5} \quad (4.2)$$

and that of the heterogenous reaction over a supported Pt catalyst (washcoat) is obtained from Schefer et al. [62] and given by

$$r_c = a_c k_{0c} \exp \left[-\frac{E_c}{RT_w} \right] c_{H_2}. \quad (4.3)$$

Here, a_c is the active (exposed) surface area of platinum catalyst available for reaction per unit volume of the washcoat, which can be estimated from the catalyst loading, dispersion and other catalyst bulk properties. It is well known that hydrogen oxidation over Pt is very fast even at room temperatures [63]. In order to keep the ignition temperature close to ambient, we have chosen a nominal value of 1000 m² Pt/m³ of washcoat for a_c as the base case, which corresponds to a catalyst loading of <0.05 m² Pt/gm of washcoat. The various kinetic and transport parameters used in this model are listed in Table 4.1.

For the above kinetic model of the catalytic reaction, the activation energy E_c equates to 14.9 kJ/mol. In the literature, the activation energy of Pt-catalyzed hydrogen oxidation is found to vary over a wide range (7 - 45 kJ/mol). Joshi et al. [63] studied hydrogen oxidation on Pt/Al₂O₃ monolithic catalyst and observed an activation energy of 44.6 kJ/mol with fresh catalyst. On another study, Bhatia et al. [64] computed the activation energy to be 8.7 kJ/mol for Pt catalyst in a monolith reactor. Based on the experimental observations in a packed bed reactor, Younis [65] calculated an activation energy of 9.4 kJ/mol. More recently, Nguyen et al. [66] performed catalytic hydrogen combustion on Pt washcoated cordierite monolith and reported an activation energy of 12.1 kJ/mol. The activation energy used in our study

Table 4.1: List of parameters for hydrogen combustion in short monolith model

Parameter	Unit	Value
k_{0h}	$\text{mol}^{-0.5}.\text{m}^{1.5}.\text{s}^{-1}$	1.8×10^{10}
k_{0c}	m/s	14
E_h/R	K	17609
E_c/R	K	1792
a_c	$\text{m}^2 \text{ Pt/m}^3 \text{ washcoat}$	$10^3, 10^4 \text{ or } 10^5$
R_{Ω_f}	μm	250 or 1000
$R_{\Omega_{wc}}$	μm	50
R_{Ω_w}	μm	140
D_{f,H_2}	m^2/s	$3.40 \times 10^{-9} \frac{T_f^{1.75}}{P}$
D_{f,O_2}	m^2/s	$9.23 \times 10^{-10} \frac{T_f^{1.75}}{P}$
D_{f,H_2O}	m^2/s	$1.18 \times 10^{-9} \frac{T_f^{1.75}}{P}$
α_f	m^2/s	$9.80 \times 10^{-10} \frac{T_f^{1.75}}{P}$

lies on the lower end of the reported values. Also, the catalytic reaction is taken as first order with respect to hydrogen and zero order in oxygen. This is a reasonably fair assumption since only lean mixtures of hydrogen is considered here and is also consistent with some of the aforementioned experimental findings ([63], [66]).

4.4 Steady-state bifurcation analysis of short monolith model

We analyze the steady-state bifurcation behavior of the short monolith (SM) model by solving eqns. (2.54-2.57) numerically. As discussed earlier, one of the main objectives of this study is to construct a phase diagram in the plane of inlet fuel composition and other state variables like space time or feed temperature. Typ-

ically, in the combustion literature the inlet fuel composition is expressed in terms of equivalence ratio, φ , which is defined as the ratio of fuel/air in the feed to the stoichiometric fuel/air ratio. For the case of hydrogen, the relation between inlet fuel mole fraction and equivalence ratio can be expressed by

$$\varphi = \frac{c_{f,H_2}^{in}}{2c_{f,O_2}^{in}} \quad (4.4)$$

$$\text{and } y_{f,H_2}^{in} = \frac{2\varphi}{1 + 2\varphi + \frac{79}{21}}. \quad (4.5)$$

Before diving deep into the thermally coupled case of homo-/hetero combustion, we first consider the limiting cases where only catalytic or only homogeneous reaction is present. The insight gained from these simpler cases are useful in fully understanding the bifurcation behavior of the coupled case. The various bifurcation diagrams with feed temperature or space time as the bifurcation parameter are examined and suitable operating regimes for catalytically assisted combustion applications are identified in the phase diagram. The roles of various design variables such as the channel hydraulic radius, washcoat properties and catalyst activity on the bifurcation features are also elucidated. Afterwards, we focus on including heat losses and analyze the existence of additional stable steady-states.

4.4.1 Homogeneous or catalytic reaction only

Fig. 4.1 shows the hysteresis locus of lean hydrogen oxidation in the plane of equivalence ratio vs. space time when only the catalytic reaction or only the homogeneous reaction is present using a short monolith reactor model with $R_{\Omega_f} = 250 \mu m$.

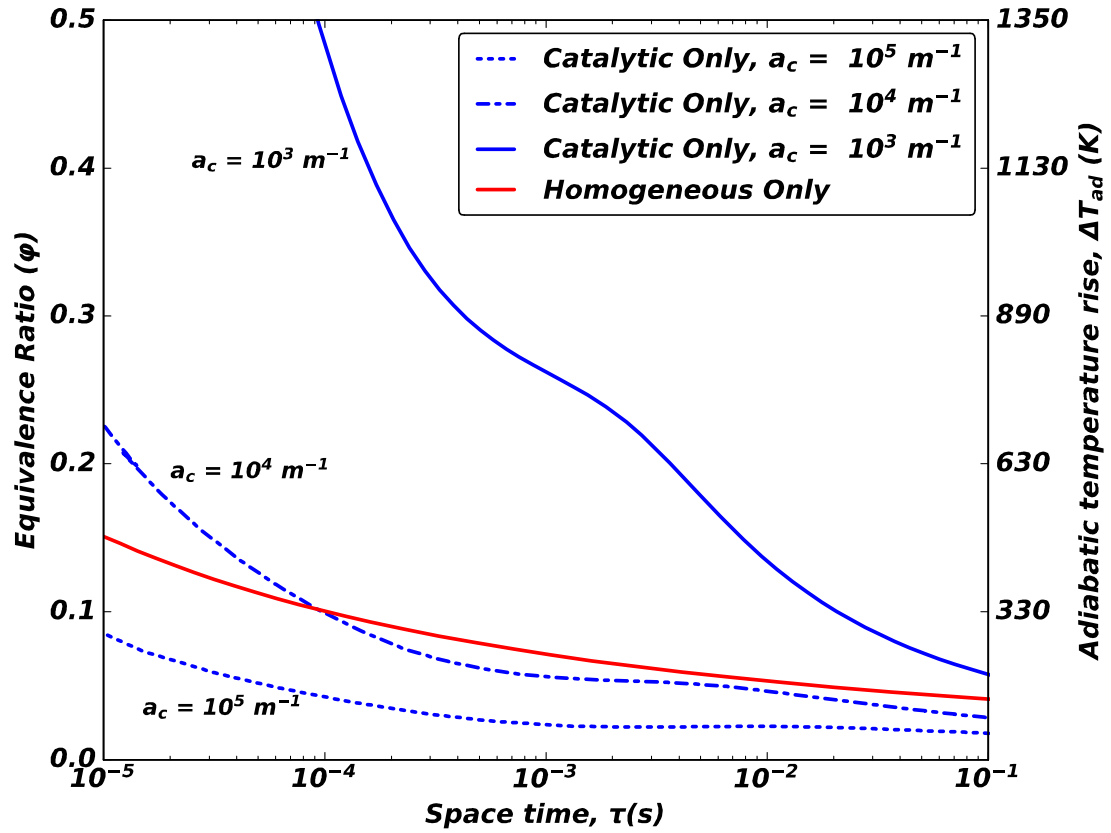


Figure 4.1: Computed hysteresis loci for adiabatic lean combustion of hydrogen with either only catalytic (at 3 different catalyst activities) or only homogeneous reaction present.

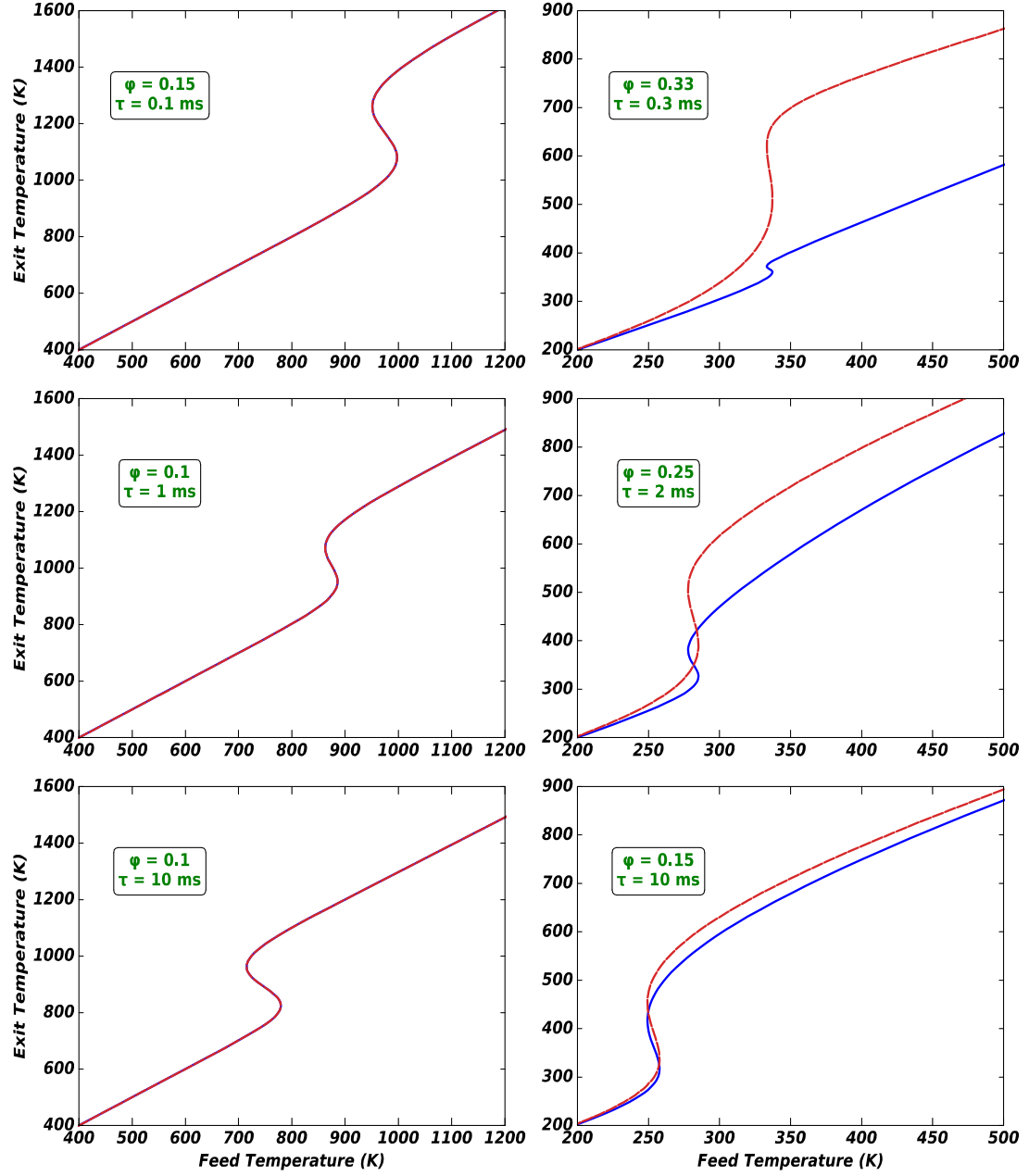


Figure 4.2: Bifurcation diagrams of exit fluid and solid temperature vs. feed temperature for hydrogen combustion with only homogeneous reaction (left) and with only catalytic reaction (right).

Along with our base Pt loading case ($a_c = 10^3 \text{ m}^{-1}$), we have also included the catalytic hysteresis loci at two higher loadings ($a_c = 10^4$ and 10^5 m^{-1}). Any combination of equivalence ratio and space time above the hysteresis loci will result in a S-shaped bifurcation diagram of exit temperature or conversion with respect to feed temperature. However, the region below the hysteresis loci will just lead to a single-valued light-off behavior. The adiabatic temperature rise associated to the equivalence ratios are calculated with a gas inlet temperature of 300 K and labeled in the right hand side axis. Typical bifurcation diagrams of exit fluid and solid temperatures for both the homogeneous and the catalytic only cases (at the base Pt loading) are shown in fig. 4.2. The left column corresponds to the case when only homogeneous reaction is present, whereas the right column represents the catalytic only case. This distinction between the homogeneous only and catalytic only cases can also be clearly determined from the relative rise in fluid and solid temperatures. [The fluid temperatures are given by solid blue lines whereas the dashed red lines represent solid temperatures]. Upon ignition of the catalytic reaction, the solid temperature reaches a higher value than the fluid temperature. On the contrary, there is practically no difference between the solid and fluid temperatures upon the ignition of homogeneous reaction. Furthermore, it is to be noted that increasing the space time shifts the bifurcation diagrams to the left while decreasing the ignition temperature.

Although the homogeneous hysteresis locus lies below the catalytic hysteresis locus for $a_c = 10^3 \text{ m}^{-1}$, the homogeneous reaction requires much higher temperature to ignite ($\sim 800 \text{ K}$) than the catalytic reaction, the ignition temperature of which is close to the ambient. This implies that the catalytic reaction will dominate over

the homogeneous chemistry in a coupled homo-/hetero system and will always ignite first for any choice of equivalence ratio and space time above the catalytic hysteresis locus. However, at lower space times (< 1 ms), while the catalytic reaction is ignited, the fuel conversion on the ignited branch can be smaller due to external diffusional limitations. Under such circumstances, the homogeneous reaction can assist in the later stages of fuel conversion when both the homogeneous and catalytic reactions are present. [We will revisit this topic while discussing the thermally coupled case in a later section]. Further, it is found that increasing the space time decreases the ignition temperature. Therefore, along the hysteresis locus, as the equivalence ratio decreases and space time increases, the corresponding inlet temperature decreases monotonically.

As the catalytic loading/activity is increased from 10^3 to 10^5 m^{-1} , the catalytic hysteresis locus shifts downwards to lower values of space time and equivalence ratio, thereby expanding the region of multiplicity. At $a_c = 10^5$ m^{-1} , it is interesting to note that the hysteresis locus of catalytic reaction lies completely below that of the homogeneous reaction. This suggests that the catalytic reaction will always dominate the homogeneous chemistry, even with extremely small values of space time, when the chosen catalytic activity is high. On the contrary, at lower loadings, this dominance of catalytic reaction over the homogeneous counterpart can only be observed at relatively higher space times.

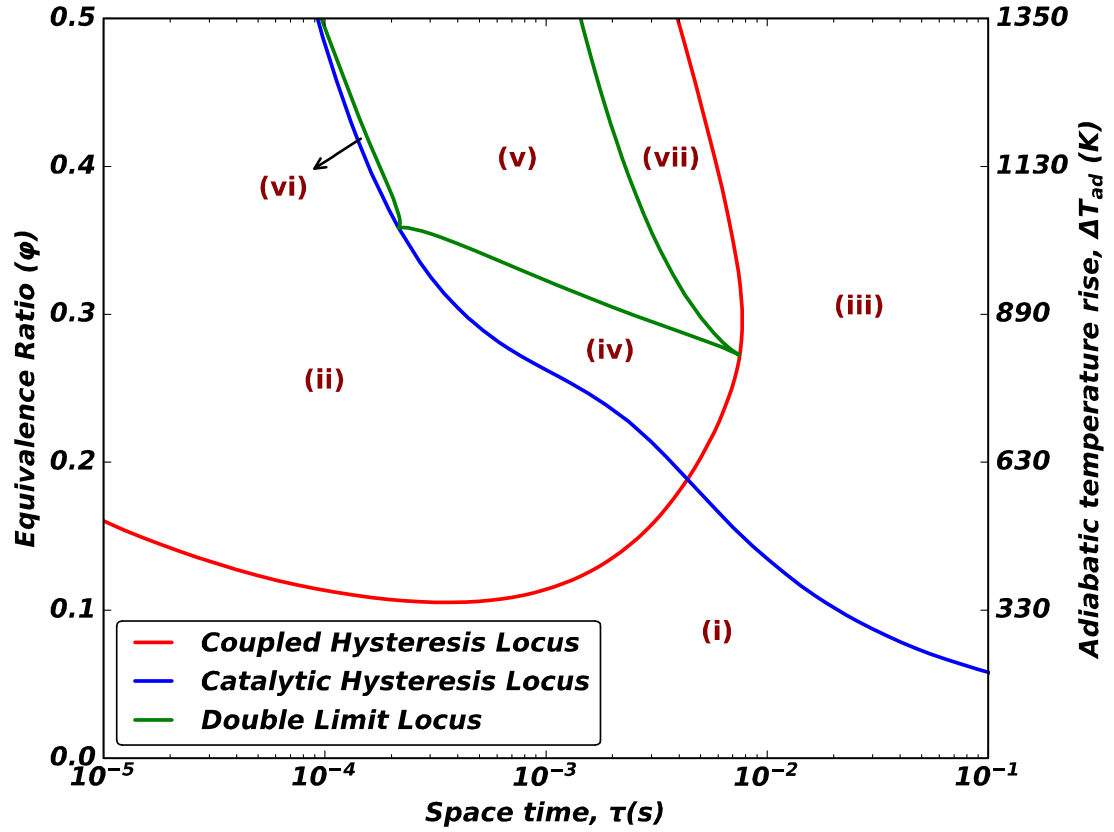


Figure 4.3: Computed phase diagram for adiabatic lean combustion of hydrogen with both catalytic and homogeneous reactions present in equivalence ratio vs. space time plane.

4.4.2 Thermally coupled system under adiabatic conditions

For the base Pt loading case, the hysteresis loci of the thermally coupled system in the plane of equivalence ratio vs. space time are illustrated in fig. 4.3. In comparison to the previously discussed standalone catalytic or homogeneous cases, here the thermally coupled hysteresis locus is non-monotonic and moves upwards towards higher equivalence ratios at intermediate space times (1 - 10 ms). At lower space times (0.1 - 5 ms) and higher equivalence ratios (0.2 - 0.5), though the catalytic reaction ignites first and results in ignition-extinction type behavior at lower feed temperatures, the

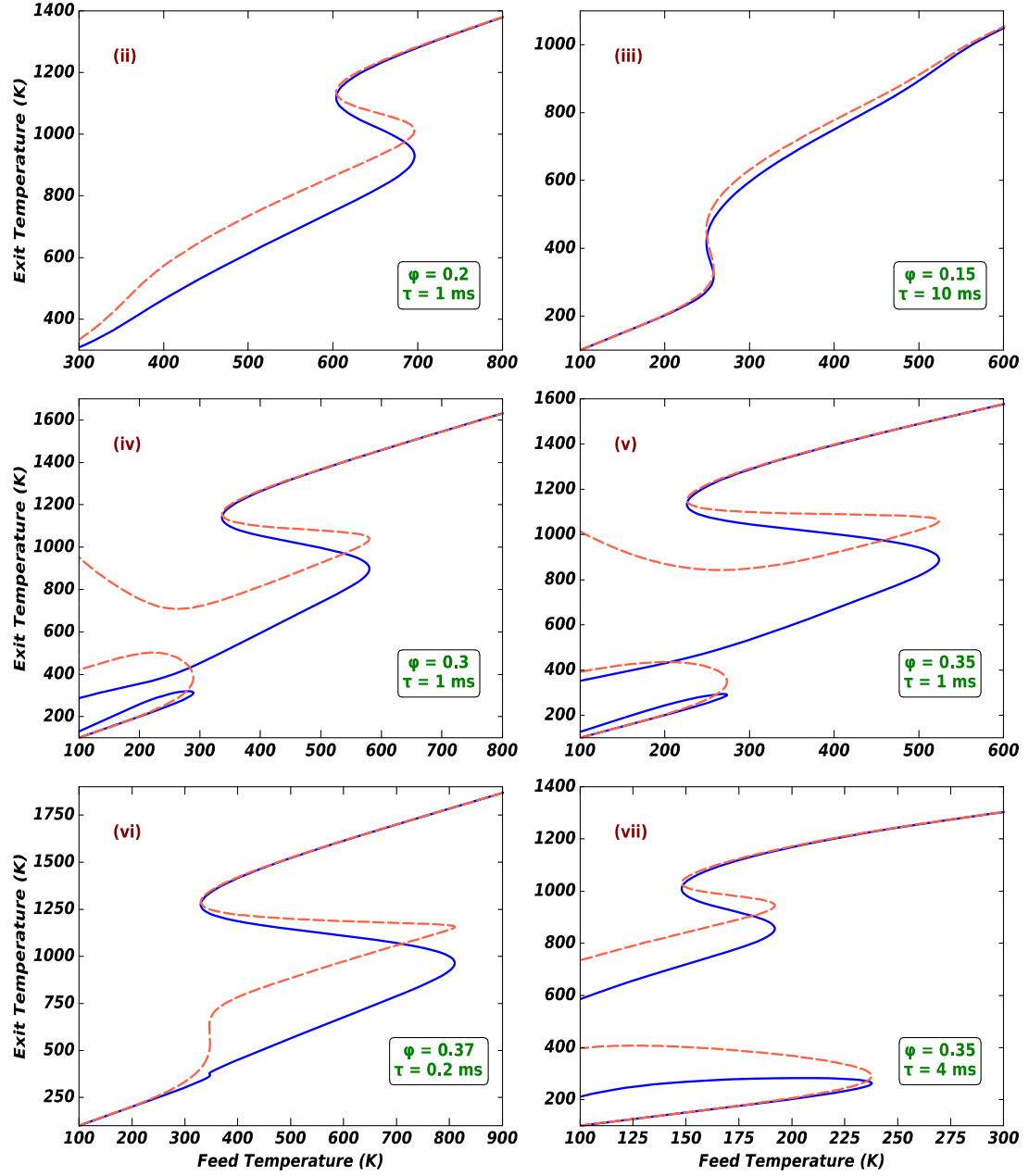


Figure 4.4: Bifurcation diagrams of exit fluid (T_f) and solid temperature (T_w) vs. feed temperature ($T_{f,in}$) for adiabatic lean combustion of hydrogen.

conversion on the ignited branch is low due to diffusional (external mass transfer) limitations. The unreacted fuel then gets converted by the thermally coupled homogeneous reaction, which may lead to a second ignition at a higher fluid temperature. Therefore, in the parameter space between the catalytic and the thermally coupled hysteresis loci ($0.1 \text{ ms} < \tau < 10 \text{ ms}$, $0.2 < \varphi < 0.5$) double S-shaped bifurcation diagrams with two ignition and two extinction points are obtained. The relative positions of the thermally coupled ignition/extinction points with respect to that of the catalytic ones further classify this parameter space into 4 regions. The distinctions between these regions can be well understood from the respective bifurcation diagrams shown in fig. 4.4. In region (iv), both the ignition and extinction points of the homogeneous reaction lie ahead of the catalytic ignition point, whereas in region (v), the extinction feed temperature of the homogeneous reaction is lower than the catalytic ignition feed temperature. The line that demarcates these two regions is known as the *double limit locus*. For this particular case, it signifies the locus of equivalence ratio and space times at which the actual value of the catalytic ignition feed temperature exactly matches with the thermally coupled extinction feed temperature. In region (vi), the second extinction point goes behind the first extinction point. Therefore, the double limit locus between region (v) and (vi) marks the locus of operating points where the two respective extinction feed temperatures coincide. It is important to note that in all these three regions, there is an intermediate stable branch between the catalytic and homogeneous ignition where fluid temperatures and conversions are low. However, in region (vii), the feed temperature at the ignition point of the thermally coupled reaction is lower than that of the catalytic reaction.

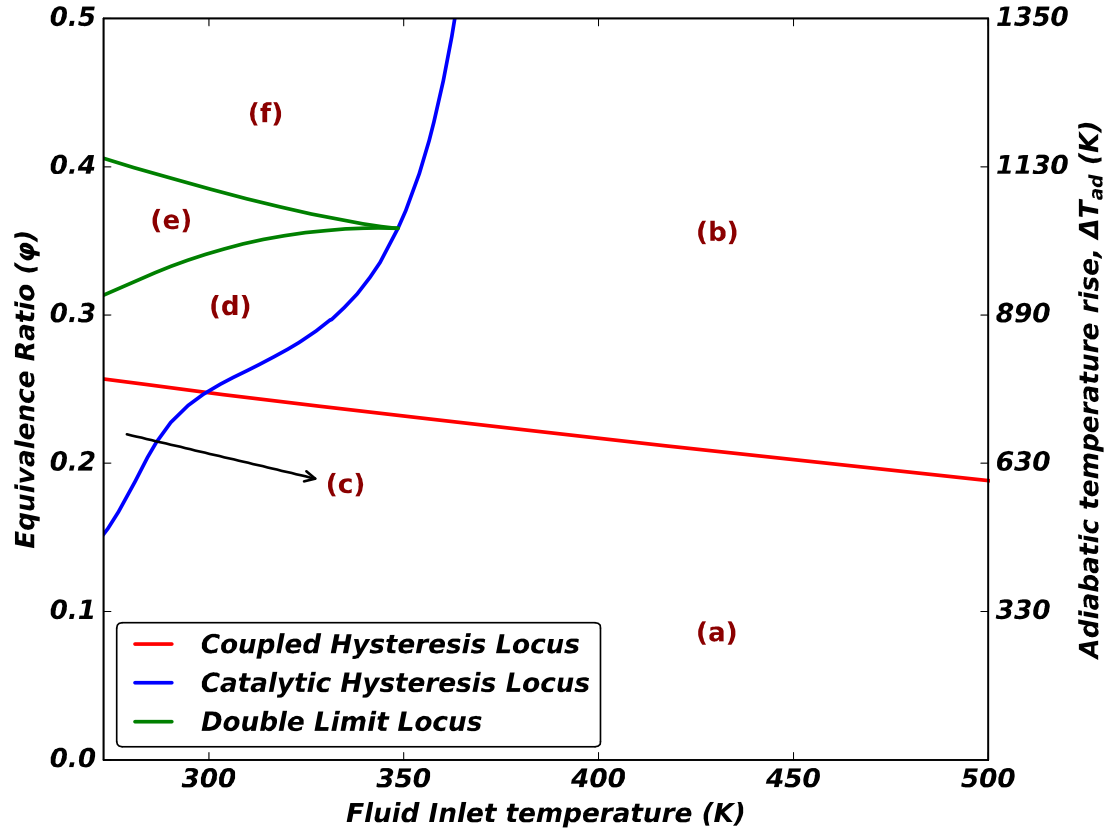


Figure 4.5: Computed phase diagram for adiabatic lean combustion of hydrogen with both catalytic and homogeneous reactions present in equivalence ratio vs. feed temperature plane.

Therefore, in this case, there is a simultaneous ignition of both catalytic and homogeneous chemistries at a lower feed temperature after which the system jumps to the high temperature/conversion branch. Naturally, the double limit locus between region (v) and (vii) represents the set of points where the ignition feed temperatures of both catalytic and thermally coupled homogeneous reactions are exactly same. The ignition-extinction phenomenon at lower space times (region ii) is primarily dominated by the homogeneous reaction, whereas that at higher space times (region iii) is due to the catalytic reaction, both resulting in one pair of ignition-extinction type behavior.

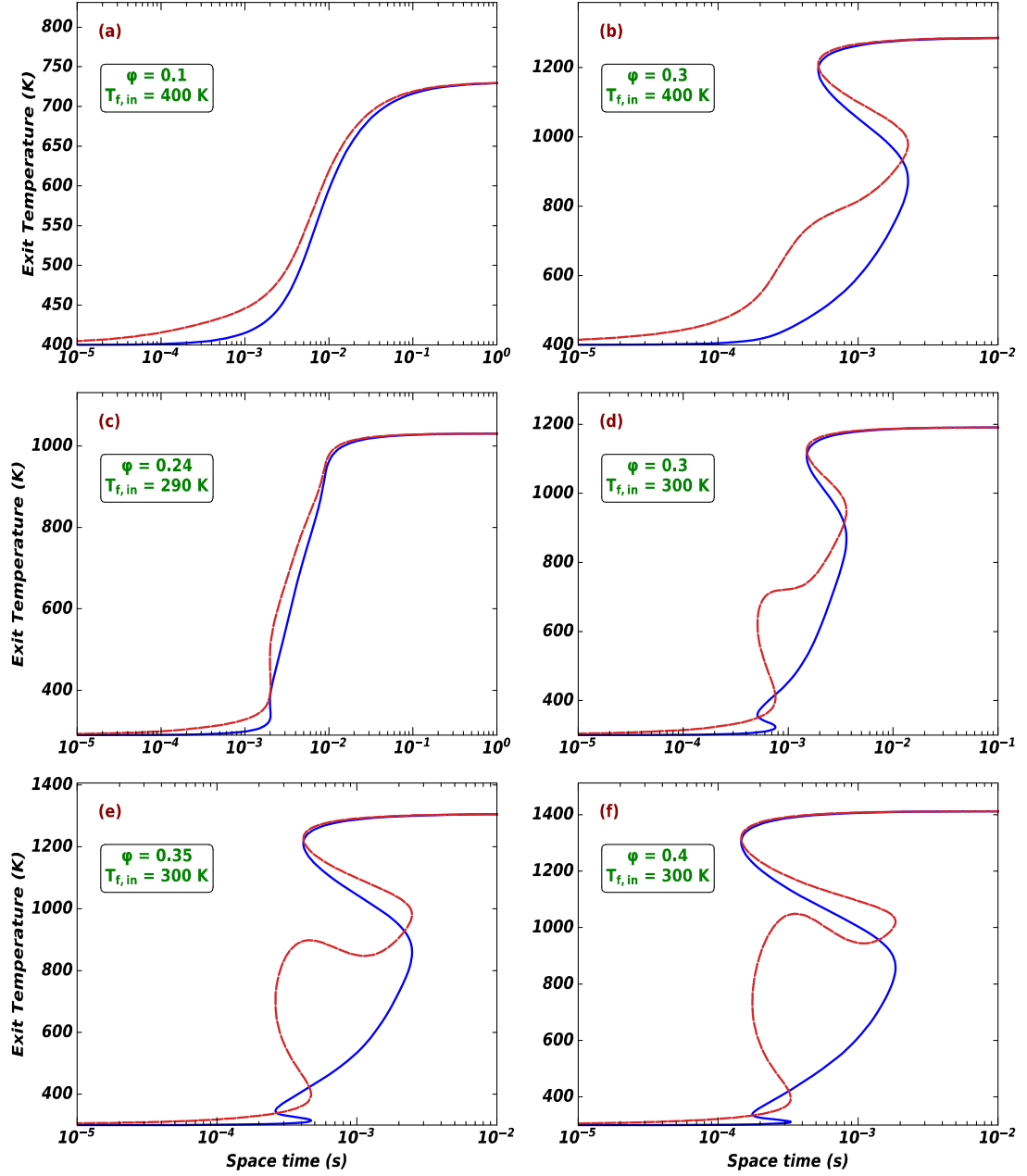


Figure 4.6: Bifurcation diagrams of exit fluid (T_f) and solid temperature (T_w) vs. space time (τ) for adiabatic lean combustion of hydrogen.

The feed temperature along the two hysteresis loci are plotted in fig. 4.5 and can serve as the respective hysteresis loci when space time is the bifurcation parameter. The two hysteresis and double limit loci classify the parameter space of equivalence ratio and feed temperature into six regions, each exhibiting a different kind of bifurcation behavior. Typical bifurcation diagrams of fluid and solid temperatures with space time as bifurcation parameter for the six different regions are shown in fig. 4.6. Any combination of equivalence ratio and feed temperature from region (a) in the phase diagram, which is below the catalytic and thermally coupled hysteresis loci, does not manifest in ignition-extinction behavior, and only shows singled valued light-off behavior. Both regions (b) and (c) exhibit one pair of ignition-extinction, however their natures are very different. Region (c) shows ignition-extinction behavior primarily because of the catalytic reaction only, whereas in region (b), it is due to the combination of both catalytic and thermally coupled homogeneous reactions. Again, this distinction can be identified from the relative rise in fluid and solid temperatures upon ignition. As shown in fig. 4.6, for a fixed equivalence ratio, $\varphi = 0.24$ and feed temperature, $T_{f,in} = 290$ K, which represents a point in region (c), the solid temperature reaches a higher value than the fluid temperature upon ignition, thereby signifying a catalytic ignition in this case. Here, the homogeneous reaction only assists in the later stages of fuel conversion and the system requires higher space time to reach complete conversion ($\tau \sim 10$ ms). On the contrary, for region (b), both the fluid and solid temperatures reach the adiabatic limit upon ignition as depicted in the fig. 4.6 with $\varphi = 0.3$ and $T_{f,in} = 400$ K. Hence, this ignition is due to the thermal coupling of the homogeneous and catalytic fuel conversion. Although, no catalytic

hysteresis is observed in the latter case, the solid temperature is found to be higher than that of the fluid before the ignition point, thereby suggesting active catalytic chemistry even at lower values of space time or just near the reactor entrance. It is due to this active catalytic chemistry, the thermally coupled homogeneous system ignites at such low space times (~ 2 ms) and can be maintained in an ignited state with much smaller space times (~ 0.5 ms), till the extinction point is reached.

In this context, it is noteworthy that, the behavior of the state variables at significantly small values of space time is kinetically controlled and that at higher values of space time is thermodynamically controlled. Therefore, at sufficiently high space times both the fluid and solid temperature reach the adiabatic flame temperature limit when there is no heat loss. The behavior at intermediate space times are due to the combined effects of kinetics and transport. Since the SM model is derived through axial averaging of the detailed model, the state variables are independent of spatial variations. However, qualitative insights on the spatial profiles can be derived when space time is taken as bifurcation parameter. As space time is directly proportional to reactor length for a fixed gas velocity, the bifurcation behavior along the reactor length is qualitatively similar to that computed with space time as bifurcation parameter.

Regions (d), (e) and (f) exhibit two pairs of ignition-extinction with the first one corresponding to the catalytic reaction, while the second one is due to the thermally coupled homogeneous reaction. Again, the relative position of the catalytic ignition-extinction points with respect to that of the coupled homogeneous reaction is the main difference among these 3 regions. In region (d), the extinction point of the thermally

coupled homogeneous reaction lies ahead of the catalytic ignition point, whereas in region (e) the actual value of space time required to extinguish the homogeneous reaction is lower than that required to ignite the catalytic reaction. The double limit locus that demarcates these two regions signifies the locus of fuel composition and space time where the actual values of catalytic ignition point is same as that of the homogeneous extinction point. Similarly, the upper double limit locus between regions (e) and (f) is the set of all equivalence ratios and space times for which the numerical values of space time required for extinction of both catalytic and thermally coupled homogeneous reactions are same. As we move from region (e) into region (f), the extinction point of thermally coupled homogeneous reaction crosses and goes behind the extinction point of the catalytic reaction. Additionally, upon extinction of the thermally coupled homogeneous reaction in regions (d) and (e), the system can still be maintained in a stable state where catalytic reactions are active. However, in region (f), the whole reaction system (both catalytic and homogeneous) quenches upon extinction of the thermally coupled homogeneous reaction.

4.4.3 Impact of channel hydraulic radius on thermal coupling

A closer look at the bifurcation diagrams representing regions (e) and (f) in fig. 4.6 reveal that the solid temperature decreases in the stable ignited branch upon ignition of the catalytic reaction, while the fluid temperature increases. This non-monotonicity of the solid temperature with respect to space time is due to the Lewis number effect. Hydrogen has a higher molecular diffusivity as compared to the thermal diffusivity of the fluid system, resulting in a Lewis number, $Le_f = \frac{\alpha_f}{D_f}$ around 0.3 in a lean

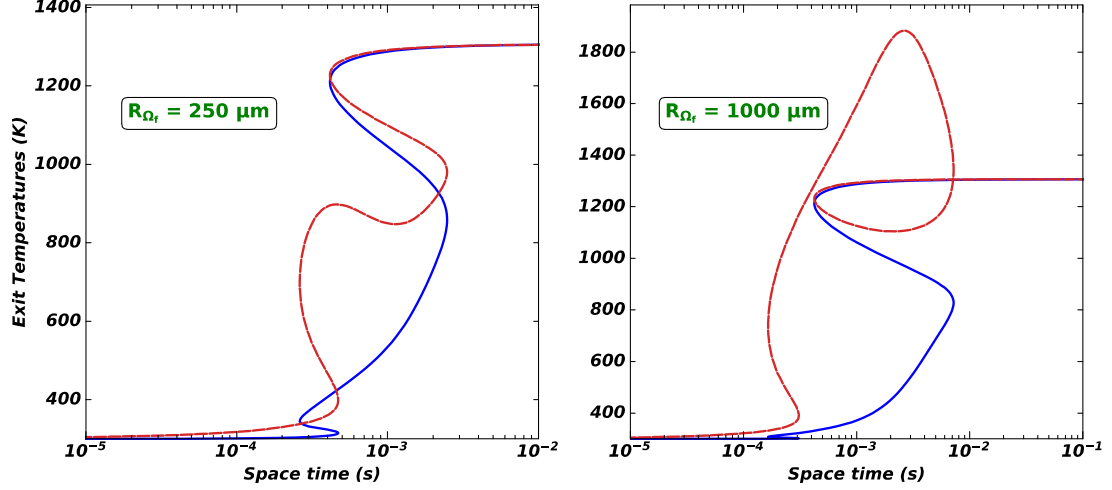


Figure 4.7: Bifurcation diagrams of exit fluid (T_f) and solid temperature (T_w) for adiabatic lean combustion of hydrogen with space time as bifurcation parameter.

mixture. Upon ignition of the catalytic reaction, the solid temperature goes to a very high value. However, due to the slower heat diffusion times, the increase in fluid temperature at the ignition point is considerably low, creating a large interfacial gradient in temperatures right after ignition. These gradients are further amplified at higher channel hydraulic radius. In fact, due to these relative differences in species and heat diffusion times, the solid temperatures can even go beyond the adiabatic temperature limit creating super-adiabatic hot spots right near the reactor inlet, as shown in fig. 4.7. Such hot spots can quickly deactivate the catalyst and hence caution should be exercised to avoid them. After the catalytic ignition, the solid catalyst acts like a heat source till the homogeneous reaction ignites. Therefore, as space time, τ increases, the fluid temperature increases while the solid temperature decreases. Finally, upon the ignition of the gas phase reaction, both solid and fluid reach the adiabatic limit.

In the limiting case where the catalytic reaction enters the external mass transfer controlled regime right near the reactor inlet ($\tau \rightarrow 0$), Alam et al. [17] showed that the surface temperature can be derived as

$$T_s = T_{f,in} + \frac{\Delta T_{ad}}{Le_f^{0.5}} \quad (4.6)$$

where, ΔT_{ad} denotes the adiabatic temperature rise and the exponent of the Le_f depends on the flow conditions at inlet. Following the above equation, it is evident that for fluid systems with $Le_f < 1$, the solid temperature can attain super-adiabatic values. In fact, for hydrogen combustion at an equivalence ratio of 0.35, eqn. 4.6 predicts a maximum surface temperature of 2125 K. In our calculations, the maximum solid temperature attained with a channel hydraulic radius of 1 mm is 1900 K, which compares fairly with the predicted value. Increasing the channel hydraulic radius will further increase this maximum value till the given predicted limit is reached. [Remark: The exponent on the Lewis number in eqn. 4.6 depends on the flow conditions in the channel. For developing flow, the exponent is 0.5 as shown above but changes to $\frac{2}{3}$ for fully developed conditions or parabolic velocity profile].

The impact of channel hydraulic radius on the hysteresis loci and thermal coupling between homo-/hetero reactions is demonstrated in fig. 4.8. At a fixed washcoat thickness and catalyst activity, as the channel hydraulic radius is increased from 250 μm to 1 mm, both the catalytic and thermally coupled hysteresis regions are found to expand, thereby enlarging the region of multiplicity. [The solid curves correspond to $R_{\Omega_f} = 250 \mu m$ and the dashed curves represent $R_{\Omega_f} = 1 mm$]. The expansion of the

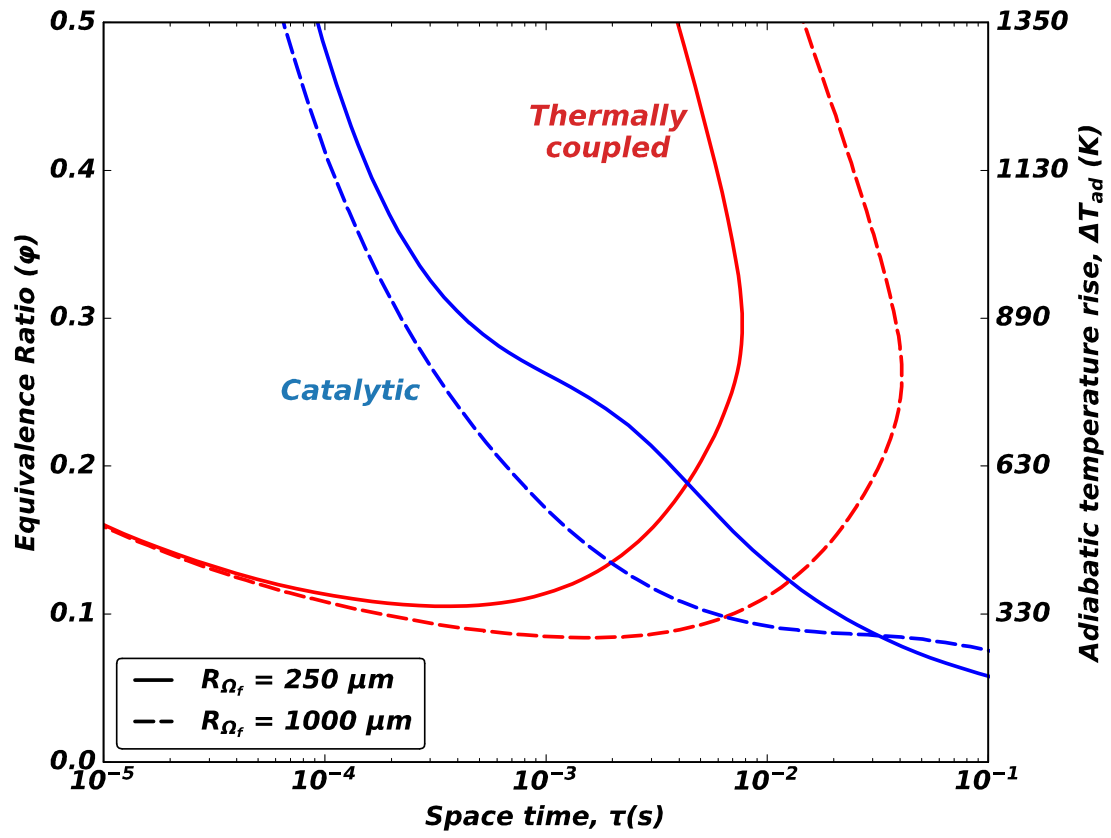


Figure 4.8: Comparison of catalytic and thermally coupled hysteresis loci for adiabatic lean hydrogen combustion at two different channel hydraulic radii.

catalytic hysteresis locus can be possibly attributed to the delay in heat propagation between the solid and fluid phases by transport processes. Even though catalytic hysteresis can be observed at lower space times for a fixed equivalence ratio with higher channel hydraulic radius, the fuel conversion through catalytic route will be significantly lower due to higher diffusion times (higher values of transverse Peclet number, P_{H_2}). Consequently, followed by the catalytic ignition, considerable amount of reactant will get converted through the homogeneous route at such higher channel radius, resulting in an expansion of the thermally coupled hysteresis region. It is also interesting to note that the intersection point of the catalytic and thermally coupled hysteresis loci moves right towards higher space time and lower equivalence ratio as the channel hydraulic radius is increased. The branch of the thermally coupled hysteresis locus left to the intersection point is primarily dominated by the homogeneous reaction, and hence is closer to the hysteresis locus for homogeneous reaction only.

4.4.4 Impact of washcoat properties

The catalyst loading and activity plays an important role in determining the actual NOx emissions in catalytically assisted combustion applications as shown by Basavaraju et al. [67]. In this subsection, we look into the impact of catalyst loading from the standpoint of bifurcation behavior and coupling effects between homo-/hetero reactions. Fig. 4.9 demonstrates the impact of a_c on the hysteresis loci of catalytic and thermally coupled homogeneous reactions while other washcoat properties like porosity, diffusivity and thickness are kept constant. In order to declutter the plot, we have emphasized the catalytic hysteresis loci on the top diagram and

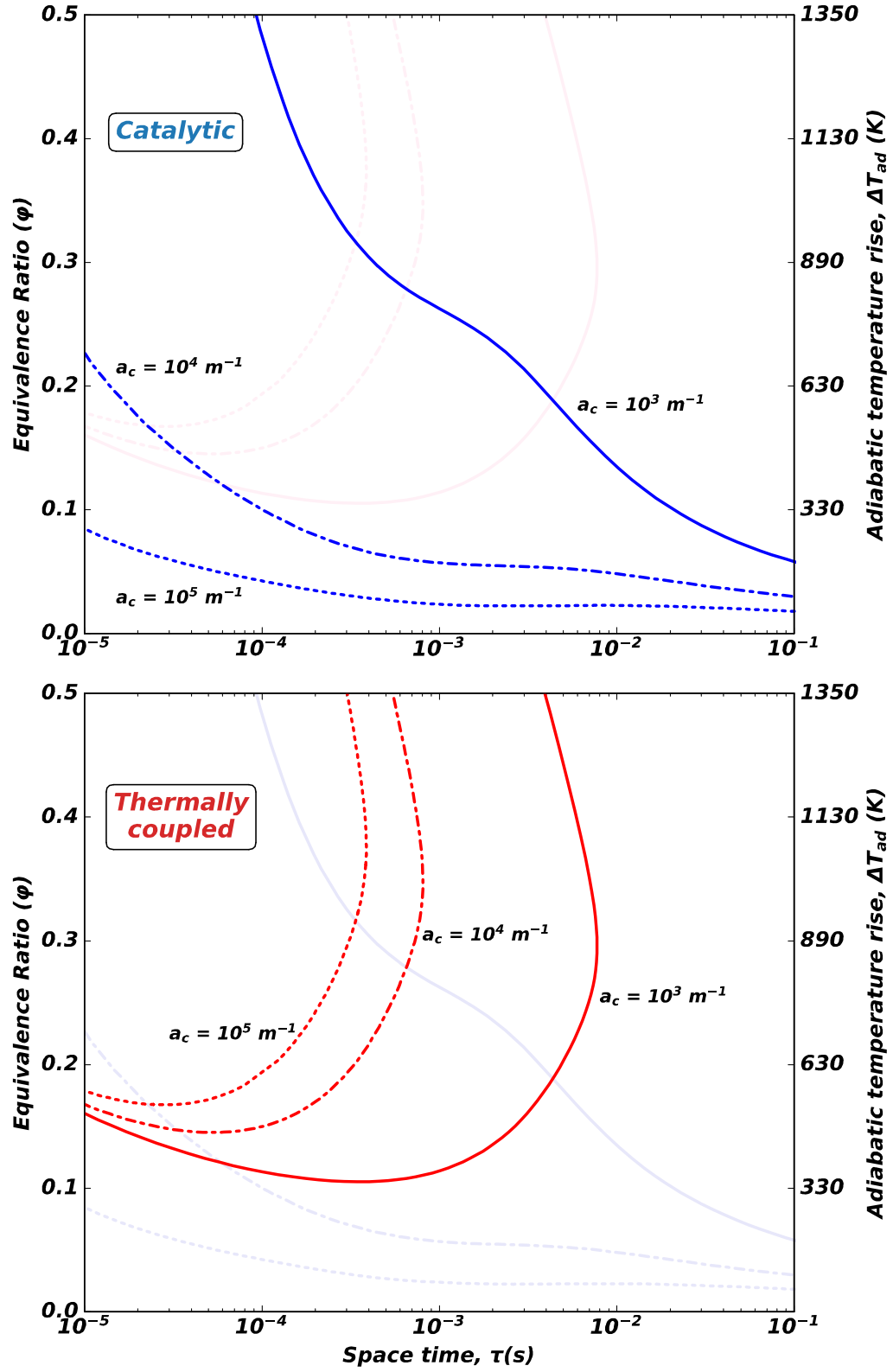


Figure 4.9: Computed catalytic (top) and thermally coupled hysteresis loci (bottom) for adiabatic lean combustion of hydrogen at different catalyst activities in equivalence ratio vs. space time plane.

the thermally coupled counterpart in the bottom. As discussed earlier, with the increase of active Pt surface area from $10^3 - 10^5 \text{ m}^{-1}$, the catalytic hysteresis locus shifts left and down towards lower space times and equivalence ratios expanding the region of multiplicity. At lower catalytic activity like 10^3 m^{-1} , the coupling between the homogeneous and catalytic reactions can only occur at higher space times ($\tau \sim 1 \text{ ms}$). However, with the increase of Pt loading, the catalytic reaction starts to dominate over the homogeneous chemistry even at significantly lower space times, thereby shifting the thermally coupled region left towards smaller space times ($\tau \sim 0.1 \text{ ms}$).

Another important aspect that affects the region of multiplicity is washcoat pore (internal) diffusion. The internal diffusivity is dependent on the washcoat structure and can be varied by changing the ratio of porosity to tortuosity in our simplified pore diffusion model. It can be intuitively expected that lower washcoat diffusivities will create stronger pore diffusional limitations, and hence shrink the region of catalytic hysteresis. This is confirmed in fig. 4.10 which illustrates the impact of pore diffusion on the hysteresis loci for a fixed washcoat thickness $R_{\Omega_{wc}} = 50 \text{ }\mu\text{m}$ and catalytic activity $a_c = 10^3 \text{ m}^{-1}$. As shown in the top diagram, with the decrease of washcoat pore diffusivity, the catalytic hysteresis locus translates to the right towards higher values of space times, since the pore diffusional limitations are dominant when space times are low (0.1 - 5 ms). However, at high enough space times ($\tau > 10 \text{ ms}$), the pore diffusivity has negligible impact on the catalytic hysteresis locus. A slight expansion of the thermally coupled hysteresis region can also be noticed in fig. 4.10 where we have plotted it at the two extreme values of $\mathbf{D}_{wc}/\mathbf{D}_f$ (0.1 and 0.01). Since the catalytic reaction is suppressed at lower pore diffusivities, there are more reactants

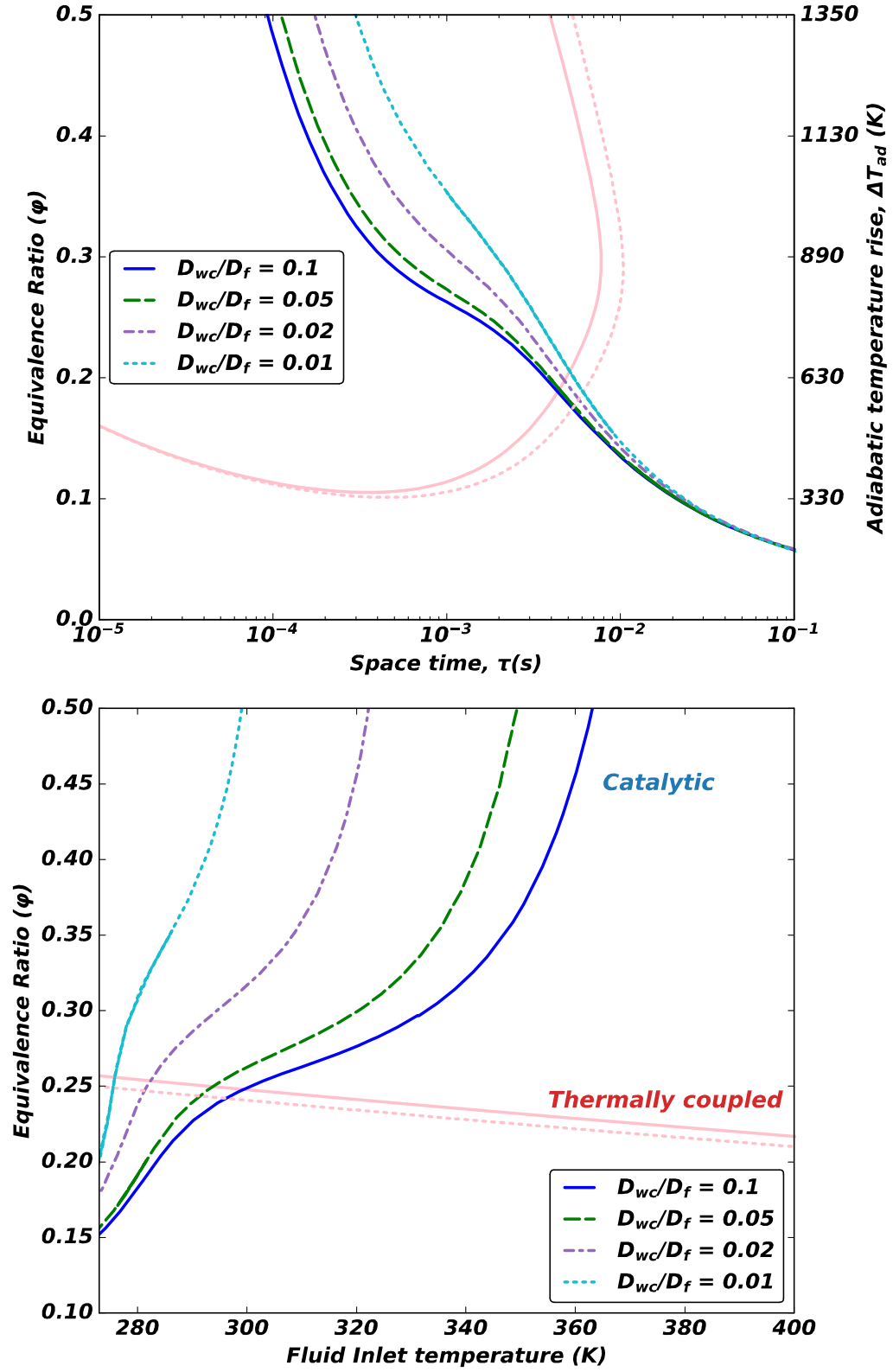


Figure 4.10: Comparison of catalytic hysteresis loci for adiabatic lean hydrogen combustion at different washcoat diffusivities.

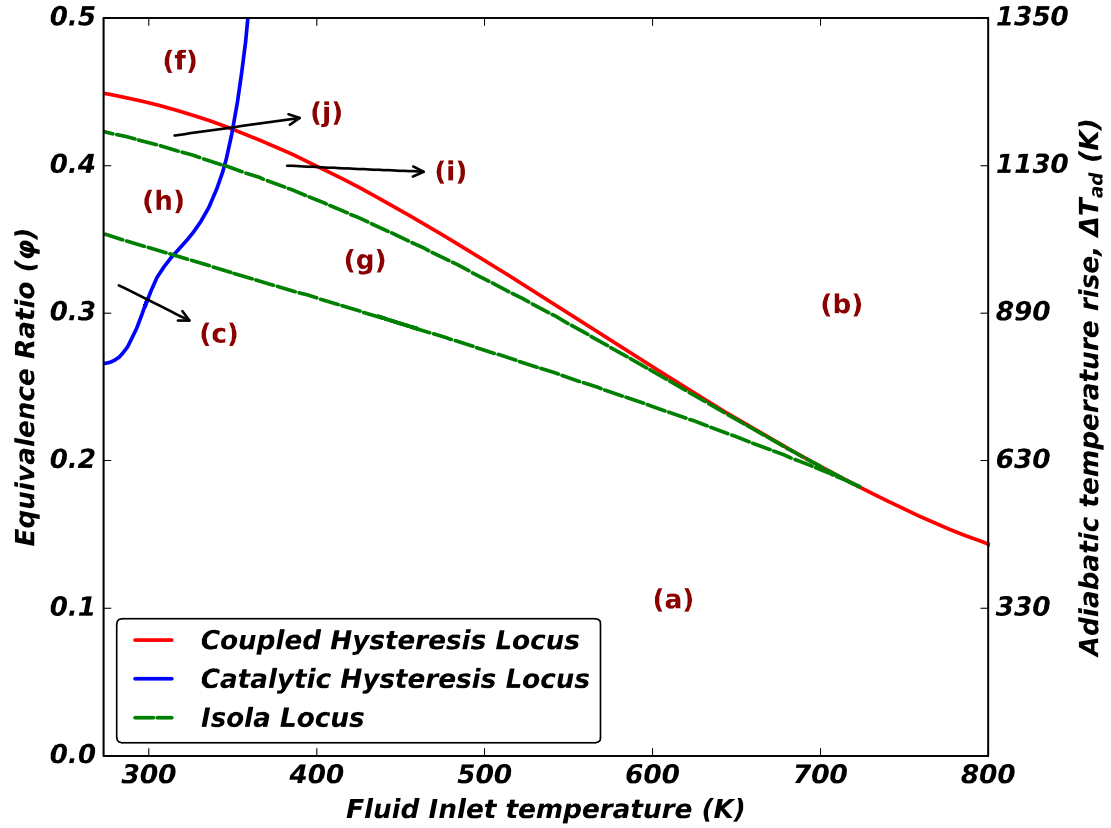


Figure 4.11: Computed phase diagram for non-adiabatic lean combustion of hydrogen in presence of washcoat diffusion.

available for the homogeneous reaction which eventually results in this expansion. In the plane of equivalence ratio vs. feed temperature, as the washcoat diffusivity is decreased, the catalytic hysteresis locus shifts towards higher equivalence ratios and lower feed temperatures.

4.4.5 Impact of heat loss

The inclusion of heat loss effects can lead to complicated bifurcation behavior and further classifies the phase diagram into new regions. As discussed earlier, we have simulated the effect of heat loss between the reactor wall and surroundings through a lumped overall heat loss coefficient, h_a . Fig. 4.11 shows the phase diagram of

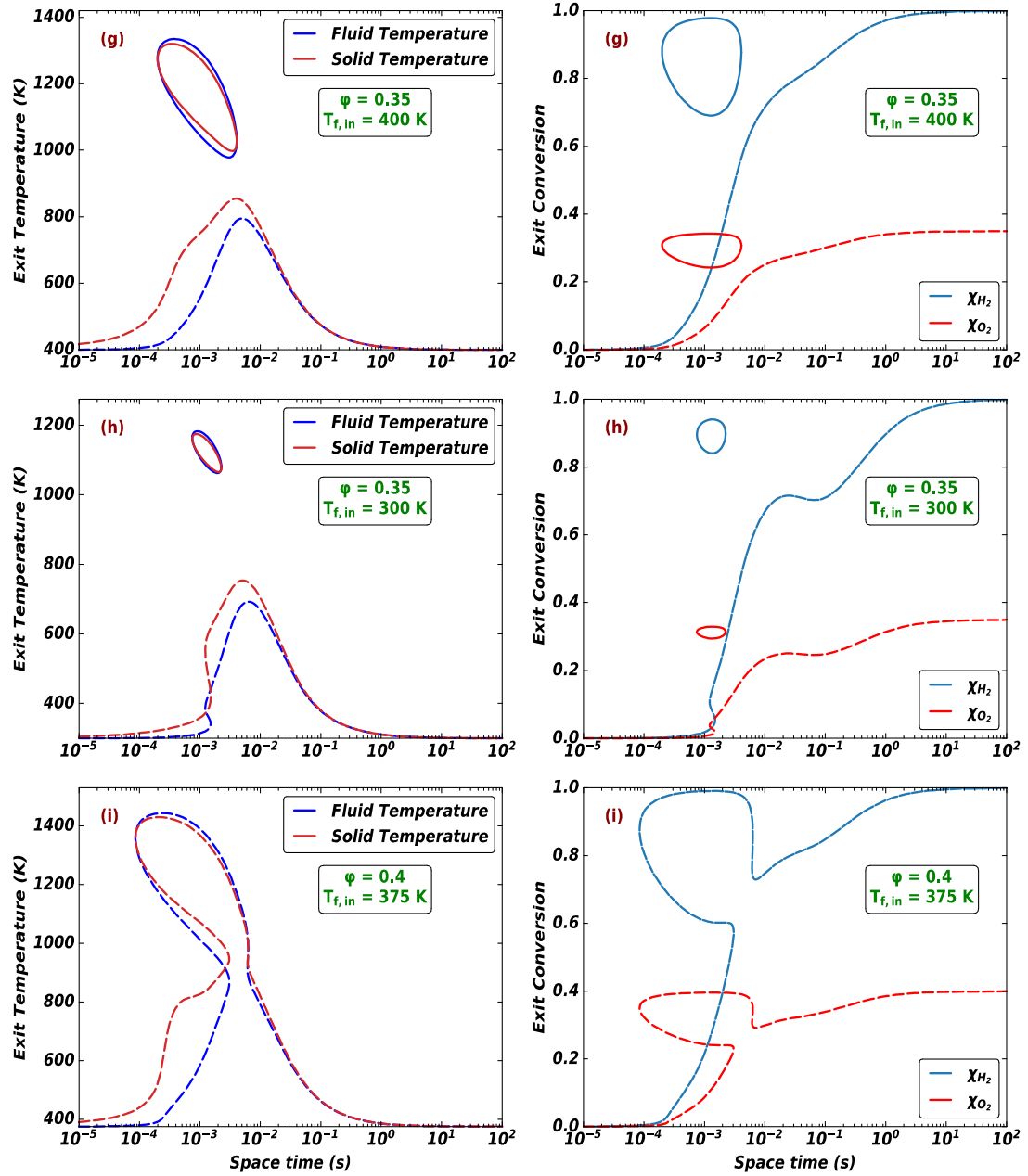


Figure 4.12: Bifurcation diagrams of fluid and solid temperatures (left) and reactant conversions (right) for lean hydrogen combustion in presence of external heat loss.

lean hydrogen combustion with an average value of heat loss coefficient, $h_a = 25$ W/m²K. Similar to the adiabatic case (refer fig. 4.5), region (a) shows no ignition-extinction behavior, region (b) exhibits one pair of ignition-extinction feature due to the combined effects of catalytic and gas phase reactions, and region (c) corresponds to mainly catalytic ignition-extinction case only. However, due to the presence of strong heat loss effects, region (a) has expanded in this case and both the catalytic and thermally coupled hysteresis loci moved upwards towards higher equivalence ratios. Also, isolated solution branches with two extinction points can exist when heat loss effects are considered (see fig. 4.12). Therefore, in addition to the hysteresis loci, there is an isola variety locus in this case, which further divides the parameter space into 4 new regions. The lower branch of the isola variety is the set of all equivalence ratios and space times where the two extinction points coalesce and above which an isolated branch appears over the low conversion branch (refer top two rows in fig. 4.12). On the other hand, the isolated solution branch merges with the continuous branch and forms a mushroom shaped bifurcation diagram with two ignition and two extinction points in the upper branch of the isola variety (bottom row of fig. 4.12). Furthermore, there can be catalytic ignition-extinction together with the isola and mushroom shaped diagrams, the respective regions of which are named as region (h) and (j) in the phase diagram. Region (f) again exhibits two pairs of ignition-extinction feature, the first one corresponding to the catalytic reaction and second one due to thermally coupled homogeneous reaction. As we move towards higher equivalence ratios, the adiabatic temperature rise increases while decreasing the characteristic heat generation times. Thereby, the heat generation effects dominate over the heat loss effects at such higher

equivalence ratios, which does not manifest in isola formation. The heat loss effects only decreases the maximum value of solid or fluid temperature at intermediate space times.

Typical bifurcation diagrams of exit temperatures and conversions for region (g), (h) and (i) are shown in fig. 4.12. The bifurcation diagram with $\varphi = 0.35$ and $T_{f,in} = 400$ K, which corresponds to an example point from region (g) in fig. 4.11, shows a high temperature isolated branch over the low temperature continuous solution. The extinction point at low space times is called blow-out in the literature and is primarily caused due to the faster rate of heat removal through convection. The fluid temperature attained at this point is much closer to the adiabatic limit. The other extinction point at high space times is caused by heat loss through the reactor wall. As shown in the bifurcation diagram, with the increase of space time, the fluid and solid temperatures start to fall in the isolated branch till the extinction point where the characteristic heat loss time becomes comparable to the heat generation time. Only the upper branch of the isola is stable and can be attained physically through proper reactor start-up strategies. It is also interesting to note that the fluid temperature is slightly higher than the solid temperature in the isola, thereby suggesting active homogeneous chemistry in this branch. On the contrary, higher solid temperature in the lower continuous branch signifies dominant catalytic chemistry. Due to lower activation energy of the catalytic reaction and high molecular diffusivity of hydrogen, the catalytic reaction times and associated heat generation times scales are much smaller than the characteristic heat loss times. For the choices of parameters undertaken here, the isola formation is only observed due to thermally coupled

homogeneous reaction. Unlike the adiabatic case, here the thermodynamic branch of the bifurcation diagram reaches the furnace temperature (inlet temperature in our calculations) at high enough space times. Conversion increases monotonically in the continuous branch.

The bifurcation diagram in region (h) is shown in the figure with $\varphi = 0.35$ and $T_{f,in} = 300$ K. Catalytic ignition along with an isola can be observed in this case. Since this particular operating point is much closer to the lower branch of the isola variety in the phase diagram (refer fig. 4.11), here the isola is much smaller and the conversion is lower than the previous case. After the initial catalytic ignition, reactant conversion along with fluid and solid temperatures are found to increase with increasing space time in the continuous branch. However, at higher space times ($\tau > 10$ ms), as the fluid and solid temperatures start to decrease, the conversion goes through a shallow minimum and then increases again with increasing space time. Eventually, the reactor behavior approaches the isothermal limit at sufficiently high space times ($\tau > 1$ s) and 100% conversion of the limiting reactant (hydrogen) is achieved. The bifurcation diagrams in the bottom row of fig. 4.12 with $\varphi = 0.4$ and $T_{f,in} = 375$ K represent an operating point of region (i). As per the phase diagram, this region lies above the upper branch of the isola variety. The isolated solution branch is thereby expected to merge with the continuous branch to form a mushroom shaped bifurcation diagram. The non-monotonic nature of conversion discussed previously is much more prominent in this case. At lower space times, the reactor behavior is close to adiabatic and the system jumps to a high temperature, high conversion branch upon the first ignition. However, as the solid and fluid temperature starts to decrease with increasing space

time, conversion decreases rapidly until it reaches a minimum and then starts to increase again. The bifurcation behavior of region (j) would be much similar to that of region (i), with an added catalytic ignition-extinction pair.

4.5 Bifurcation analysis of two-mode long channel model

One of the limitations of the SM model is the spatial independence of the state variables. Also, it assumes perfect species and thermal backmixing along the axial direction. These two constraints can be relaxed and the impact of finite mixing effects can thereby be analyzed through the use of two-mode long channel model given by eqns. (2.46 - 2.53). Since the steady-state version of this model turns into a differential-algebraic system [68], pseudo steady-state analysis of the transient model is addressed here. Therefore, instead of the steady state bifurcation diagrams, dynamic hysteresis plots consisting of only the stable solution branches are calculated by increasing and then decreasing the feed temperature slowly at a rate of 1 K/min in between the range 40 - 600 K. The extent of species and thermal backmixing depends on axial diffusion and convection time scales, and can be succinctly expressed in terms of dimensionless effective axial mass and heat Peclet numbers (ratio of axial diffusion/conduction time scales of species/heat to it's corresponding convection time scales) as given by

$$Pe_{m,j} = \frac{\langle u \rangle L}{D_{f,j}} \text{ and } Pe_{h,eff} = \frac{\langle u \rangle \widetilde{C_{pf}} R_{\Omega_f} L}{R_{\Omega_w} \kappa_w}. \quad (4.7)$$

Smaller values of $Pe_{m,j}$ and $Pe_{h,eff}$ ($Pe_{m,j}, Pe_{h,eff} \ll 1$) suggest stronger mixing effects where the reactor almost approaches the short monolith limit. As the values of $Pe_{m,j}$ and $Pe_{h,eff}$ are increased, the reactor behavior deviates from that limit and starts to exhibit spatial gradients, while reaching the plug-flow limit eventually. The additional parameters used in the simulation of the long channel model are given in Table 4.2.

Table 4.2: List of parameters for the two-mode long channel model - hydrogen

Parameter	Unit	Value
L	cm	0.1, 1, 2 or 10
$L / \langle u \rangle$	ms	10
R_{Ω_f}	μm	250 or 1000
$R_{\Omega_{wc}}$	μm	50
R_{Ω_w}	μm	140
a_c	m ² Pt/m ³ washcoat	10 ³
C_{pw}	J/kg.K	1000
ρ_w	kg/m ³	2000
κ_w	W/m.K	1.5 or 15
φ	-	0.25

In fig. 4.13, the dynamic hysteresis plots of exit fluid temperature and hydrogen conversion are compared at different reactor lengths for a fixed average space time under adiabatic conditions. As per the phase diagram in fig. 4.3, one pair of ignition-extinction behavior can be observed with a short monolith type reactor at a feed equivalence ratio of 0.25 and space time of 10 ms. The species and thermal mixing effects approach the short monolith limit when the reactor length is 1 mm and

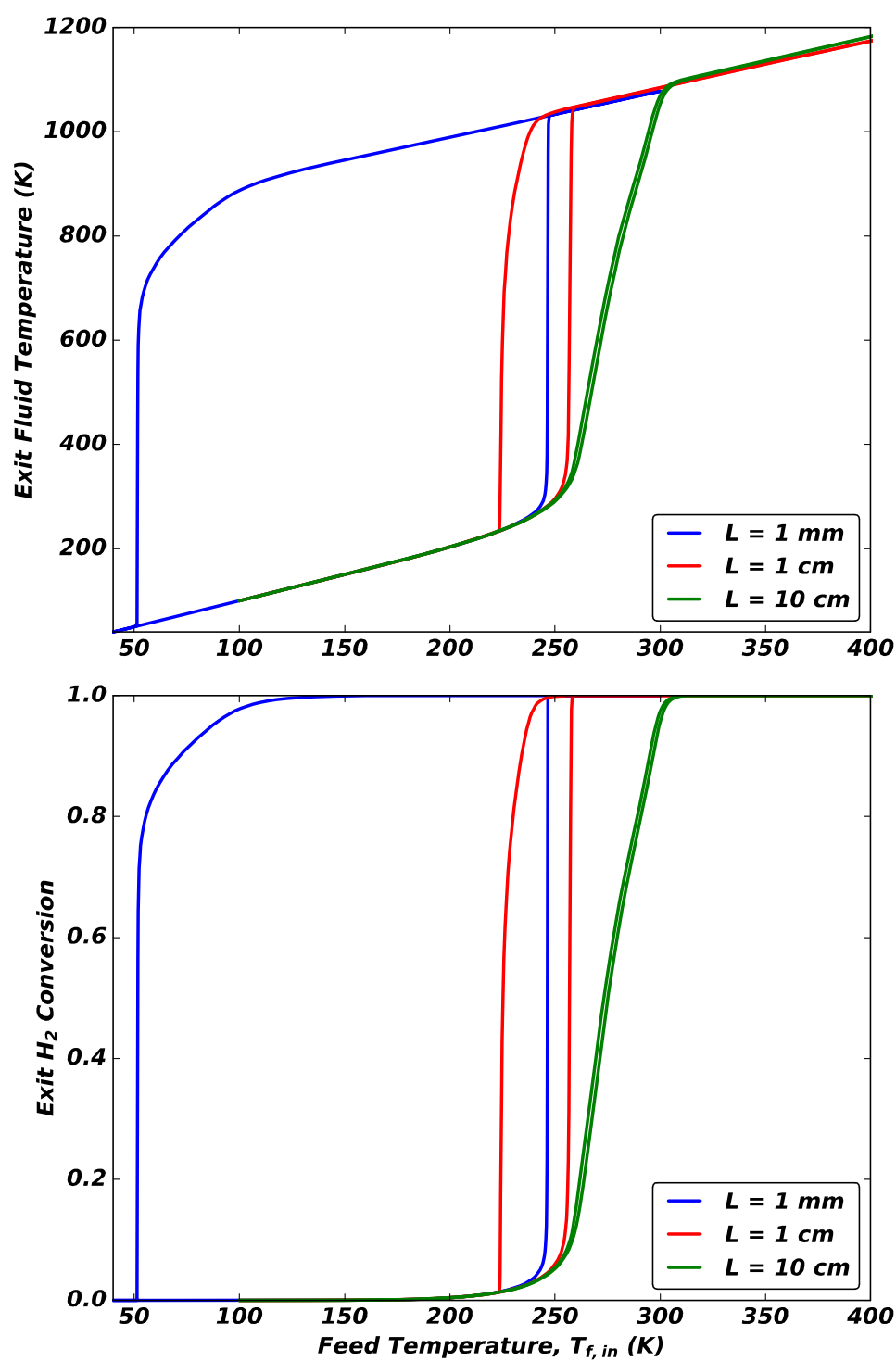


Figure 4.13: Computed dynamic hysteresis plots of exit fluid temperature (top) and H_2 conversion (bottom) versus feed temperature at different reactor lengths.

the substrate conductivity is 1.5 W/m.K ($Pe_{m,H_2} \simeq 1, Pe_{h,eff} \simeq 0.1$). Thereby, the qualitative as well as the quantitative nature of the ignition-extinction phenomenon at $L = 1$ mm resembles the behavior of a short monolith reactor. However, increasing the reactor length by a factor of 10 at a fixed space time increases the axial Peclet numbers by 100 times, thereby reducing the extent of species and thermal backflow. As a result, the reactor behavior deviates from the short monolith limit and the extinction point moves to much higher feed temperature while shrinking the width of hysteresis. At much longer channel lengths such as 10 cm, the hysteresis phenomenon may completely disappear, and the reactor may exhibit a single-valued light-off behavior. Also, it requires higher feed temperature to attain complete fuel conversions in reactors with longer channels.

Fig. 4.14 demonstrates the impact of substrate conductivity on exit fluid temperature and hydrogen conversion at a reactor length of 2 cm, in absence of any external heat losses. Since, higher values of substrate conductivity enhances the extent of bed scale thermal mixing, ignition-extinction phenomena with a wider region of hysteresis can again be observed with $\kappa_w = 15$ W/m.K ($Pe_{h,eff} \simeq 4$). The computed results are in qualitative agreement with the experimental data obtained by Specchia et al. [60] using silicon carbide monoliths ($\kappa_w = 65$ W/m.K reported at 1000 K). Such reactor model with high mass and low heat Peclet numbers ($Pe_{m,H_2} \simeq 400, Pe_{h,eff} \simeq 4$) is widely referred as Lumped Thermal Reactor (LTR) model in the literature and is known to have the largest region of multiplicity [22]. Higher substrate conductivity monoliths also exhibit temperature profiles in the solid phase with smaller gradient as can be seen from the top diagram in fig. 4.15 which plots the axial fluid and solid

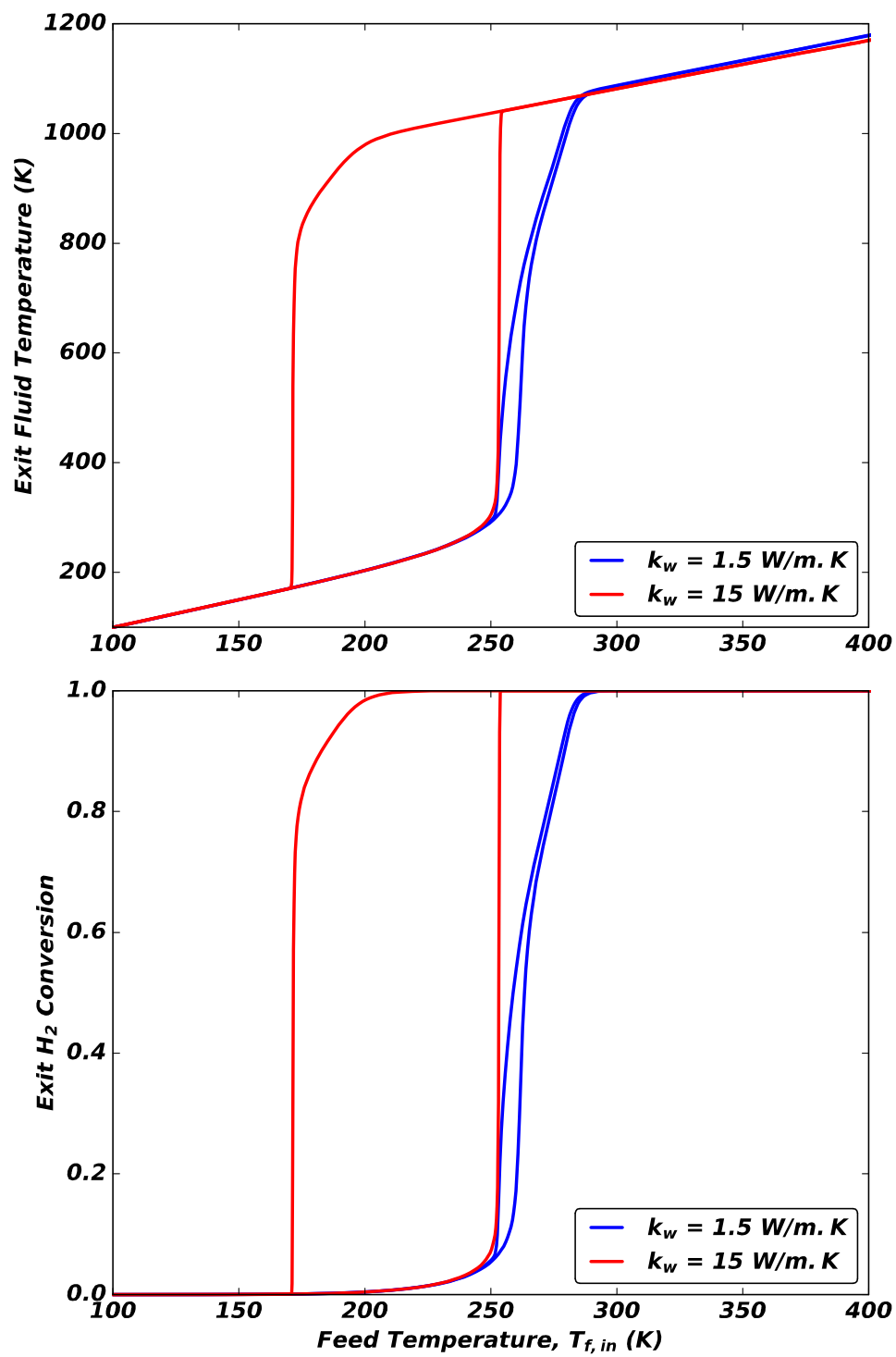


Figure 4.14: Computed dynamic hysteresis plots of exit fluid temperature (top) and H_2 conversion (bottom) versus feed temperature at different substrate conductivities.

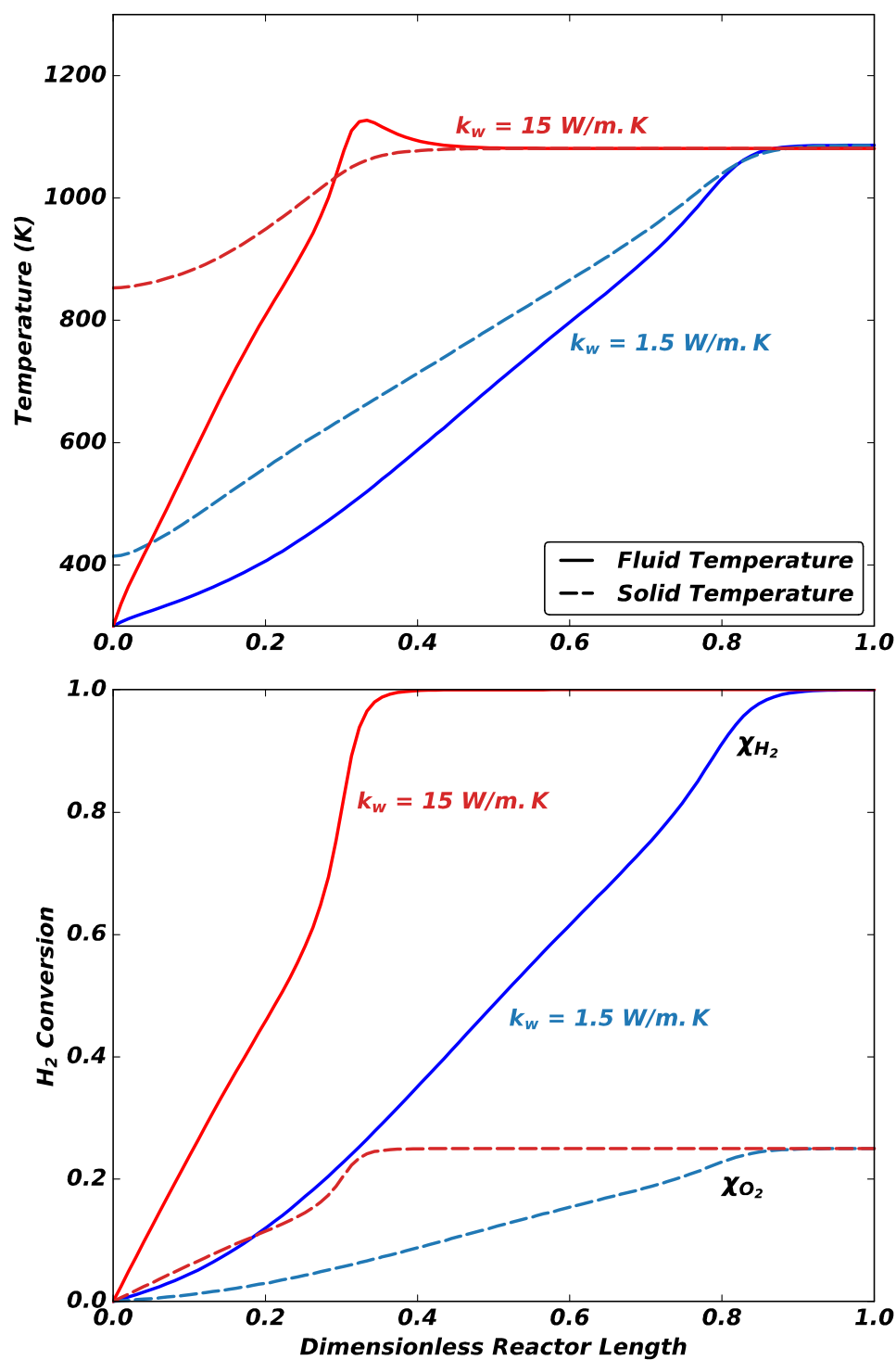


Figure 4.15: Temperature (top) and conversion (bottom) profiles along the reactor length in the ignited branch at different substrate conductivities for a feed temperature of 300 K.

temperatures of the ignited reactor at a feed temperature of 300 K. Contrastingly, pronounced spatial gradients in both solid and fluid phases can be noticed with the lower conductivity substrate. Furthermore, due to enhanced heat backflow, the reaction zone (the axial distance to reach maximum fluid or solid temperature from reactor inlet) is found to be closer to the reactor entrance with $\kappa_w = 15$ W/m.K. Monoliths with higher substrate conductivities (metallic monoliths, SiC substrate, stacked wire-meshes etc.) can also aid in absorbing the thermal shock and hence are favorable for combustion applications [32].

Interestingly, the fluid temperature is found to go through a maximum, attending super-adiabatic values for the case of $\kappa_w = 15$ W/m.K. In general, this kind of overshoot in fluid temperature is observed only at higher feed temperatures and on the ignited branches. Comparing the axial temperature and the conversion profiles (bottom diagram in fig. 4.15), it is quite evident that the catalytic reaction practically ignites at the inlet of the channel and enters external mass transfer controlled regime. As a result, there is a gradual linear type increase in fluid temperature, while the solid temperature is at a significantly higher value. The conversion profile is also observed to increase monotonically till the H_2 conversion reaches 60%, after which the slope of the profile changes. This sudden change in slope marks the ignition of the homogeneous reaction. The instantaneous conversion of the limiting reactant through the homogeneous route combined with the Lewis number effect drives the fluid temperature locally to super-adiabatic values. Such local high temperatures can also lead to NOx formation and hence are important to consider while designing reactors for combustion applications. Since these local super-adiabatic fluid temperature are

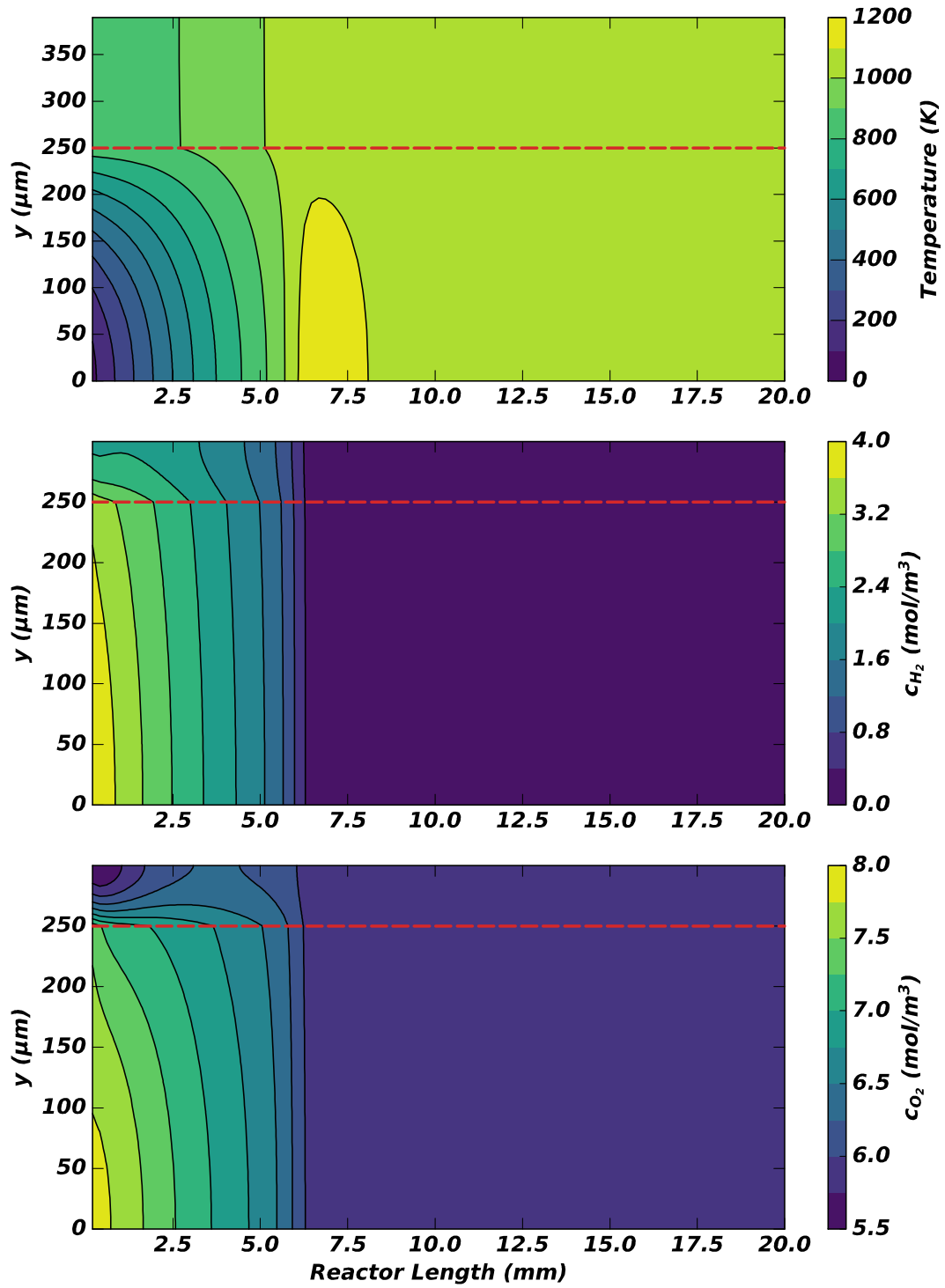


Figure 4.16: Temperature and concentration contour plots in the flow channel and washcoat for $L = 2$ cm and substrate conductivity, $\kappa_w = 15$ W/m.K.

only observed in the ignited branches at higher values of feed temperatures, one way to prevent them is by operating the reactor at lower feed temperatures, i.e., in the ignited branch closer to the extinction point. Also, in this context it is important to note that the fluid or solid temperatures can only attend super-adiabatic values when $Le_f < 1$. For fuel mixtures with $Le_f > 1$, the maximum temperature can never exceed the adiabatic limit [28].

While the previous figure shows the axial variation of temperature and conversion, we can also construct the transverse profiles by plugging in the phase-averaged quantities into eqns. (2.87-2.88). Fig. 4.16 shows the contour plot of temperature and reactant concentrations in 2D domain (horizontal axis is the axial coordinate while the vertical axis being transverse coordinate) for the case of $L = 2 \text{ cm}$, $\kappa_w = 15 \text{ W/m.K}$ and $T_{f,in} = 300 \text{ K}$. The horizontal red dashed line at $y = 250 \text{ }\mu\text{m}$ in each of the subplots represents the fluid-washcoat interface where the flow channel lies below the red line ($0 \leq y \leq 250 \text{ }\mu\text{m}$) and above is the washcoat phase ($250 \leq y \leq 300 \text{ }\mu\text{m}$) or the solid phase (washcoat + support, $250 \leq y \leq 390 \text{ }\mu\text{m}$). It can be seen that temperature and concentrations are continuous at the interface while the slope is discontinuous (due to the flux continuity but different diffusivities in each phase). Pronounced temperature gradients exist in both x and y directions in the fluid phase. Also, the super-adiabatic zone in the fluid phase can be clearly spotted around $x \simeq 7.5 \text{ mm}$. As expected, there is negligible variation of temperature in transverse direction of the solid phase owing to its high thermal conductivity. On the contrary, the transverse concentration gradients in the flow channel are negligible due to higher diffusivities while the gradient is stronger in the washcoat, especially near the interface.

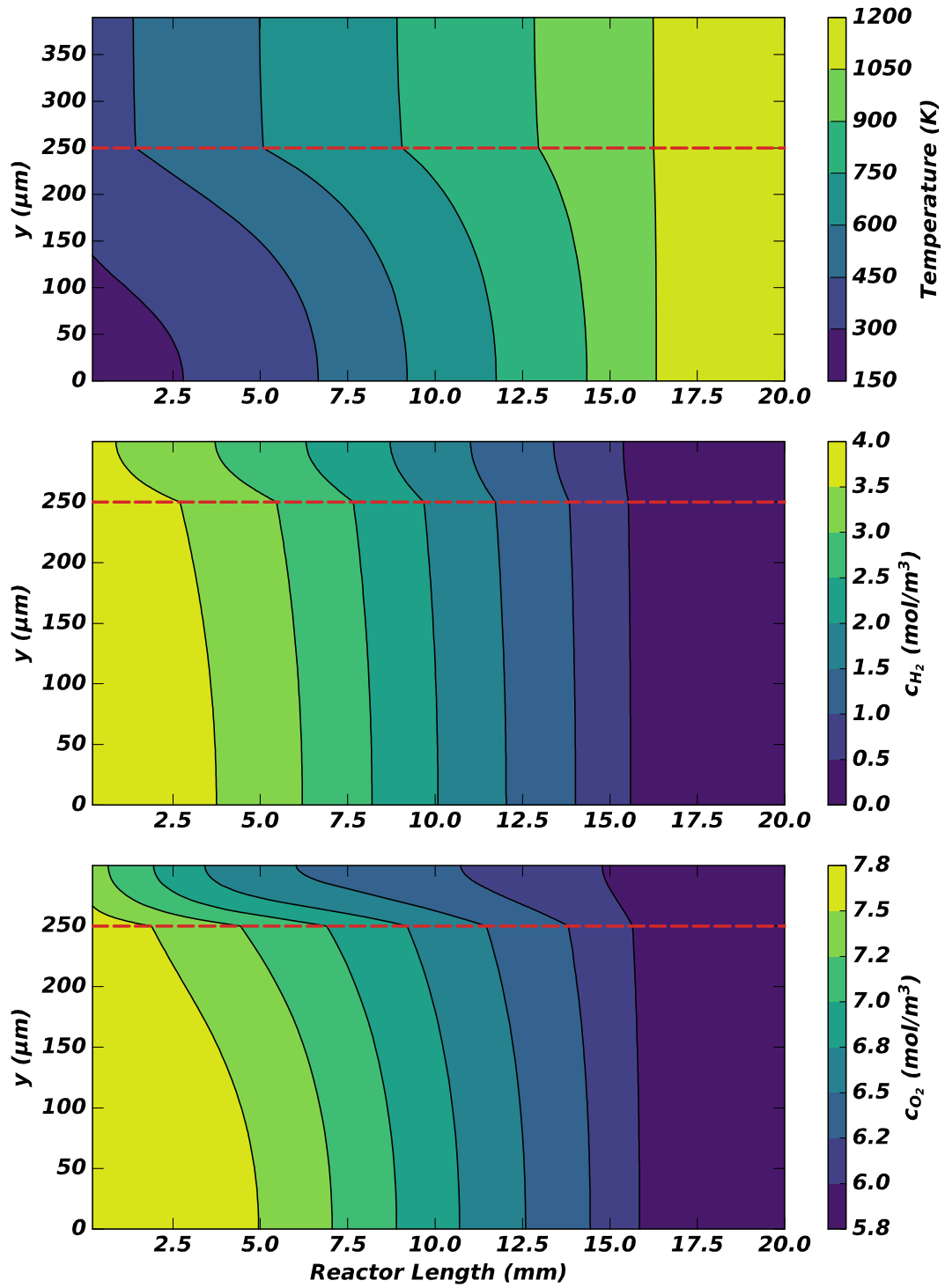


Figure 4.17: Temperature and concentration contour plots inside the reactor of length, $L = 2$ cm and substrate conductivity, $\kappa_w = 1.5$ W/m.K.

In addition, due to non-linear transport effects and reaction kinetics, the concentrations may also be non-monotonic in the washcoat as can be seen from the contour plot of oxygen concentration. Keeping all other parameters constant, similar spatial profiles for the case of $\kappa_w = 1.5 \text{ W/m.K}$ are shown in fig. 4.17. Unlike the previous case, the transverse variations are not so strong for this low conductivity case. Significant transverse gradients can only be observed in washcoat concentrations. The O_2 concentration decreases monotonically in x direction and shows relatively steeper gradients inside the washcoat due to its lower diffusivity.

Our simulations also reveal that there is negligible difference between the solid and fluid temperatures at the reactor exit when the channel hydraulic radius is $250 \mu m$ or smaller (high cell density monolith). However, that may not hold true for a low cell density monolith where the channel hydraulic radius is large. Firstly, in a low cell density monolith, due to larger transverse diffusion times $\left(\tau_{D,j} = \frac{R_{\Omega_f}^2}{D_{f,j}} \right)$ the conversion on the ignited branch is limited by external mass transfer and is significantly poor when the space times are low. As shown in fig. 4.18, only 50% fuel conversion is achieved upon the ignition of the catalytic reaction when the channel hydraulic radius is chosen to be 1 mm, space time is 10 ms and reactor length is 1 cm. The thermally coupled homogeneous reaction only assists in the later stages of fuel conversion and does not manifest in any hysteresis in this case. In comparison to that, complete conversion is attained after the first ignition at a channel hydraulic radius of $250 \mu m$. Furthermore, the solid temperatures shoot up to very high values upon the ignition of the catalytic reaction due to the Lewis number effect at higher channel hydraulic radius. We have plotted the axial temperature profiles at different

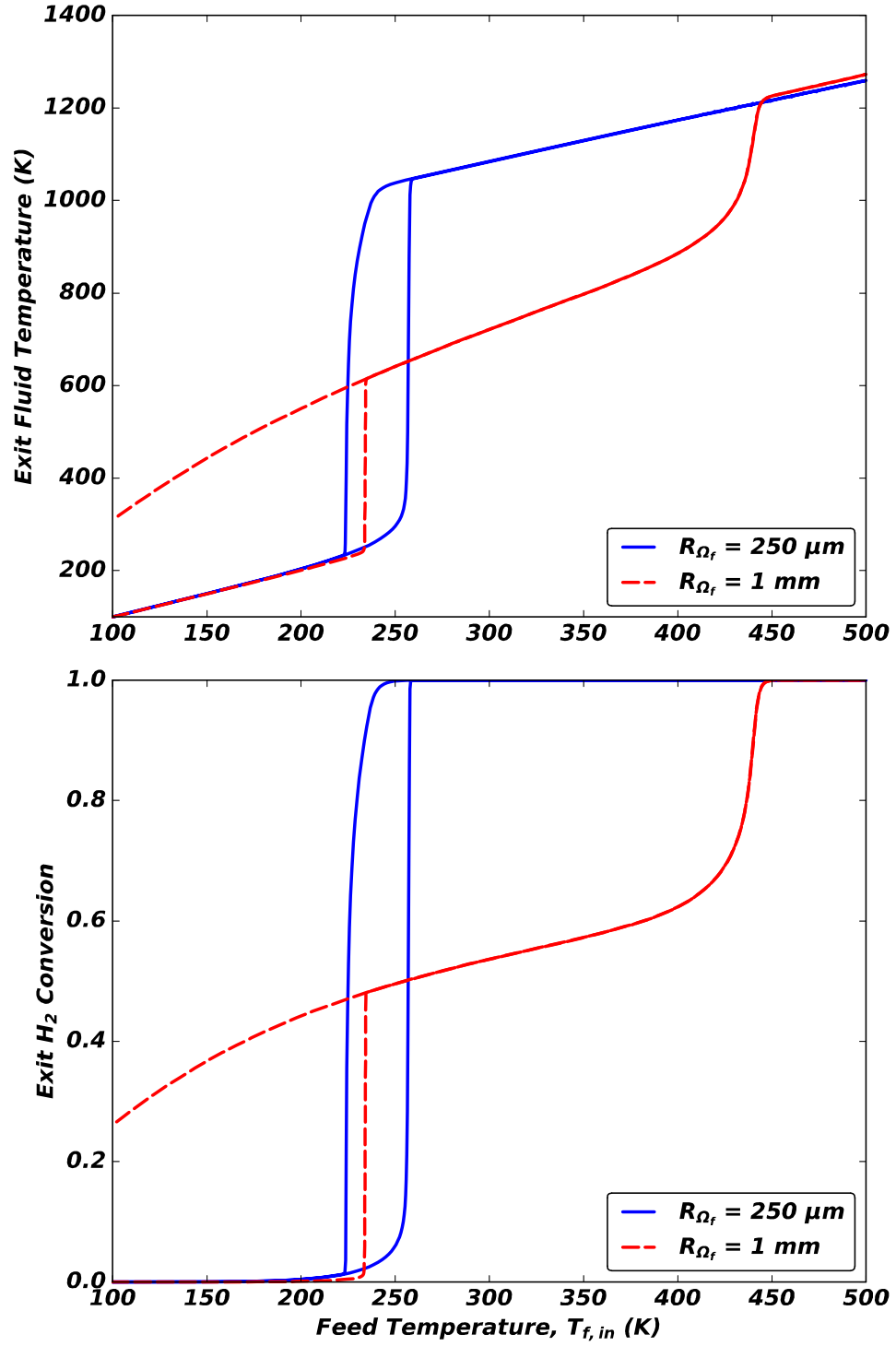


Figure 4.18: Computed dynamic hysteresis plots of exit fluid temperature (top) and H_2 conversion (bottom) versus feed temperature at two different channel hydraulic radii.

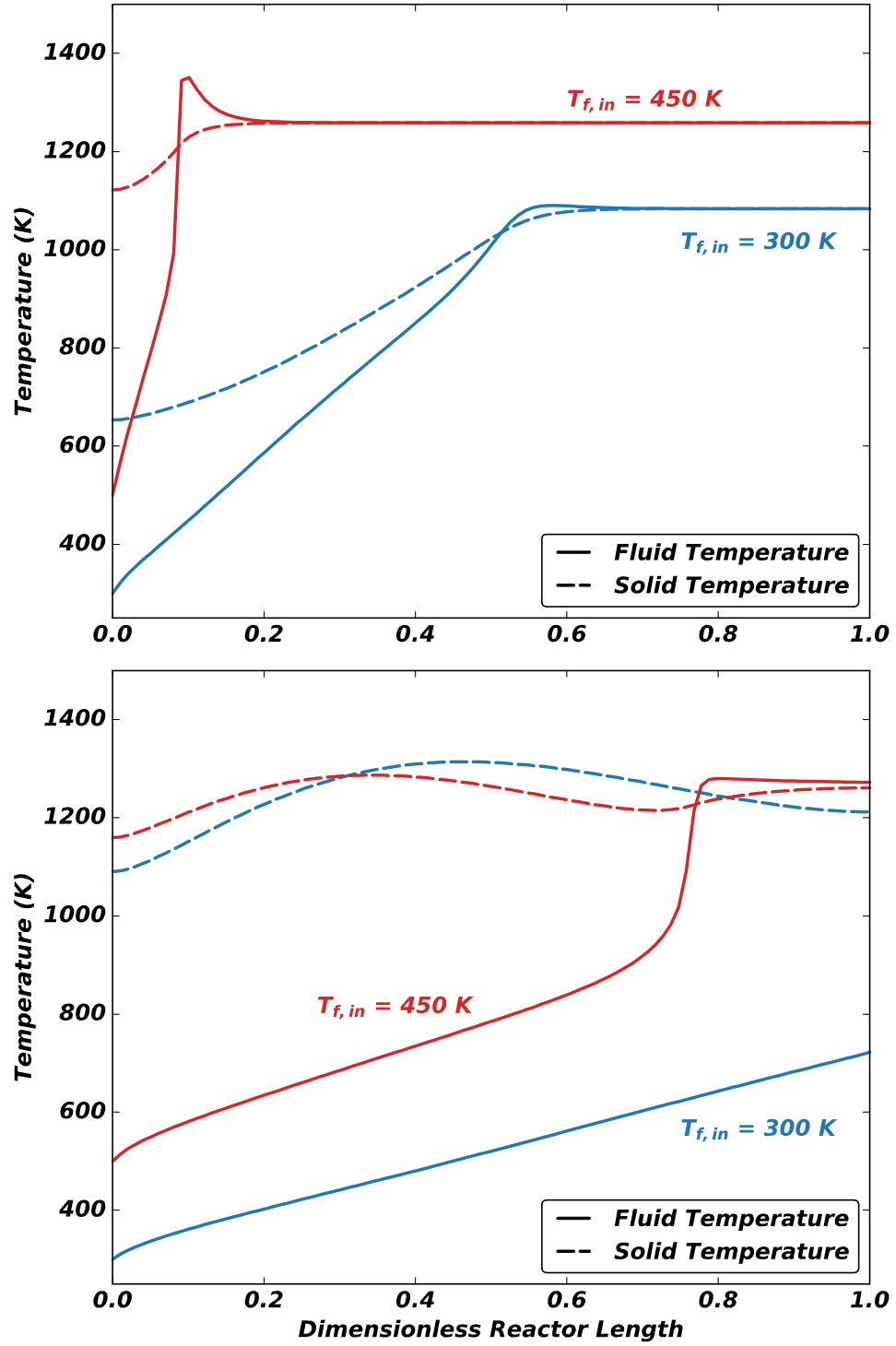


Figure 4.19: Temperature profiles along the reactor length on the ignited branch at two different feed temperatures for $R_{\Omega_f} = 250 \mu m$ (top) and $R_{\Omega_f} = 1 mm$ (bottom).

feed temperatures in fig. 4.19 to illustrate the interfacial gradients of these two channel hydraulic radii. From the top diagram of fig. 4.19, which refers to $R_{\Omega_f} = 250 \mu m$, it is apparent that the solid temperatures are monotonic with respect to reactor length and approach the adiabatic limit at reactor exit. With the increase of feed temperature from 300 K to 450 K, the reaction zone comes closer to the reactor inlet and the aforementioned overshoot in fluid temperatures can again be observed. On the contrary, for the case $R_{\Omega_f} = 1 \text{ mm}$ (bottom plot) at a feed temperature of 300 K when the catalytic chemistry is only active, the solid temperatures reach as high as 1300 K resulting in huge interfacial gradients. It is interesting to note that the solid temperatures are non-monotonic inside the reactor in this case. Initially it increases due to the catalytic reaction and then decreases while acting as a heat source to the fluid phase. The ignition of the homogeneous reaction can be spotted with a feed temperature of 450 K in the reactor downstream. At both these feed temperatures, the solid temperatures are found to be super-adiabatic inside the reactor. It is due to this difference in fluid and solid temperatures, a wider region of dynamic hysteresis is observed with the catalytic reaction at $R_{\Omega_f} = 1 \text{ mm}$.

4.6 Summary

The main contribution of this work is the comprehensive analysis of the ignition-extinction behavior of the catalytically assisted lean combustion of hydrogen in monolith reactors. We have examined the different types of ignition and extinction behaviors that could occur in the catalytically assisted lean combustion of hydrogen and constructed phase diagrams in the plane of equivalence ratio versus feed temperature

when space time is taken as the bifurcation variable. Similarly, we constructed phase diagrams in the plane of equivalence ratio versus space time when the inlet (feed) temperature is taken as the bifurcation variable. These phase diagrams classify all the different types of steady-state phenomena occurring and the extent of coupling between the homogeneous and catalytic conversion of the fuel. We have also examined in detail the impact of monolith channel hydraulic diameter, the precious metal (Pt) loading and/or dispersion, effective diffusivity of hydrogen in the washcoat, heat loss from the reactor, reactor length and the monolith substrate thermal conductivity on the ignition-extinction behavior. The results of this analysis lead to the following major conclusions: (i) the coupling between homogeneous and catalytic conversion is strongest when the effective axial heat and mass Peclet numbers are of order unity or smaller (or more precisely, the thermal coupling is strongest when the effective heat Peclet number approaches zero while the species coupling is also strong when the mass Peclet number is of order unity or smaller). In practice, Peclet values of order unity or smaller can be attained by either using shorter monoliths and/or substrates with high conductivity and/or low flow rates (or space velocities). In fact, in our opinion, this observation is extremely important as it can be used to control the extent of the coupling between homogeneous and catalytic chemistries not only in the problem studied here but also in other applications. (ii) as can be expected intuitively, a reduction in the flow channel hydraulic diameter and/or increase in Pt dispersion or loading makes the catalytic reaction as well as the coupling stronger and moves the ignition and extinction points to lower values of feed temperature or space time (iii) washcoat diffusional limitations always weaken the catalytic reaction

as well as the coupling (iv) since the Lewis number for hydrogen (in a lean mixture) is less than unity, ignition of the catalytic reaction in wider channels (higher values of channel hydraulic diameter) could lead to solid/catalyst temperature exceeding the adiabatic value, especially at lower space times where the conversion of the fuel is incomplete. Surprisingly, for larger values of the space time and for some range of channel hydraulic radii and length, the maximum fluid temperature in the channel could also exceed the adiabatic value when catalytic ignition is followed by homogeneous ignition. It is possible to potentially mitigate these super-adiabatic fluid and solid temperatures by using high cell density monoliths and operating the reactor at lower feed temperatures in the ignited branches.

The bifurcation analysis presented for the adiabatic case was also extended to include heat losses from the reactors. In this case, as expected, isolated solution branches exist, especially when the heat loss from the reactor is significant and space time is taken as the bifurcation parameter. The computed bifurcation diagrams under adiabatic conditions are qualitatively comparable to the experimental results of Vlachos and Bui [48]. They observed catalytic ignition-extinction behavior near ambient temperatures along with onset of gas phase chemistry around $T_s = 1000$ K at 1% H_2 and 50 s^{-1} strain rate on a stagnation flow reactor. As per our phase diagrams (fig. 4.5 and 4.9), such an operating point falls in region (iii) where only catalytic ignition-extinction behavior can be observed, while the homogeneous reaction lights-off at higher fluid temperatures. Furthermore, the trends in axial temperature/ H_2 conversion profiles with respect to thermal conductivity and channel diameter calculated in our study match with the CFD simulation results of Chen et al. [57].

Chapter 5

Bifurcation analysis of oxidative coupling of methane

5.1 Introduction

The discovery and recent development (during the past 10 years) of abundant shale gas, and its concomitant drop in price have renewed interest in the production of useful chemicals from natural gas [69]. Currently, natural gas is predominantly combusted as a clean fuel for heat and power generation owing to its high calorific values and low CO_2 emission rates as compared to other hydrocarbon resources like petroleum or coal[70]. However, it also has huge potential as a feedstock material for both direct and indirect synthesis of fuels and chemicals. Some of the industrially practiced indirect routes of natural gas utilization are methanol synthesis followed by methanol-to-gasoline (MTG) process, Fischer-Tropsch (F-T) synthesis, and ammonia production, all of which involve syngas production as a first step. The direct conversion of methane to chemicals, bypassing the costly intermediate syngas step is seen as an attractive option. However, because of poor C_{2+} yields, low CH_4 conversions and high operating temperatures, these processes have not been commercialized ([71]-[72]).

In one of the direct routes, oxidative coupling of methane (OCM), CH_4 is activated on a mixed metal oxide catalyst to form $CH_3\bullet$ radicals, which combine in the gas phase to form C_2H_6 [73]. The yields of C_2H_6 and C_2H_4 (primarily formed through oxidative dehydrogenation [74]), are limited by the catalytic and gas phase secondary reactions of $CH_3\bullet$ radicals and combustion reactions of intermediate products, leading to formation of undesirable CO and CO_2 [75]. Since the discovery of OCM by Keller and Bhasin[76] and Sofranko [77], there has been an extensive amount of work in the last four decades in search of a suitable catalyst as demonstrated in the recent review by Galadima et al.[78]. However, failing to meet the industrial requirements of CH_4 conversion ($>20\%$) and C_2 selectivity ($>80\%$) per reactor pass ([79]-[85]), the pursuit of an active catalyst is still ongoing. In this chapter, instead of delving into improved catalyst development and mechanistic studies, we take a different approach and examine in some detail the ignition-extinction behavior of OCM in monolith, gauze or wire-mesh type reactors. The main objectives of this work are to determine the impact of design and operating conditions such as the feed temperature, space time, inlet CH_4/O_2 mole ratio and reactor dimensions on the ignition-extinction behavior of OCM and to identify an optimum operating window where the conversions and selectivities are maximized.

5.2 Literature review

Annapragada and Gulari[80] observed hysteresis in OCM experimentally in 1990. Afterwards, Lee et al.[81] observed ignition-extinction behavior while investigating OCM with pelletized $Na_2WO_4/Mn/SiO_2$ catalyst, Noon et al.[82] studied the La_2O_3 -

CeO_2 catalyst and reported a lower ignition temperature with nano-fiber catalysts, Sarsani et al.[18] studied both these catalysts and successfully carried out OCM autothermally using $La-Ce$ catalyst with feed at ambient temperature. They also demonstrated autothermal operation with $Na_2WO_4/Mn/SiO_2$ catalyst at somewhat higher feed temperature. More recently, Aseem et al.[83] observed steady-state multiplicity using different mixed metal oxide catalysts and compared their performances over a range of feed conditions. In spite of all these experimental results, there have been only few efforts in modeling such ignition-extinction phenomenon in OCM reactors. Using a thin-bed model with single step first order kinetics, Sarsani et al.[18] computed the hysteresis behavior of OCM on La-Ce oxide and $Na_2WO_4/Mn/SiO_2$ catalysts for the first time. Sun et al.[84] performed bifurcation analysis on three adiabatic ideal reactor models using a global reaction network for gas phase OCM and concluded that the lumped thermal type reactor (high thermal backmixing and negligible mass dispersion) is optimal to sustain autothermal operation while exhibiting higher C_2 selectivity and CH_4 conversion. Following the recent progress of bifurcation analysis on complex kinetic mechanisms [86], Vandewalle et al. [87] examined the ideal reactor models using 317 elementary homogeneous reactions and 26 surface reactions for catalytic OCM. Although, these are some of the pioneering works in application of bifurcation theory to OCM, it is noteworthy that all the aforementioned studies used ideal reactor types derived from 1-D pseudo-homogeneous model, which neglects axial and transverse gradients in the flow channel, diffusional limitations inside the catalyst and/or physical property variations with temperature, and hence may not be applicable for large scale systems (reactors with large diameter,

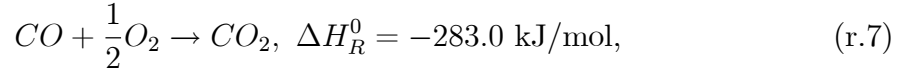
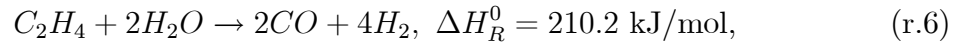
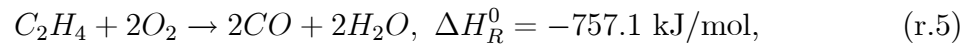
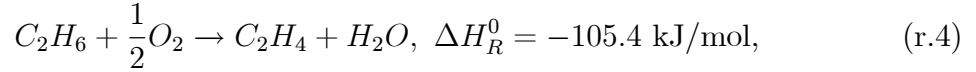
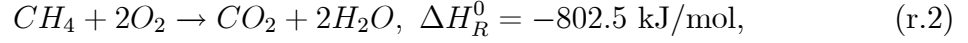
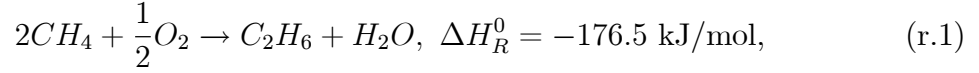
large catalyst particles/thick washcoats for monolith reactors). Moreover, a detailed quantitative analysis of practically constructing a lumped thermal reactor (optimal reactor type for OCM, [84]-[88]) is also missing.

In this chapter, we use our multi-scale multi-mode reduced order model for coupled homogeneous-catalytic reactions in monolith, gauze or wire-mesh types reactors to analyze the bifurcation features in the presence of washcoat diffusion. A monolith reactor with high thermal conductivity substrate (silicon carbide or metallic substrate) and appropriate length can enhance the thermal backflow while limiting the species backmixing, and therefore is a suitable choice for OCM ([22],[84], [87], [88]). Aigler and Lunsford [89] performed OCM experiments on MgO and Li^+/MgO catalysts and concluded that monoliths are relatively less efficient than the traditional packed bed reactors. However, Liu et al. [90] compared the temperature profiles between Na_2WO_4-Mn/SiC monolithic foam catalyst and conventional $Na_2WO_4/Mn/SiO_2$ catalyst and found that the SiC substrate largely reduces the chances of hot spot formation due to its high thermal conductivity. Also, the honeycomb structure in monoliths can provide a homogeneous flow distribution leading to reduced diffusional limitations between the reactants and catalyst. This is demonstrated by Sollier et al. [91], who observed an improvement in both methane conversion and C_2 yields using a cordierite monolith. With a different reaction scheme, Merino et al. [92] showed that monoliths with higher effective thermal conductivity can allow operation with higher catalyst loading (washcoat thickness) than ceramic monoliths while reducing the chances of thermal and selectivity runaway.

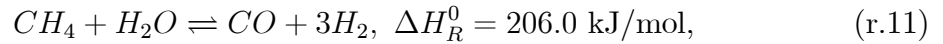
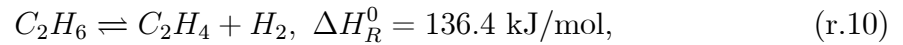
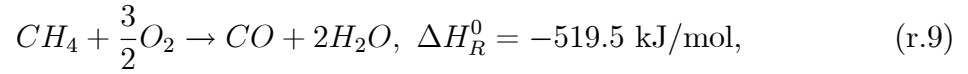
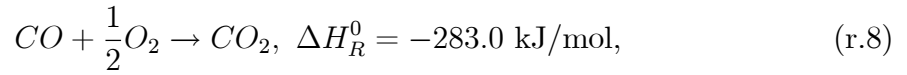
5.3 Kinetic model

We used a twelve reaction global kinetic network, consisting of seven catalytic reactions over La_2O_3/CaO catalyst and five homogeneous gas phase reactions in this study. The catalytic reaction scheme is adopted from Stansch et al. [93] who proposed a ten step global reaction mechanism for catalytic OCM over La_2O_3/CaO catalyst. Although this reaction network has been widely used for OCM calculations [22] and also been modified to represent other catalyst data as well [94], one of the most important drawbacks of this reaction scheme is that, it does not take any gas phase reaction into account except thermal decomposition of ethane, thereby limiting the validity of the model. To circumvent this problem and, increase the accuracy and range of validity of our analysis, we have taken a slight variation of this kinetic scheme. First of all, the catalytic oxidation reactions of CH_4 , C_2H_6 , C_2H_4 and CO along with the C_2H_4 reforming reactions are kept same as found in the original literature. Secondly, the water gas shift reaction, which is reported as a catalytic reaction in the original reference, has been taken as homogeneous reaction here. Our calculations show that adding water gas shift reaction in the catalytic reaction network has negligible effect on the overall results. And finally, we have considered five gas phase reactions. Note that there are total of eight species (CH_4 , C_2H_6 , C_2H_4 , CO_2 , CO , O_2 , H_2 , H_2O) made up of three atoms (C , H , O). Since the rank of atomic matrix is three, there are five independent reactions. Though not all reactions in the catalytic scheme are independent, they are chosen based on the experimental observations recorded in the original

reference. The catalytic reactions are given as follows:



and the homogeneous reactions are taken as,



The rate expressions for the catalytic reactions are listed in Table 5.1, and the reaction parameters as obtained from Stansch et al. [93] are listed in Table 5.2. In Table 5.1, r_j with $j = 2 - 5, 7$ denote the generalized rate expressions of the catalytic reactions given by eqns. (r.2 - r.5, r.7), respectively, where p_{C_j} ($j = 2 - 5, 7$)

represents the partial pressure of the reactants other than O_2 in those respective reactions. The values of frequency factors ($k_{0,j}$) were originally in terms of weight of catalyst ($mol/gm-s-Pa^{m_j+n_j}$). Here, we have used a catalyst particle density of $3600 kg/m^3$ and expressed the frequency factors in terms of catalyst volume ($mol/m^3-s-Pa^{m_j+n_j}$) in Table 5.2. As per the experimental observations noted in the original reference, the rate of C_2 hydrocarbon formation goes through a maximum with respect to oxygen partial pressures at lower temperatures, whereas at higher temperatures ($T > 1073$ K) the inhibiting effect of oxygen is negligible. Furthermore, the rate of hydrocarbon formation is also observed to significantly decrease with increase of carbon dioxide partial pressures. It is assumed that, for the coupling reaction of methane to ethane (r.1) there is a competition for adsorption between oxygen and carbon dioxide for an active site. That's why the inhibiting effects of oxygen and carbon-dioxide are considered through the Hougen-Watson type rate equation for the primary selective coupling reaction. However, for other oxidation reactions such as partial/deep oxidation of methane, ethane, ethylene and carbon monoxide (r.2 - r.5, r.7), inhibiting effect of only carbon dioxide is considered in the Hougen-Watson type rate equations and no oxygen inhibition is detected. For steam reforming of ethylene (r.6), power-law type rate equation is considered.

The homogenous reaction rate expressions are taken from available kinetic data on homogeneous OCM [84] and are given in Table 5.3. It should be noted that all these rate expressions are expressed in terms of mole fractions here (e.g., y_{CH_4} , y_{CO} , y_{CO_2} , etc.)

that are defined for j^{th} component as

$$y_j = \frac{c_j}{C_0} = \frac{c_j R_g T}{P_T} = \frac{p_j}{P_T} \quad (5.1)$$

where c_j and p_j are the species concentration and partial pressure respectively, R_g is the gas constant, T is temperature, P_T is pressure and $C_0 \left(= \frac{P_T}{R_g T} \right)$ is the total concentration,. Among the twelve reactions, only the thermal cracking of ethane (r.10), steam reforming of methane (r.11) and water gas shift reactions (r.12) are reversible, equilibrium constants of which can be estimated from thermodynamics [27].

Table 5.1: Rate expressions for catalytic reactions

r_1	$= \frac{k_{0,1} \exp \left[-\frac{E_{a,1}}{RT} \right] \left(K_{O_2} \exp \left[\frac{-\Delta H_{ad,O_2}}{RT} \right] p_{O_2} \right)^{n_1} p_{CH_4}}{\left[1 + \left(K_{O_2} \exp \left[-\frac{\Delta H_{ad,O_2}}{RT} \right] p_{O_2} \right)^{n_1} + K_{1,CO_2} \exp \left[\frac{-\Delta H_{ad,CO_2,1}}{RT} \right] p_{CO_2} \right]^2}$
r_j	$= \frac{k_{0,j} \exp \left[\frac{-E_{a,j}}{RT} \right] p_{C_j}^{m_j} \cdot p_{O_2}^{n_j}}{\left[1 + K_{j,CO_2} \exp \left[\frac{-\Delta H_{ad,CO_2,j}}{RT} \right] p_{CO_2} \right]^2}, \quad j = 2 - 5, 7$
r_6	$= k_{0,6} \exp \left[\frac{-E_{a,6}}{RT} \right] p_{C_2H_4}^{m_6} \cdot p_{H_2O}^{n_6}$

Table 5.2: Kinetic parameters of catalytic reactions

Reaction No.	$k_{0,j}$	Ea, j	K_{j,CO_2}	$\Delta H_{ad,CO_2}$	m_j	n_j
Units	$\frac{mol}{m^3-s-Pa^{m_j+n_j}}$	$\frac{kJ}{mol}$	Pa^{-1}	$\frac{kJ}{mol}$	-	-
r_1	83.52×10^6	182	0.83×10^{-13}	-186	1.0	0.40
r_2	7.20	48	0.25×10^{-12}	-175	0.24	0.76
r_3	1.87	68	0.36×10^{-13}	-187	0.57	0.85
r_4	6.12×10^5	157	0.45×10^{-12}	-166	0.95	0.37
r_5	2.16×10^5	166	0.16×10^{-12}	-211	1.0	0.96
r_6	33.48×10^9	300	-	-	0.97	0
r_7	396	104	0.40×10^{-12}	-168	1.0	0.55
Note: For reaction r_{c1} , $K_{O_2} = 0.23 \times 10^{-11} Pa^{-1}$ and $\Delta H_{ad,O_2} = -124 kJ/mol$.						

Table 5.3: Rate expressions for homogeneous reactions

Reaction No.	$k_{0,j} (s^{-1})$	$\frac{Ea,j}{R} (K)$	Rate Expression
r_8	1.9×10^9	25500	$k_{0,9} \exp \left[\frac{-E_{a,9}}{RT} \right] y_{CO} \cdot y_{O_2}^{0.5}$
r_9	3.8×10^9	26220	$k_{0,8} \exp \left[\frac{-E_{a,8}}{RT} \right] y_{CH_4}^{-0.3} \cdot y_{O_2}^{1.3}$
r_{10}	4.0×10^{12}	32836	$k_{0,10} \exp \left[\frac{-E_{a,10}}{RT} \right] (y_{C_2H_6} - y_{C_2H_4} \cdot y_{H_2} / K_{eq,10})$
r_{11}	1.5×10^9	24056	$k_{0,11} \exp \left[\frac{-E_{a,11}}{RT} \right] (y_{CH_4} \cdot y_{H_2O} - y_{CO} \cdot y_{H_2}^3 / K_{eq,11})$
r_{12}	4.5×10^8	29830	$k_{0,12} \exp \left[\frac{-E_{a,12}}{RT} \right] (y_{CO_2} \cdot y_{H_2} - y_{CO} \cdot y_{H_2O} / K_{eq,12})$

5.4 Steady-state bifurcation analysis of short monolith or gauze or wire-mesh type reactors

The steady state multi-component short monolith model as given by eqns. (2.54 - 2.57) is solved numerically using the arc-length continuation algorithm to generate the bifurcation diagrams of state variables versus feed (inlet) temperature. As mentioned earlier, the main objective of this study is to analyze the impact of various design and operating parameters on the ignition-extinction behavior of the system. In addition, other quantities of particular interest in OCM reactor design are CH_4 and O_2 conversion, C_2 product ($C_2H_6 + C_2H_4$) yield and selectivity. Since there are various definitions of yield and selectivity in the literature, it is pertinent to explicitly provide the expressions of these terms here. The reactant (CH_4 and/or O_2) conversion (χ_j), product yield (Y_j) and selectivity (S_j) are given by:

$$\chi_j = 1 - \frac{F_j}{F_j^{in}}, \quad (5.2)$$

$$Y_j = \frac{n_{c,j} F_j}{F_{CH_4}^{in}}, \quad (5.3)$$

$$\text{and } S_j = \frac{n_{c,j} F_j}{F_{CH_4}^{in} - F_{CH_4}}, \quad (5.4)$$

where, F_j^{in} and F_j are the inlet and exit molar flow rates of species j and $n_{c,j}$ represents the number of carbon atoms in species j . The number of carbon atoms in the undesired products (CO and CO_2) is 1, and for desired products (C_2H_6 and C_2H_4) is 2. From the above expressions, it is clear that, $Y_j = \chi_{CH_4} S_j$. In what follows, we present only

the selectivity plots.

In the following sections, we investigate the role of various design and operating conditions such as feed CH_4/O_2 ratio, space time, channel hydraulic radius, pressure and heat loss on the bifurcation features, as well as the overall performance of the reactor. All of our analyses are done under atmospheric pressure in adiabatic conditions, except the cases where we investigate the impact of operating pressure or heat loss.

5.4.1 Impact of inlet CH_4/O_2 mole ratio:

Fig. 5.1 shows the computed bifurcation diagrams of fluid exit temperature, CH_4 conversion, O_2 conversion and C_2 selectivity for different feed CH_4/O_2 mole ratio at fixed space time $\tau = 50$ ms, channel hydraulic radius $R_{\Omega_f} = 250 \mu m$ and washcoat thickness $R_{\Omega_{wc}} = 100 \mu m$. [The wall half-thickness $R_{\Omega_s} = 90 \mu m$ in all the calculations]. From these bifurcation diagrams, it can be observed that with the increase of inlet CH_4/O_2 mole ratio, the maximum C_2 selectivity on the ignited branch near the extinction point increases, while the CH_4 conversion decreases. This is due to the relative difference in reaction orders of methane and oxygen between the desired dimerization reaction (r.1) and undesired partial/deep oxidation reactions (r.2-r.3). For two parallel reactions with rates r_1 and r_2 , effective orders of m_i and n_i ($i = 1, 2$) w.r.t methane and oxygen, and Arrhenius type dependence of effective rate constants, the instantaneous selectivity is given by

$$\frac{r_1}{r_2} = \frac{k_1 [CH_4]^{m_1} [O_2]^{n_1}}{k_2 [CH_4]^{m_2} [O_2]^{n_2}} = \frac{k_{10}}{k_{20}} \exp \left(\frac{E_2 - E_1}{R_g T} \right) [CH_4]^{m_1 - m_2} [O_2]^{n_1 - n_2}. \quad (5.5)$$

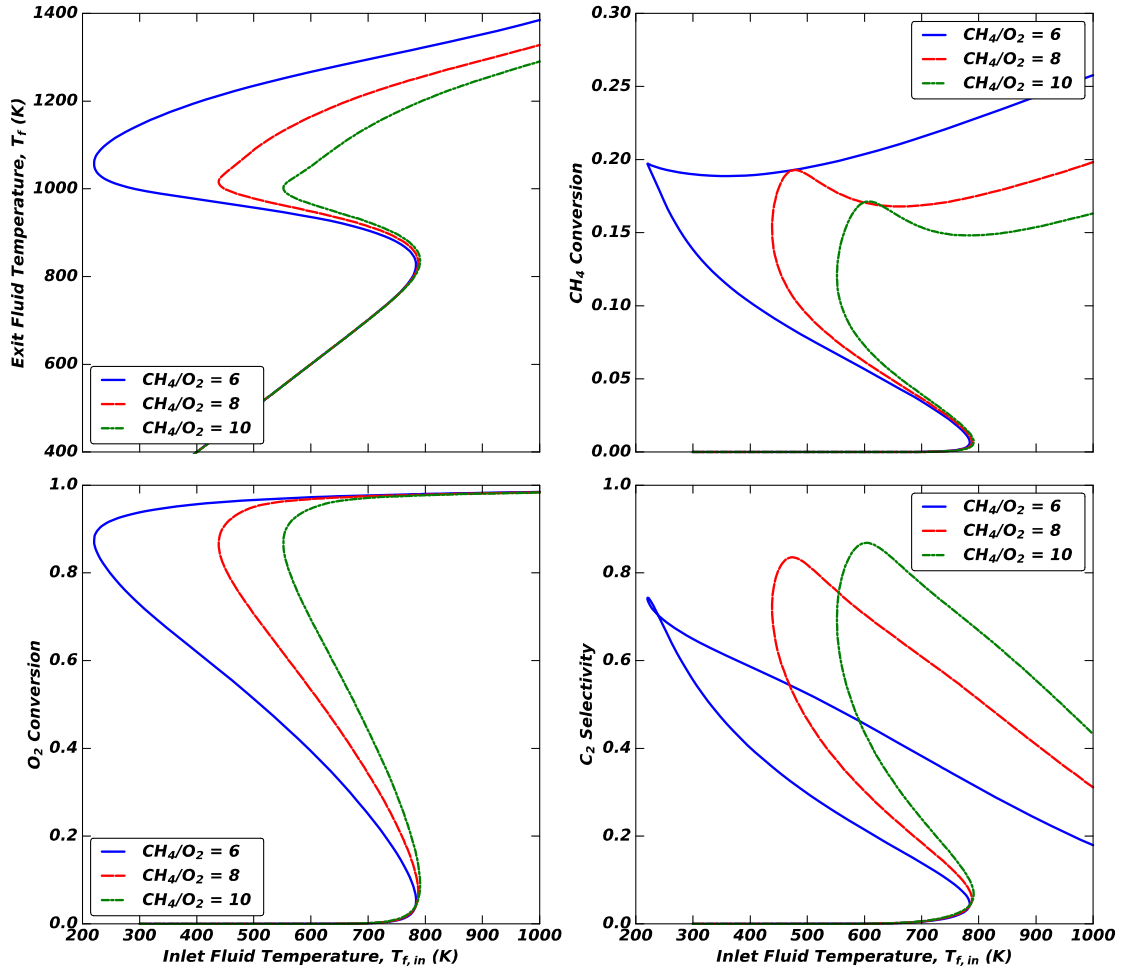


Figure 5.1: Computed bifurcation diagrams of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different inlet CH_4/O_2 mole ratio.

In the kinetic scheme used, the methane coupling reaction has the lowest apparent reaction order in oxygen ($n_1 < n_2$) but highest reaction order with respect to methane ($m_1 > m_2$), as pointed out by Balakotaiah et al. [22]. Further, the effective activation energy of the coupling reaction is higher than that of the deep oxidations ($E_1 > E_2$). Therefore, the methane coupling reaction (r.1) is favored over the undesired oxidation reactions (r.2 - r.3) at high concentration of methane and low concentration of oxygen which explains the increased C_2 selectivity at high inlet CH_4/O_2 mole ratio. Also, higher operating temperature favors the coupling reaction until secondary oxidations and reforming reactions become important. Therefore, the maximum C_2 selectivities are found to occur right next to the extinction point where oxygen concentrations are low and fluid/solid temperatures are high. It is interesting to note that the maximum C_2 selectivity for inlet $CH_4/O_2 = 6$ is found only on the unstable branch of the bifurcation curve for the choices of operating conditions taken here. However, for inlet CH_4/O_2 mole ratios between 8 and 10, there is a suitable stable operating window around the extinction point where both inlet and exit fluid temperatures are low as well as CH_4 conversion ($\sim 20\%$) and C_2 selectivity ($\sim 80\%$) are highest.

After a local maximum, CH_4 conversion is found to go through a shallow minimum before increasing monotonically again with respect to fluid inlet temperatures. Following the initial conversion of methane to ethane through the primary selective dimerization reaction there is a competition for oxygen among the parallel oxidation reactions of methane and C_2 products. At higher fluid inlet temperatures beyond the extinction point, these non-selective reactions of methane dominate over the selective ones. Since these reactions consume less number of moles of methane than the

C_2 forming reaction, the resulting methane conversion is lower. Furthermore, as the system proceeds towards complete oxygen conversion, methane conversion increases again with respect to fluid inlet temperature due to its consumption through the reforming reaction (r.11).

Though the ignition temperatures are negligibly effected by the feed mole ratio, the feed temperature at extinction increases while decreasing the region of multiplicity as we increase the inlet CH_4/O_2 mole ratio. The exit fluid temperatures are also found to decrease with the increase of inlet CH_4/O_2 mole ratio which is consistent with the combined inferences that higher inlet mole ratios produce more C_2 products per mole of converted methane and C_2 forming reactions release less heat than partial/deep oxidation reactions. Our calculations reveal no significant differences between fluid and solid temperatures (not shown in figure) which suggest that the system is well within the homogeneous limit (negligible interphase gradients) at such small value of hydraulic radius.

5.4.2 Impact of space time

The impact of space time on exit fluid temperature, reactant conversions and C_2 selectivity at constant feed CH_4/O_2 mole ratio = 8, channel hydraulic radius $R_{\Omega_f} = 250 \mu m$ and washcoat thickness $R_{\Omega_{wc}} = 100 \mu m$ is illustrated in fig. 5.2. With the increase of space time τ from 1 to 100 ms, both the ignition and extinction temperatures decrease, while increasing the region of hysteresis. At a lower space time such as $\tau = 1$ ms, the external and internal mass transfer times are of the same order of magnitude as the space time, thereby resulting in moderate reactant conversion

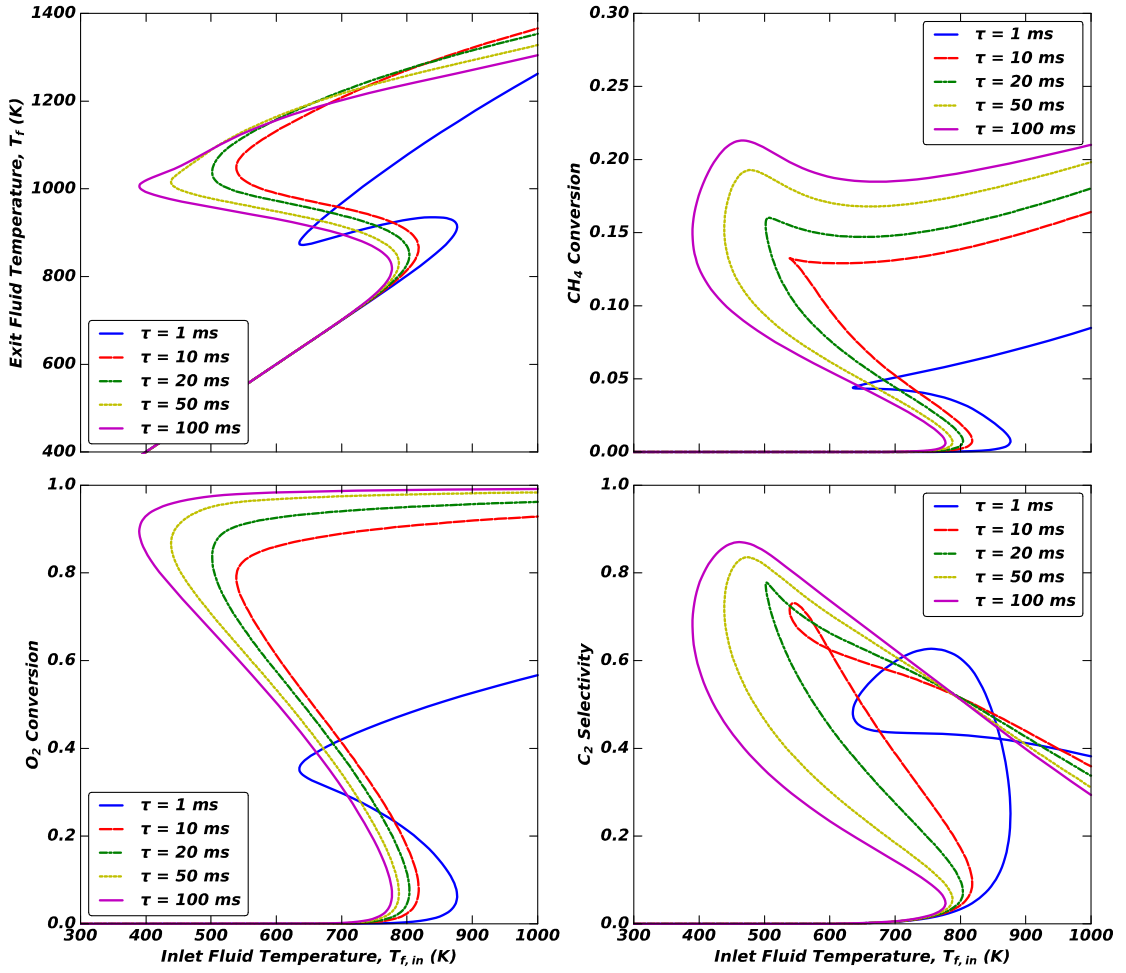


Figure 5.2: Computed bifurcation diagrams of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different space times, τ .

and lower adiabatic temperature rise. Moreover, the maximum C_2 selectivities for the cases of lower space times (e.g., 1 - 10 ms) are also found to occur on the unstable branches of the bifurcation diagram. The best combinations of methane conversion, C_2 selectivity and oxygen conversions are only achieved on the ignited branches close to the extinction points at increased space times (50 - 100 ms). Only impractically low values are obtained for space times less than or equal to 20 ms. Larger space times assist in reactor level species backmixing, and hence favor the production of intermediate C_2 products while expanding the region of multiplicity [22]. It can also be noted that at a higher space time such as $\tau = 100$ ms, the ignited branch at high values of the exit fluid temperature is no longer parallel to the quenched branch, which implies the presence of dominant endothermic chemistry at elevated temperatures. Under such high space times and temperatures, the system reaches almost complete oxygen conversion and proceeds towards attaining thermodynamic equilibrium through the reversible and predominantly endothermic reactions such as ethane cracking (r.10), methane and ethylene reforming (r.11, r.7) and reverse water-gas shift (r.12) reaction.

It is also relevant to point out that, we have chosen an inlet CH_4/O_2 mole ratio of 8 here because it leads to a reasonable extinction feed temperature of 440 K at a space time of 50 ms, with maximum selectivity being achieved around 480 K. An inlet CH_4/O_2 mole ratio lower than 8 will further decrease the extinction point and may bring it below the ambient temperature, whereas feed molar ratio higher than 8 will result in relatively higher extinction feed temperature, henceforth making the autothermal operation of the reactor unfeasible. Although an increased space time of

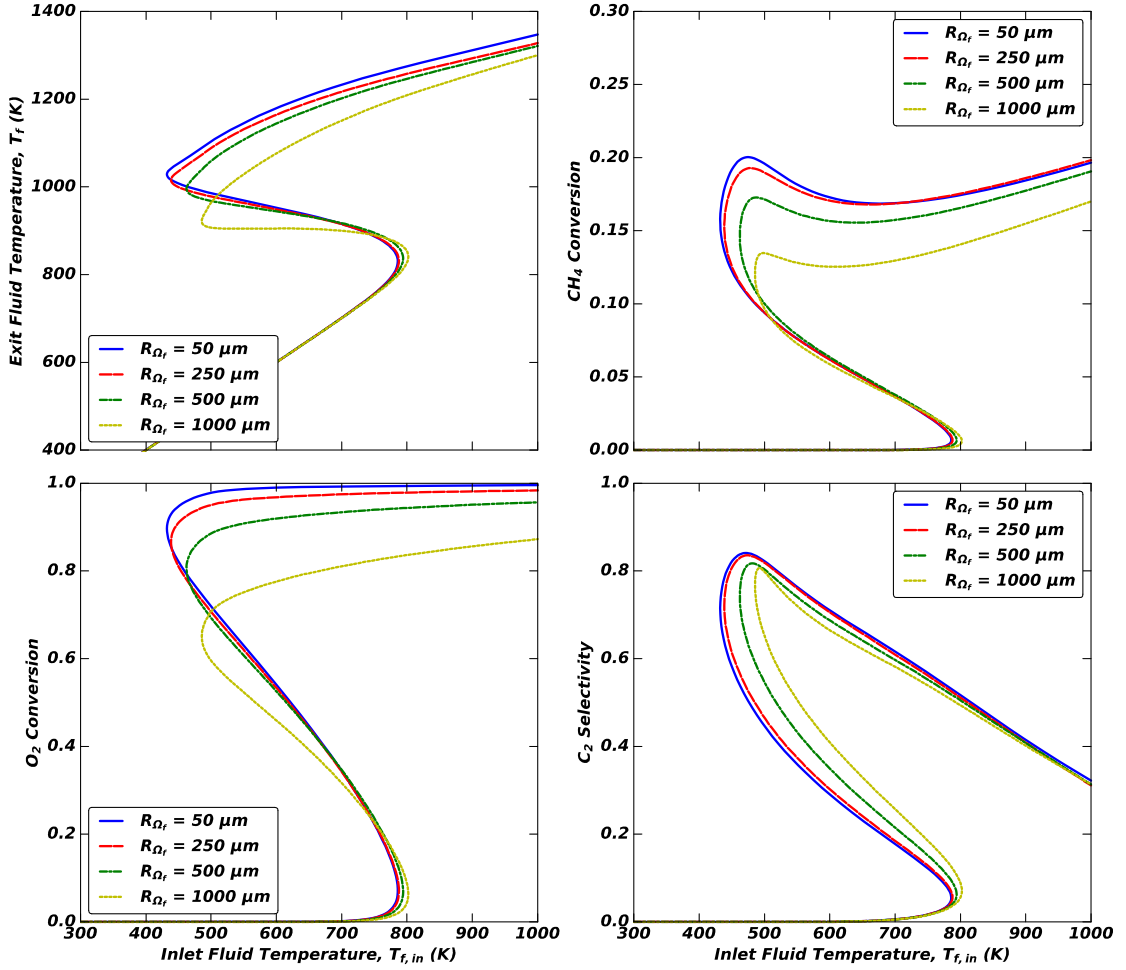


Figure 5.3: Computed bifurcation diagrams of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature for different channel hydraulic radii.

100 ms further decreases the extinction feed temperature to 390 K and improves C_2 selectivity, such a high space time can lead to lower productivity.

5.4.3 Impact of channel hydraulic radius

One of the important parameters of coupled homogeneous-catalytic reaction systems is the volume to surface ratio, which plays a crucial role in determining the degree of coupling (species as well as thermal) and also the dominance of one over

the other [95]. In practice, this ratio can be changed by tuning the channel hydraulic radius (or cell density) and/or washcoat thickness in a monolith reactor. Keeping the inlet CH_4/O_2 mole ratio, space time and washcoat thickness constant at 8, 50 ms and 100 μm , respectively, increasing the channel hydraulic radius R_{Ω_f} from 50 μm to 1 mm, decreases the maximum CH_4 conversion and C_2 selectivity, as shown in fig. 5.3. Although, CH_4 conversion and C_2 selectivity goes through a maximum on the stable ignited branches close to the extinction points for all the cases studied here, the suitable operating window which lies between the extinction point and the point of maximum C_2 selectivity/ CH_4 conversion shrinks with the increase of channel hydraulic radius. The extinction temperature is also found to increase more than the ignition temperature at higher channel hydraulic radius, thereby reducing the region of multiplicity. In this context it is extremely important to reintroduce the transverse Peclet number for species j , P_j , which is defined as the ratio of transverse diffusion time $\left(\tau_{D,j} = \frac{R_{\Omega_f}^2}{D_{f,j}}\right)$ to the space time (τ) and is given by eqn. 2.86. As noted by Alam et al. [17], catalytic reactions can ignite at high values of channel hydraulic radius, however reactant conversions are only higher when $\tau_{D,j}$ is much smaller than τ ($P_j < 0.2$). For the selected space time of $\tau = 50$ ms, at higher channel radii (500 $\mu m - 1$ mm), the system is controlled significantly by external mass transfer which leads to lower conversion and selectivity. In addition, higher volume to surface ratio (channel hydraulic radius) results in a region where the homogeneous reactions become more dominant than the catalytic reactions in the coupled homogeneous-heterogeneous system ([17],[24]), which reduces the C_2 selectivity in this case.

However, this external diffusional limitation can be circumvented if both the chan-

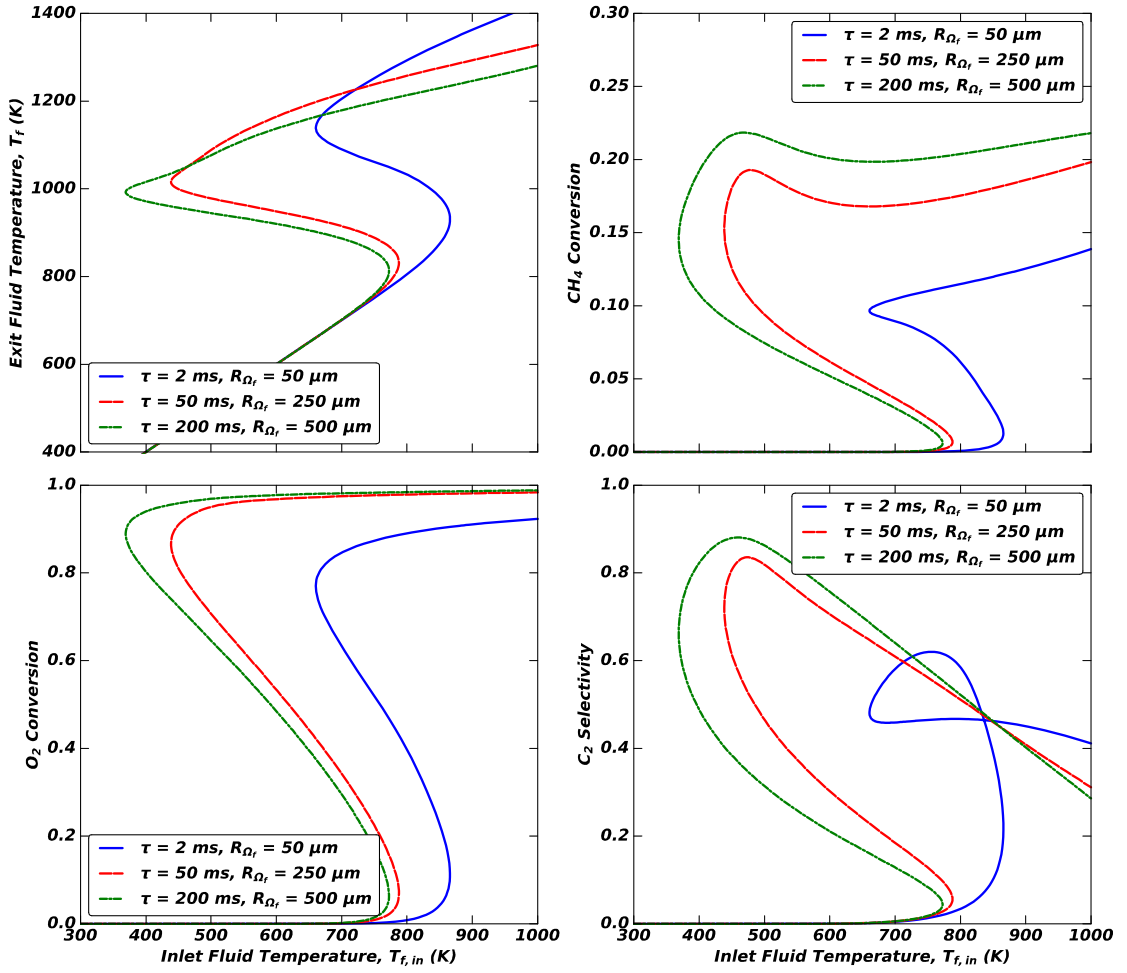


Figure 5.4: Computed bifurcation diagrams of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different channel hydraulic radii and space time.

nel hydraulic radius and space time are changed simultaneously such that the transverse Peclet number remains constant. In fig. 5.4, we have taken the transverse Peclet number of limiting reactant oxygen, P_{O_2} at $R_{\Omega_f} = 250 \mu m$ and $\tau = 50$ ms as the base case and changed R_{Ω_f} and τ accordingly to keep P_{O_2} constant. Other parameters such as inlet CH_4/O_2 mole ratio and washcoat thickness are kept at their prior values. Unlike the previous case, it can be observed here that, the highest CH_4 conversion and C_2 selectivity occurs at a higher channel hydraulic radius, $R_{\Omega_f} = 500 \mu m$ and space time $\tau = 200$ ms. Moreover, the extinction temperature is found to be lower under such design and operating conditions, resulting in an expansion of the operating window. On the other hand, the conversions at $R_{\Omega_f} = 50 \mu m$ and $\tau = 2$ ms are still poorer on the ignited branches even with a lower P_{O_2} value. This is due to strong washcoat diffusional limitation at such low space time, an estimate of which can be calculated by comparing the transverse diffusion time in washcoat $\left(\tau_{D_{wc,j}} = \frac{R_{\Omega_{wc}}^2}{D_{wc,j}}\right)$ to space time τ .

The enhanced selectivity and conversion at higher channel hydraulic radius and space time can be attributed to the difference in diffusivities between methane and oxygen. Since, the bulk diffusivity of methane is higher compared to that of oxygen, the diffusion time in fluid phase is greater for oxygen, allowing relatively higher CH_4/O_2 ratio on the catalyst surface than in the bulk or inlet. This effect will be more amplified at higher channel radii or when the system is not in the homogeneous limit. As we have noticed earlier that, due to stoichiometry of OCM chemistry and reaction orders, the dimerization reaction of methane is more selective at higher CH_4/O_2 ratios. Therefore, higher channel radius will lead to substantial interfacial gradients,

which ultimately results in higher CH_4/O_2 ratio on the catalyst and improved C_2 selectivity.

The reason behind choosing the transverse Peclet number of oxygen at $R_{\Omega_f} = 250$ μm and $\tau = 50$ ms as the base case is to maintain the adiabatic nature of our system by keeping the magnitude of space time atleast one order less than the characteristic heat loss time, which is usually in the range of few seconds ([18], [22]). For example, if we have taken $R_{\Omega_f} = 50$ μm and $\tau = 50$ ms as our base case, the required space time at $R_{\Omega_f} = 250$ μm would have been 1.25 s, which will then necessitate the consideration of heat loss. For the same reason, we did not extend the constant transverse Peclet number analysis to $R_{\Omega_f} = 1$ mm and $\tau = 0.8$ s for our calculations in fig. 5.4.

5.4.4 Impact of pressure

In practice, process constraints and/or economics dictate that the partial oxidation reactions be carried out at pressures higher than atmospheric. For example, for the case of OCM, the optimal operating pressure may be in the 5 to 10 bar range [85]. In a large scale reactor operating at higher pressure, the space time can be varied either by changing the mass or volumetric flow rate. Higher operating pressure at a constant mass flow rate decreases the volumetric flow rate, thereby increasing the space time. In contrast, operation at higher pressure at the same volumetric flow rate (or linear velocity) leads to increase in productivity and is preferred. Moreover, as the downstream product separation processes are usually carried out at elevated pressures, operating OCM at high pressure can be advantageous from an economic standpoint. Here, in fig. 5.5, we demonstrate the impact of total pressure on the exit fluid

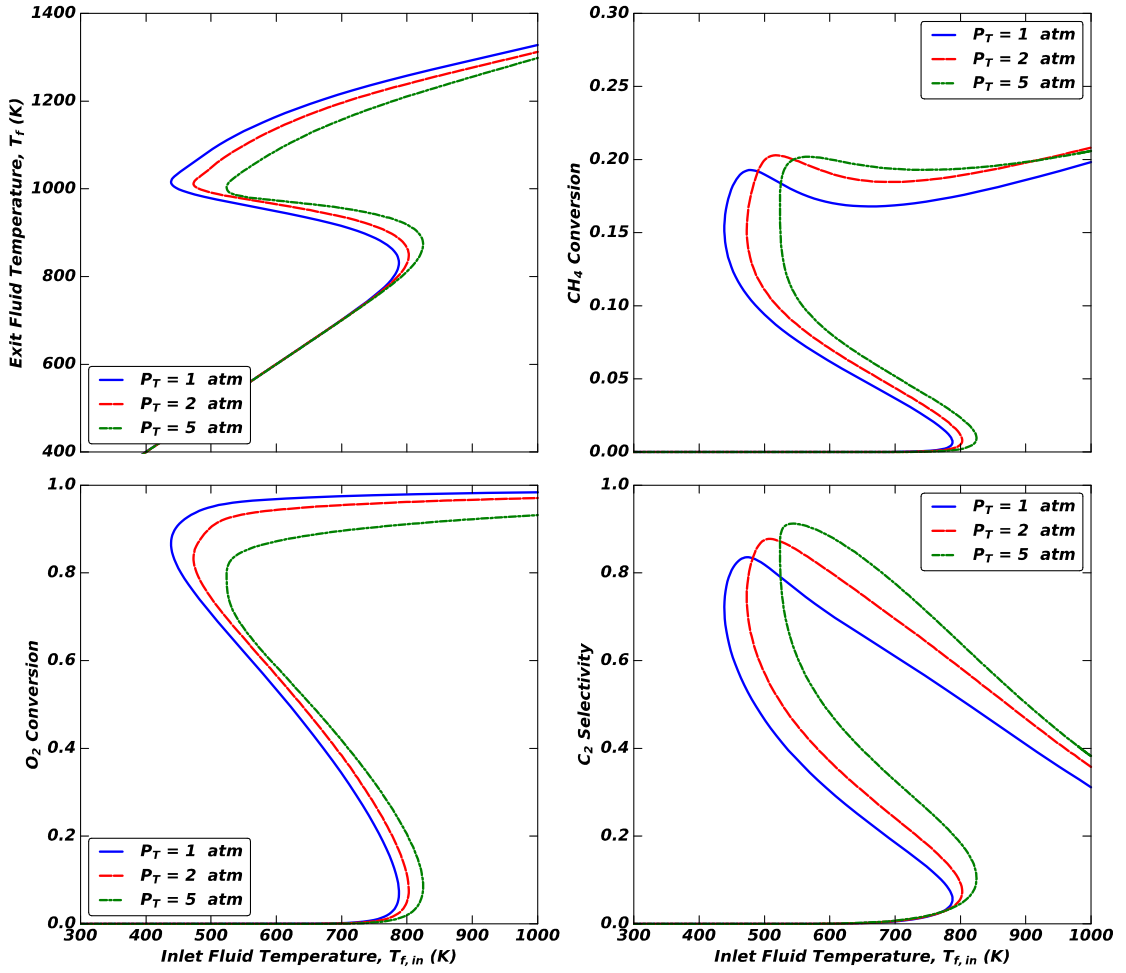


Figure 5.5: Computed bifurcation diagrams of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature for different total pressure, P_T .

temperature, reactant conversion and product selectivity for a constant molar (mass) flow rate at fixed feed CH_4/O_2 mole ratio = 8, space time $\tau = 50$ ms, channel hydraulic radius $R_{\Omega_f} = 250 \mu m$ and washcoat thickness $R_{\Omega_{wc}} = 100 \mu m$. With the increase of total pressure from 1 - 5 atm, both the ignition and extinction temperatures increase while decreasing the exit fluid temperature. The maximum CH_4 conversion is found to increase slightly with the increase of pressure, however, there is a considerable increase in C_2 selectivity and decrease in O_2 conversion at elevated pressures. Simultaneous increase in C_2 selectivity and decrease in O_2 conversion for the same amount of CH_4 converted suggests that the selective methane dimerization reaction is favored more over the non-selective oxidation reactions under such operating conditions. It also explains the lower exit fluid temperatures observed under high pressure as C_2 forming reactions release less heat than the non-selective oxidation reactions. In this context it is important to mention that apparently contradictory claims of lower selectivity at higher operating pressure with other catalysts exist in literature ([96]-[97]). Mainly these studies focused on the stability of catalyst and the decrease of selectivity is caused potentially due to catalyst deactivation under such elevated pressures.

5.4.5 Impact of heat loss from monolith to furnace or surroundings

Fig. 5.6 illustrates the effect of heat loss from the monolith reactor to the furnace (or surroundings) on exit fluid temperature, reactant conversion and product selectivity at fixed CH_4/O_2 mole ratio = 8, space time $\tau = 50$ ms, channel hydraulic radius $R_{\Omega_f} = 250 \mu m$ and washcoat thickness, $R_{\Omega_{wc}} = 100 \mu m$. Instead of actually

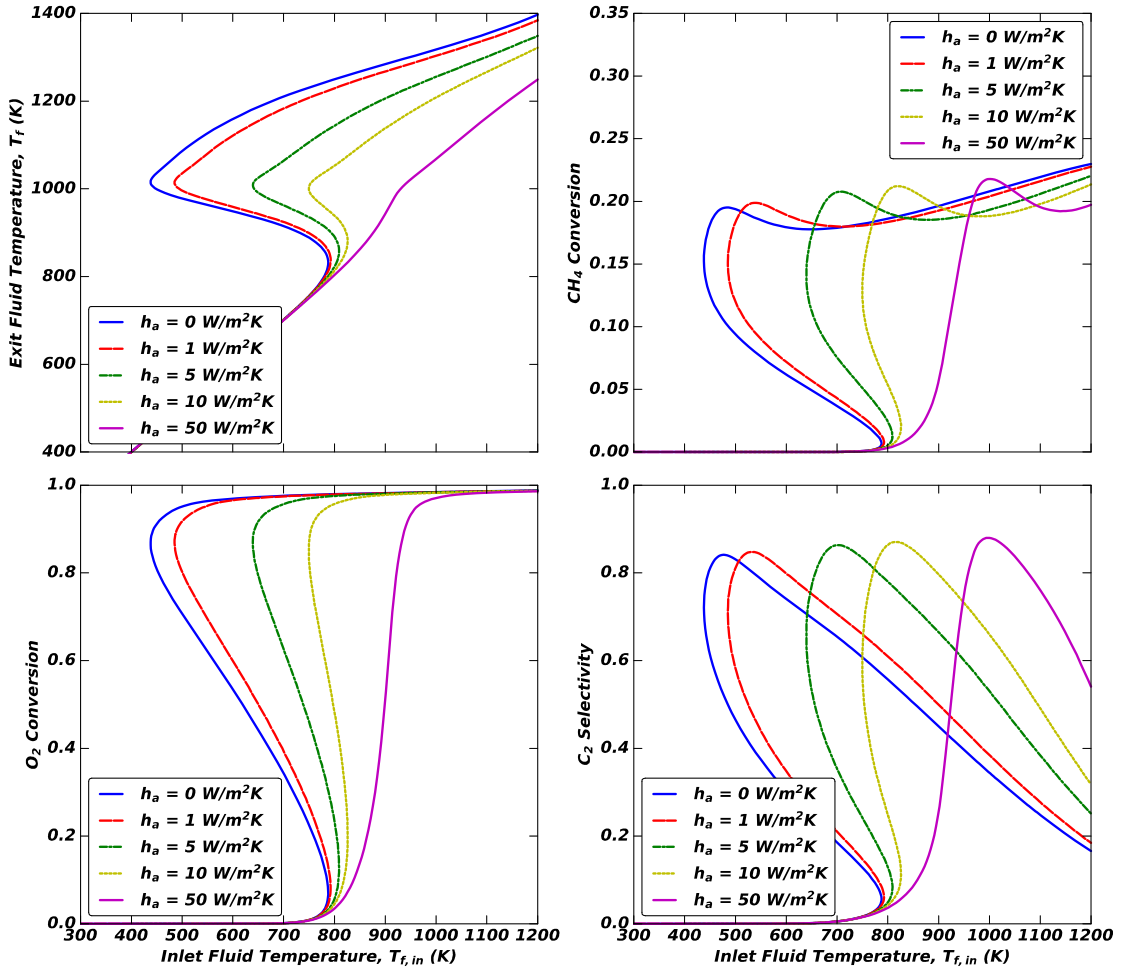


Figure 5.6: Computed bifurcation diagrams of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature in the presence of heat loss at different values of heat transfer coefficient, h_a .

calculating the proportions of convective and radiative heat losses, we have assumed here an average value of heat transfer coefficient h_a between the monolith reactor and furnace or surroundings, and varied it to represent different extents of heat loss. Also, inlet temperature is taken to be equal to the ambient or furnace temperature T_a in our calculations. It can be noted from fig. 5.6 that, as the value of h_a is increased from 0 to 10 $W/m^2.K$, the extinction temperature increases while decreasing the region of hysteresis. Further increase of h_a to 50 $W/m^2.K$ leads to complete disappearance of hysteresis phenomenon and the reactor shifts closer to the isothermal regime. Although the maximum values of CH_4 conversion and C_2 selectivity are found to be same for the various sets of operating conditions chosen here, it is not surprising to find that the feed temperature at which the maximum selectivity occurs, shifts towards higher values in the presence of heat loss. As discussed by Sarsani et al.[18], the characteristic heat loss time depends on the diameter of the monolith reactor and laboratory (or furnace) conditions and could vary from about 5 ms to 100 ms. Since the space times and reaction times are also in the same range, most laboratory scale experiments are neither isothermal nor adiabatic. In contrast, for large diameter monoliths, the heat loss time could be on the order of seconds and hence these large reactors are closer to adiabatic operation. As discussed in the literature, the best way to manage heat in large scale OCM reactors is to operate the reactor autothermally under near adiabatic conditions, close to the extinction point ([22], [37]).

5.5 Bifurcation analysis of long channel model

In order to analyze the impact of these finite mixing effects and spatial gradients on the performance of OCM in a monolith reactor, we use the long channel model as described by equations (2.46 - 2.53). Similar to the hydrogen and propane combustion cases, we perform a pseudo steady-state analysis by varying the feed temperature at a very low ramp rate (1 K/min) so that quasi-steady state at every value of inlet temperature can be achieved. By increasing (beyond ignition) and then decreasing (below extinction) the feed temperature slowly, we can obtain the dynamic hysteresis plots containing the stable branches of the steady-state bifurcation diagram. The model equations are discretized in the axial direction and integrated over time using a stiff ODE solver (LSODA). The values of fixed parameters used in the model are given in Table 5.4.

Table 5.4: List of parameters for the two-mode long channel model - OCM

Quantities	Unit	Value
R_{Ω_f}	μm	250
$R_{\Omega_{wc}}$	μm	100
R_{Ω_w}	μm	190
C_{pw}	$J/kg.K$	1000
ρ_w	kg/m^3	2000
α_f	m^2/s	$9.8 \times 10^{-10} \frac{T^{1.75}}{P}$
CH_4/O_2	-	8

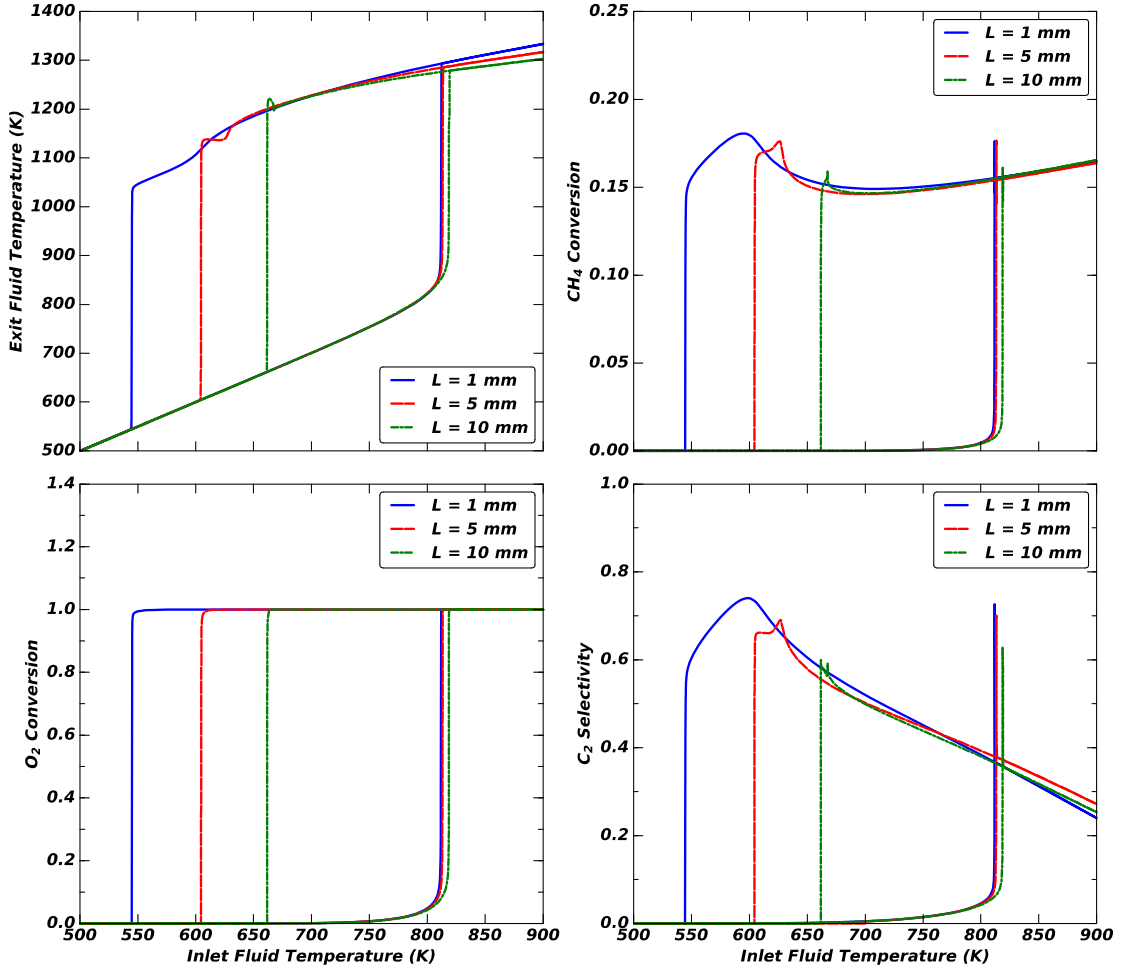


Figure 5.7: Computed dynamic hysteresis plots of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different reactor lengths.

5.5.1 Impact of reactor length and flow velocity

The extent of species and thermal backmixing, which are quantified by the axial mass and heat Peclet numbers, can be varied by changing the reactor length or the axial flow velocity or both. For a fixed space time ($\tau = \frac{L}{\langle u \rangle}$) and catalyst loading, increasing the reactor length increases (decreases) the mass and heat Peclet numbers (species and thermal backmixing), thereby gradually shifting the operation of the re-

actor from a thin bed or CSTR type behavior (infinite species/thermal backmixing) to a long bed or PFR type (zero species/thermal backmixing) ([22],[84], [87], [88]) in the homogeneous limit (or small values of hydraulic radius for which interphase gradients are small). However, it has been found that the actual magnitude of the space time (or flow velocity) also plays an important role in determining the location of the extinction temperature. As shown in fig. 5.7, when space times are low (~ 10 ms) (flow velocities are high), as the reactor length is increased from 1 - 10 mm, the extinction temperature increases while shrinking the width of hysteresis region. Although oxygen is found to reach nearly 100% conversion for all the cases we studied, the maximum CH_4 conversion and C_2 selectivity are observed to decrease with increase of the reactor length. As we increase the reactor length (at a fixed space time) and reduce the extent of species backmixing, the average concentrations of the reactants increase in the reactor. These local high concentrations of reactants (especially oxygen) promote the undesired oxidation reactions over the desired coupling reaction and bring down the selectivities of intermediate products (ethane and ethylene). Furthermore, the CH_4 conversion decreases with increasing reactor length as partial and deep oxidation reactions consume less number of moles of methane than the coupling reaction.

Fig. 5.8 shows the computed dynamic hysteresis plots for two different reactor lengths at a fixed space time, $\tau = 50$ ms and effective solid thermal conductivity, $\kappa_w = 1.5$ W/m.K. We note that the extinction temperature becomes independent of the reactor length as the effective heat and mass Peclet numbers corresponding to these values are such that the behavior approaches that of the lumped thermal

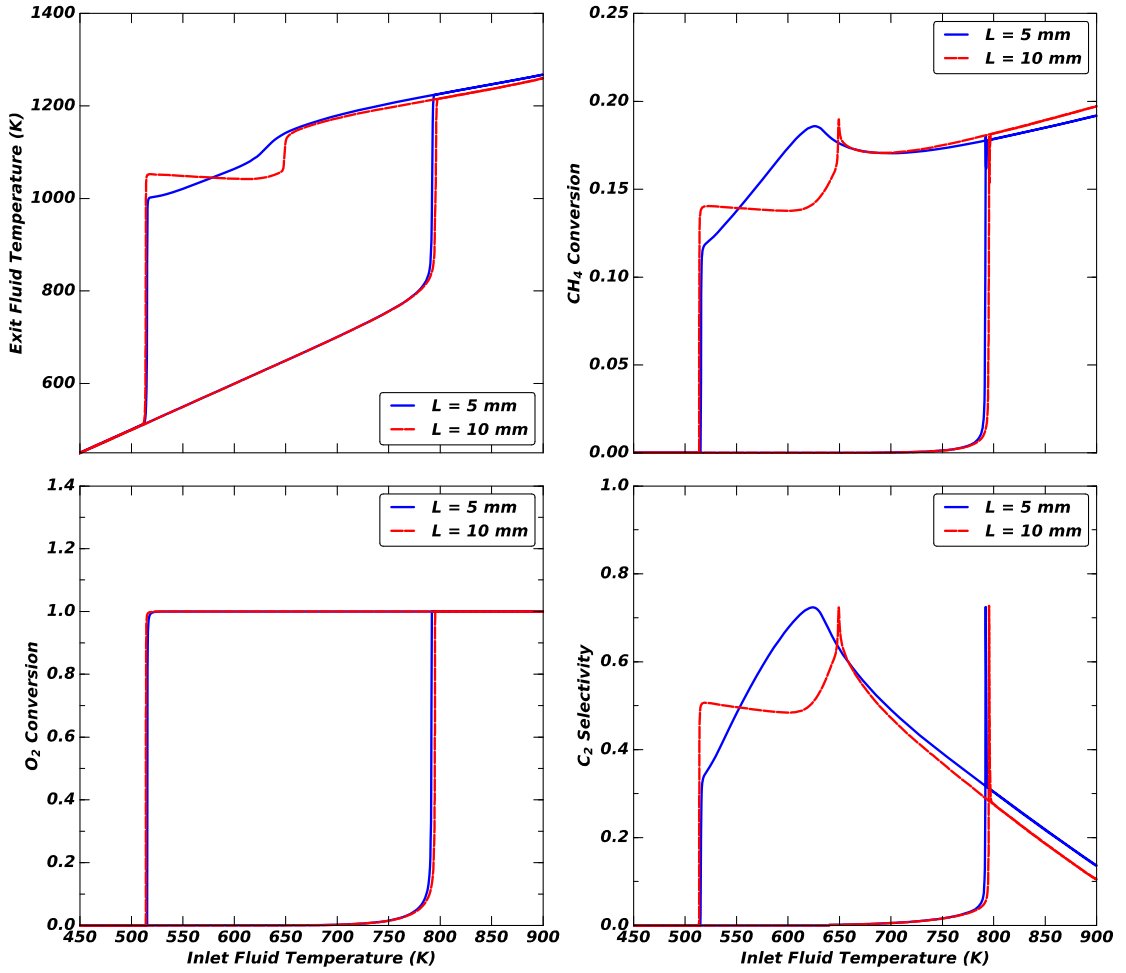


Figure 5.8: Computed dynamic hysteresis plots of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different reactor lengths.

reactor (LTR) model ($Pe_m \gg 1$, $Pe_{h,eff} \sim 1$). However, the methane conversion and C_2 selectivity on the ignited branch are different for the two cases due to the location of the reaction zone. For example, non-selective oxidation and reforming reactions occur in reactor downstream because of which C_2 selectivity decreases sharply for the longer bed. The stark difference between the two cases shown here is the nature of the ignited branch and can be attributed to the relative differences in mass and heat dispersion along the channel. As the extent of species and thermal backmixing are relatively lower in the reactor with $L = 10 \text{ mm}$, it exhibits steeper gradients and higher inlet temperature for maximum selectivity. While the extinction point is no more sensitive to reactor length, its actual value decreased by 90 K for $L = 5 \text{ mm}$ and by 145 K for $L = 10 \text{ mm}$, when space time is increased from 10 ms to 50 ms . Selectivity and conversion are found to increase substantially from 58% to 72% and from 15% to 19% , respectively, as space time is increased for the reactor with $L = 10 \text{ mm}$. Slight increase in selectivity and conversion are also observed for the 5 mm case.

It is important to note the presence of oscillations and spikes in the CH_4 conversion and C_2 selectivity plots near the ignition point. Such oscillations are not observed in fluid temperature or O_2 conversion plots. We have repeated our calculations until mesh independence is achieved, however these oscillations could not be eliminated even with the use of extremely small mesh size ($\sim 10^{-2} \text{ mm}$), which suggests that they are primarily because of the reaction kinetics and not due to numerical inaccuracies. Additionally, some of the eigenvalues of the Thiele matrices are found to be complex, confirming that these oscillations are due to kinetics and possibly due to coupling between exo and endothermic chemistries. A detailed stability analysis of the steady-

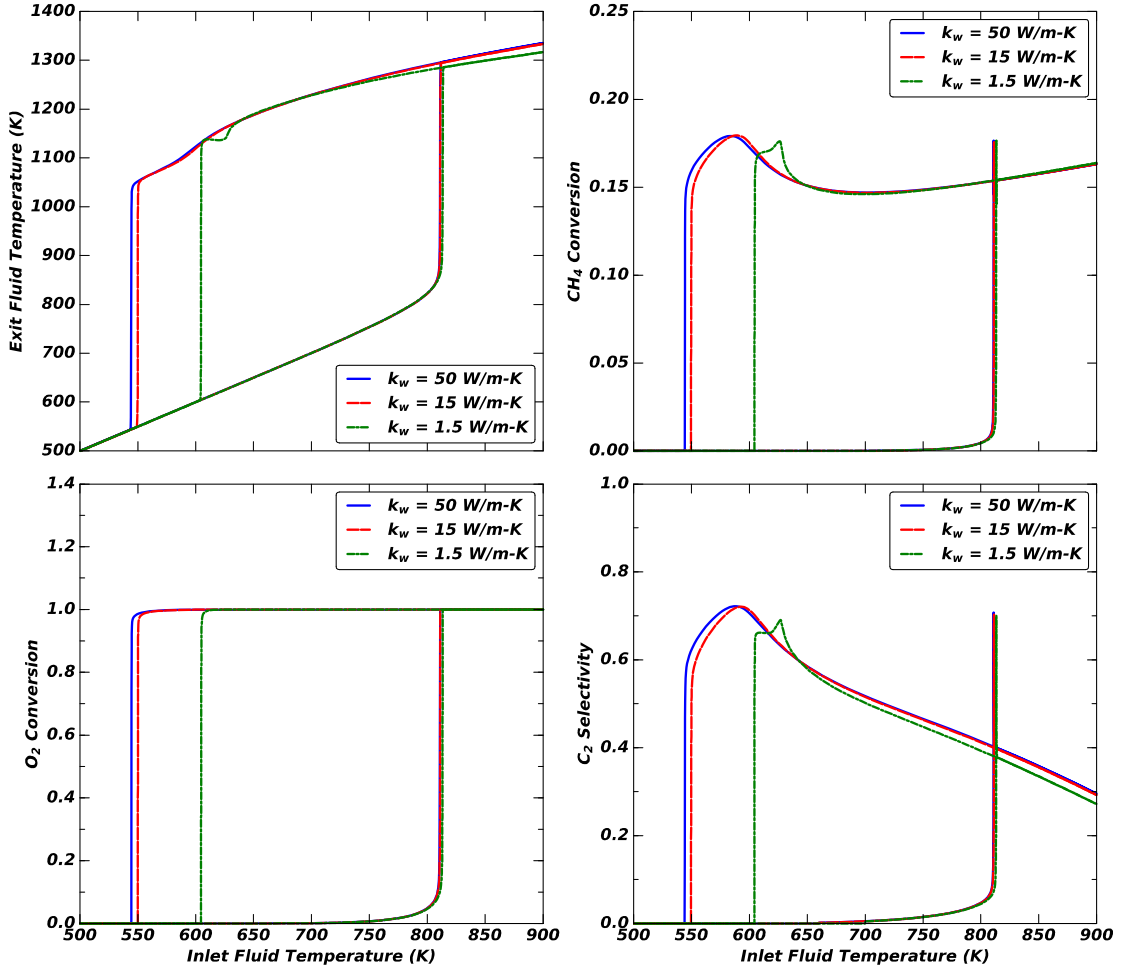


Figure 5.9: Computed dynamic hysteresis plots of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different solid conductivity.

states along with calculation of Hopf bifurcation points is necessary to thoroughly understand these behaviors. Since these underlying topics are not relevant to the focus of this current article, they are not pursued here and would be taken up in future studies.

5.5.2 Impact of thermal conductivity of the substrate material

At a fixed reactor length and axial velocity, increasing the monolith wall effective conductivity enhances the extent of thermal backmixing while increasing the ratio of mass to heat Peclet numbers $\left(\frac{Pe_m}{Pe_{h,eff}}\right)$. A monolith reactor behavior with high values of $\frac{Pe_m}{Pe_{h,eff}}$ may approach the limiting case of a Lumped Thermal Reactor (LTR) model and is considered as an optimum reactor design for OCM as it may give the largest region of autothermal operation ([22],[84], [87], [88]). In practice, the LTR limit can be approached by using a substrate material of high thermal conductivity, e.g., metallic monoliths, silicon carbide substrates, metallic wire gauzes, and so forth. At a space time $\tau = 10$ ms and reactor length $L = 5$ mm, for a tenfold increase in solid conductivity from 1.5 to 15 W/m.K, we have found the extinction point to decrease by about 50 K while widening the region of multiplicity as shown in fig. 5.9. Though, not much improvement is noted in CH_4 conversion and C_2 selectivity, the suitable operating window between the extinction point and maximum conversion/selectivity is found to expand, facilitating stable operation on the ignited branches even with longer monoliths (but with high conductivity substrates). However, a further increase of conductivity from 15 to 50 W/m.K (or higher) did not result in any further expansion of the hysteresis region, since the system has already reached the LTR limit.

In fig. 5.10, we explore the effect of conductivity for the same reactor length with a space time of 50 ms. Again, due to higher space time, the extinction temperature is

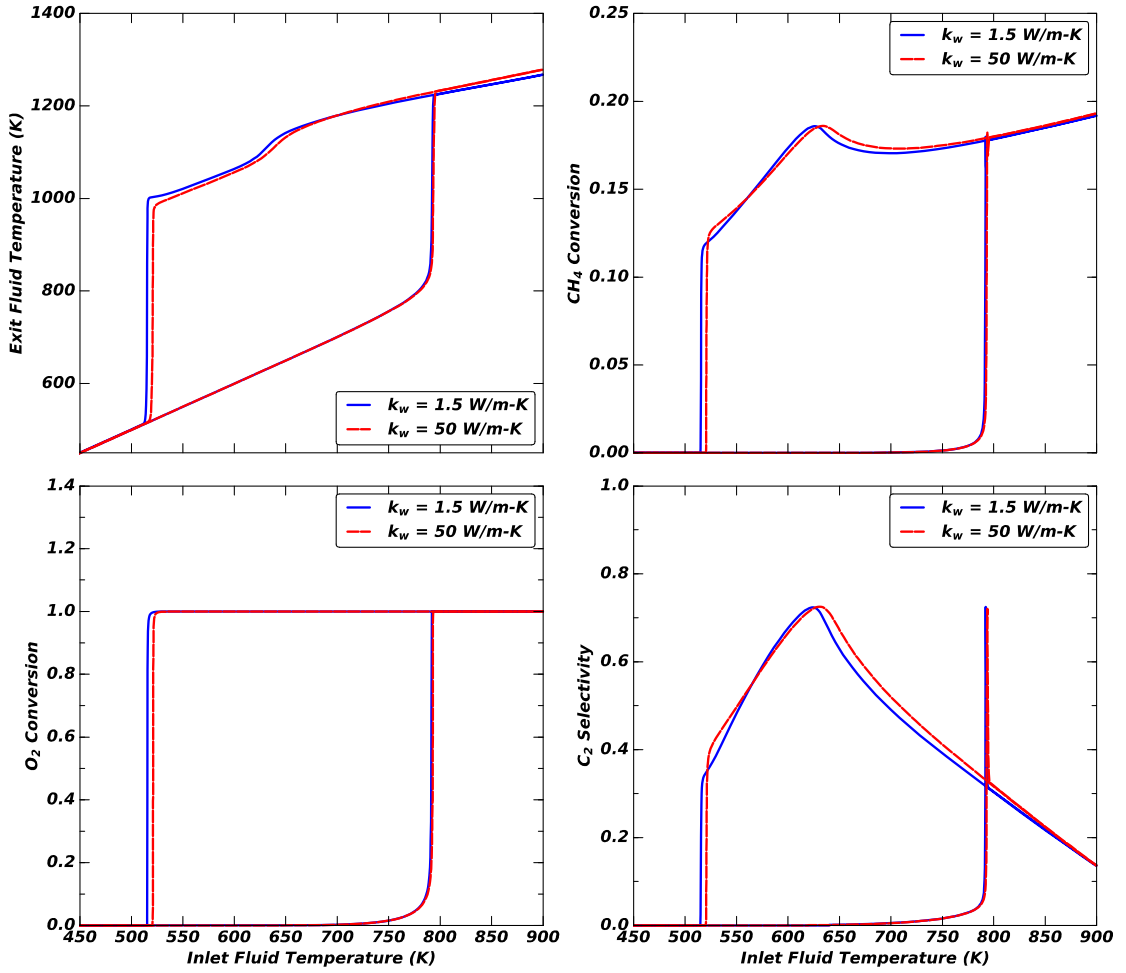


Figure 5.10: Computed dynamic hysteresis plots of exit fluid temperature, CH_4 conversion, O_2 conversion and C_2 selectivity versus feed temperature at different solid conductivity.

same for the two cases presented (the slight difference is probably due to different mesh sizes), indicating approach to the LTR limit even for this shorter channel. Since, the actual values of $Pe_{h,eff}$ are significantly small in both the cases studied ($Pe_{h,eff} \simeq 0.5$ at $\kappa_w = 1.5 \text{ W/m.K}$ and $Pe_{h,eff} \simeq 0.01$ at $\kappa_w = 50 \text{ W/m.K}$), the dynamic hysteresis plots almost coincide with each other.

The concentration profiles of reactants and products along the dimensionless reactor length for $L = 5 \text{ mm}$, $\tau = 50 \text{ ms}$ and $\kappa_w = 50 \text{ W/m.K}$ ($\frac{Pe_m}{Pe_{h,eff}} \simeq 350$) are examined in fig. 5.11. The concentrations of the reactants are normalized with their respective inlet values in order to compare them in the same scale with local selectivity of the products. H_2 and H_2O profiles are expressed in terms of mole fractions. At a higher fluid inlet temperature to the right of the ignition point ($T_{f,in} = 800 \text{ K}$), oxygen reaches complete conversion within the first 10-15% of the reactor length. Although, the profiles suggest considerable production of ethane and ethylene near the inlet, they are subsequently converted to CO_x ($CO + CO_2$) in reactor downstream resulting in poor C_2 selectivity. Whereas, at the point of maximum selectivity ($T_{f,in} = 630 \text{ K}$), the fluid and catalyst temperatures are lower which restricts the non-selective reactions and leads to much higher selectivity. With further decrease of inlet temperature, the reaction zone starts to expand and right near the extinction point, the reactor utilizes its entire length to convert the reactants. This can be observed in fig. 5.12, where we plot the concentration profiles for $L = 10 \text{ mm}$, $\tau = 50 \text{ ms}$ and $\kappa_w = 1.5 \text{ W/m.K}$ at a lower temperature, $T_{f,in} = 600 \text{ K}$. Additionally, referring to fig. 5.8 it can be noted that as the inlet temperature is decreased from 650 K to 600 K , the fluid temperature, CH_4 conversion and C_2 selectivity steeply decreases at

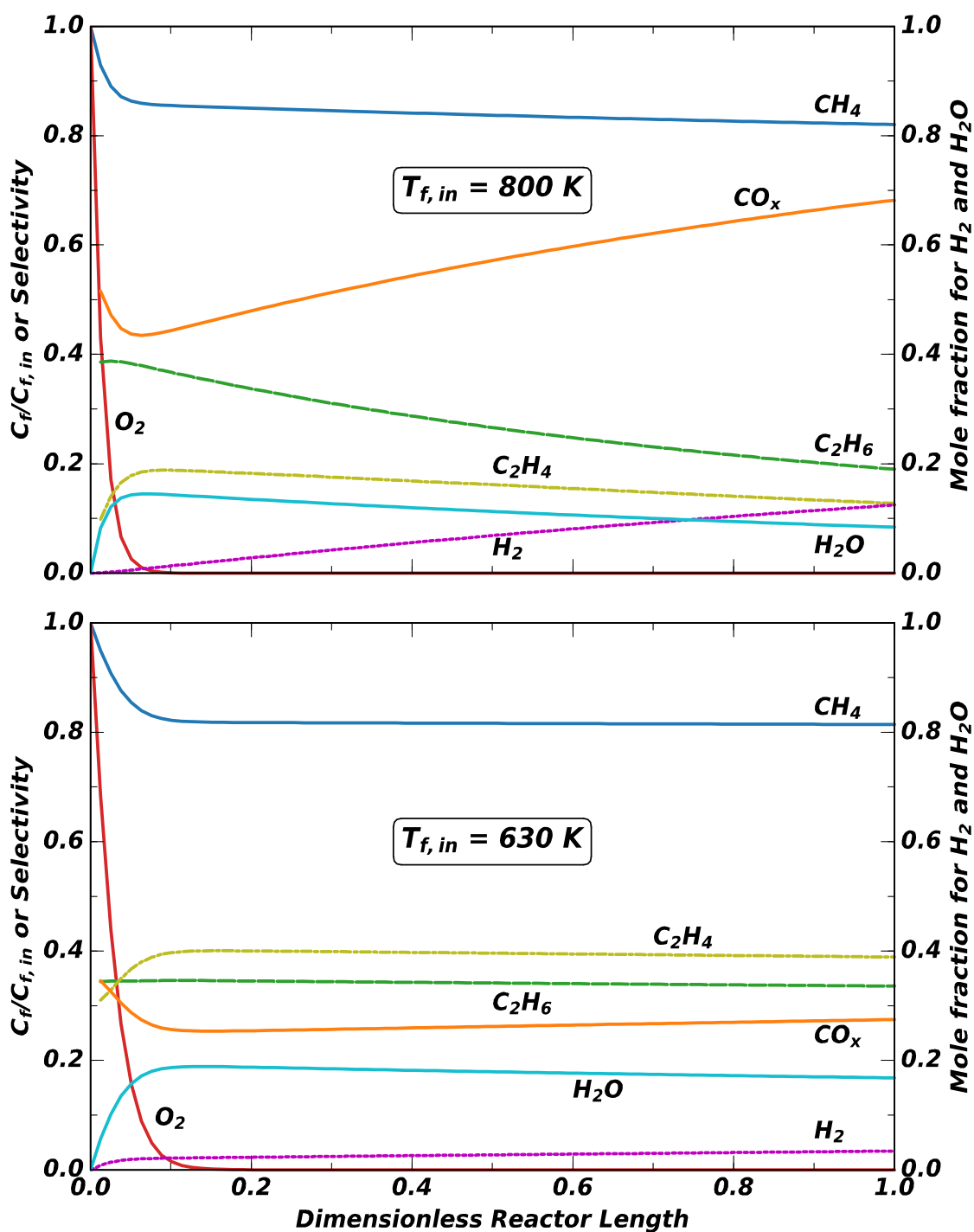


Figure 5.11: Concentration and selectivity profiles along the dimensionless reactor length on ignited branch (top) and at extinction (down).

the same time, suggesting the extinction of the methane dimerization reaction. As a result, the value of Da decreases which leads to the expansion of the reaction zone. In this context, it is noteworthy that, when space time is low (~ 10 ms) and mass/heat Peclet numbers ($Pe_m = 100$, $Pe_{h,eff} = 10$) are high, stronger concentration gradients are present inside the reactor. Under such operating conditions, as the feed temperature is decreased (while operating on the ignited branch) and extinction temperature is approached, the reaction zone entirely shifts from the left (reactor inlet) towards right, eventually leaving the reactor at the extinction point.

The fluid and solid (catalyst) temperature profiles of the aforementioned two cases are compared in fig. 5.13 and are congruent with the concentration profiles. As expected, the case with $\frac{Pe_m}{Pe_{h,eff}} \simeq 350$ (top figure) the gradient in the solid temperature is negligible while that in the fluid is confined to a small region near the inlet (reaction zone) because of stronger thermal mixing effects. For the case with $L = 10$ mm and $\kappa_w = 1.5$ W/m.K (bottom figure), the solid temperature is highest near the inlet while the fluid temperature near the ignition point goes through a peak near reactor inlet followed by a gradual drop due to the presence of endothermic cracking and reforming reactions in reactor downstream. However, $T_{f,in} = 600$ K, both solid and fluid temperatures increase along the reactor and approach each other, with only the coupling reaction dominant along the latter part of the channel.

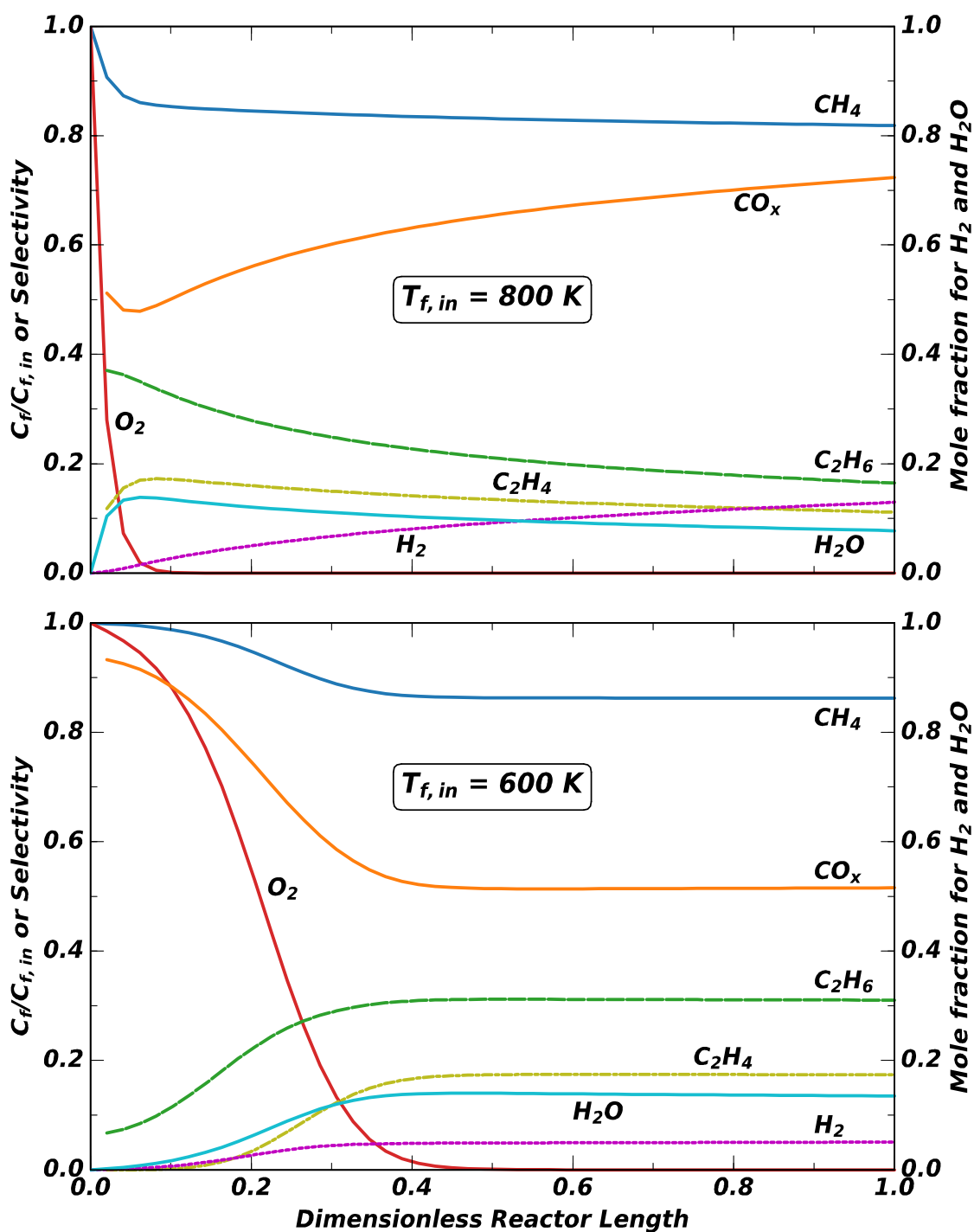


Figure 5.12: Concentration and selectivity profiles along the dimensionless reactor length on ignited branch (top) and at extinction (down) points.

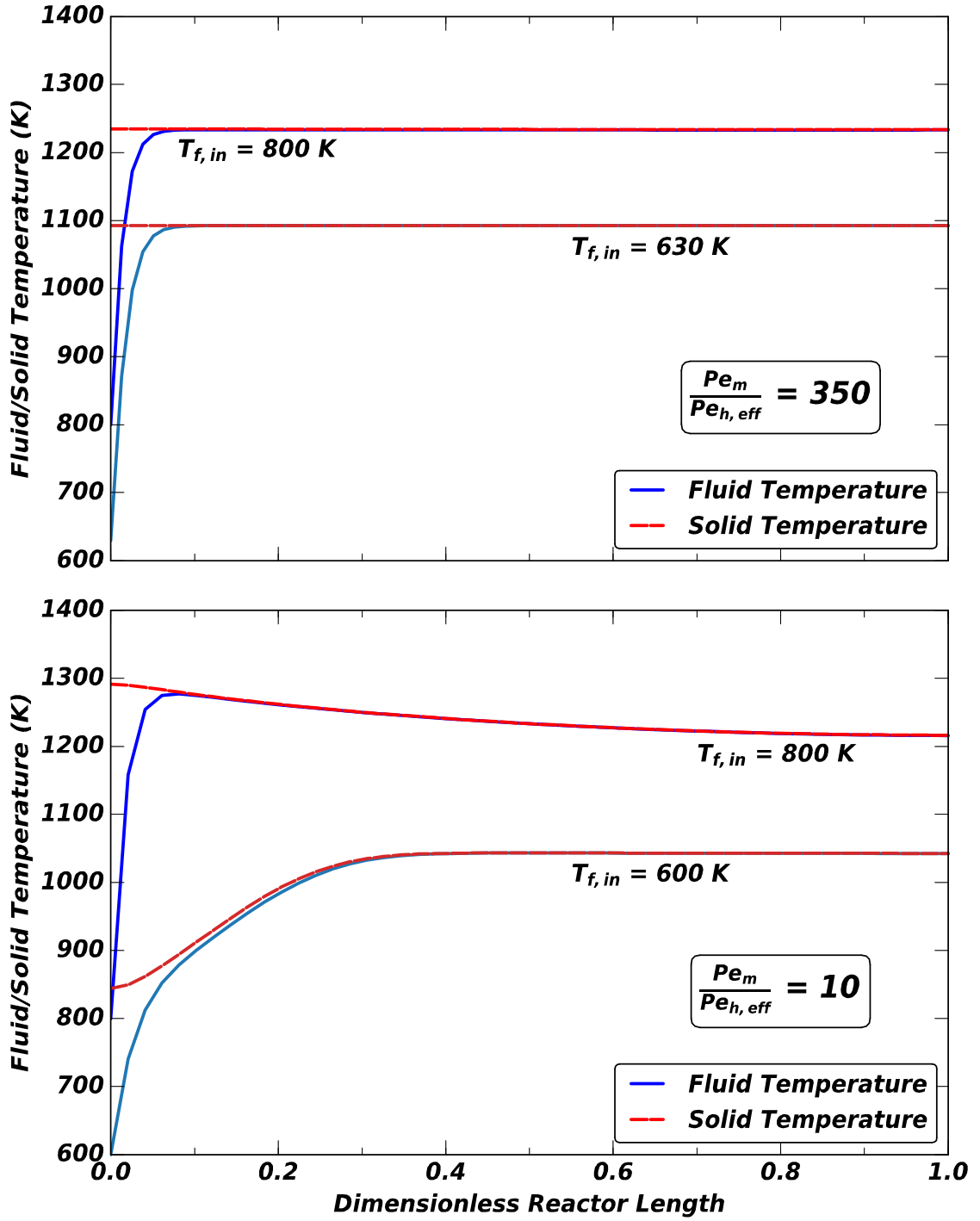


Figure 5.13: Fluid and solid temperature profiles along the dimensionless reactor length for $L = 5 \text{ mm}$, $\kappa_w = 50 \text{ W/m.K}$ (top figure) and $L = 10 \text{ mm}$, $\kappa_w = 1.5 \text{ W/m.K}$ (bottom figure).

5.5.3 Impact of heat loss

In the presence of heat loss from reactor to furnace (or surroundings) and spatial gradients, both the ignition and extinction temperatures move to higher values while shrinking the region of hysteresis, as can be seen from fig. 5.14, which shows the dynamic hysteresis plots of exit fluid temperature, reactant conversion and selectivity for $h_a = 10 \text{ W/m}^2.K$ for $L = 10 \text{ mm}$, $\tau = 50 \text{ ms}$ and $\kappa_w = 1.5 \text{ W/m.K}$. In this particular case, the maximum selectivity is noticed to occur on the ignited branch close to the extinction point. However, depending on the extent of heat loss and other operating conditions, it can further shift right towards higher temperatures and occur closer to the ignition point. Fig. 5.15 shows the concentration and temperature profiles along the dimensionless reactor length for a fixed feed temperature on the ignited branch. The calculated temperature profiles for this case are found to be qualitatively comparable to those calculated by Karakaya et al. [98] who used a detailed kinetic mechanism to validate spatially resolved experimental measurements of concentration and temperature. Though the reactor length and axial velocity used in their work are different than ours, the overall space time and mass Peclet numbers are in the similar range ($Pe_m \simeq 20$). The maximum reported reactor temperature of 1083 K at $CH_4/O_2 = 7$ attained within the first 5 mm of the catalytic bed (35% of the reactor length) matches with our calculated value of 1100 K. The disparity in the width of the reaction zone is probably due to the lower value of thermal conductivity of their reactor bed and presence of inert zone at the front of the catalyst section.

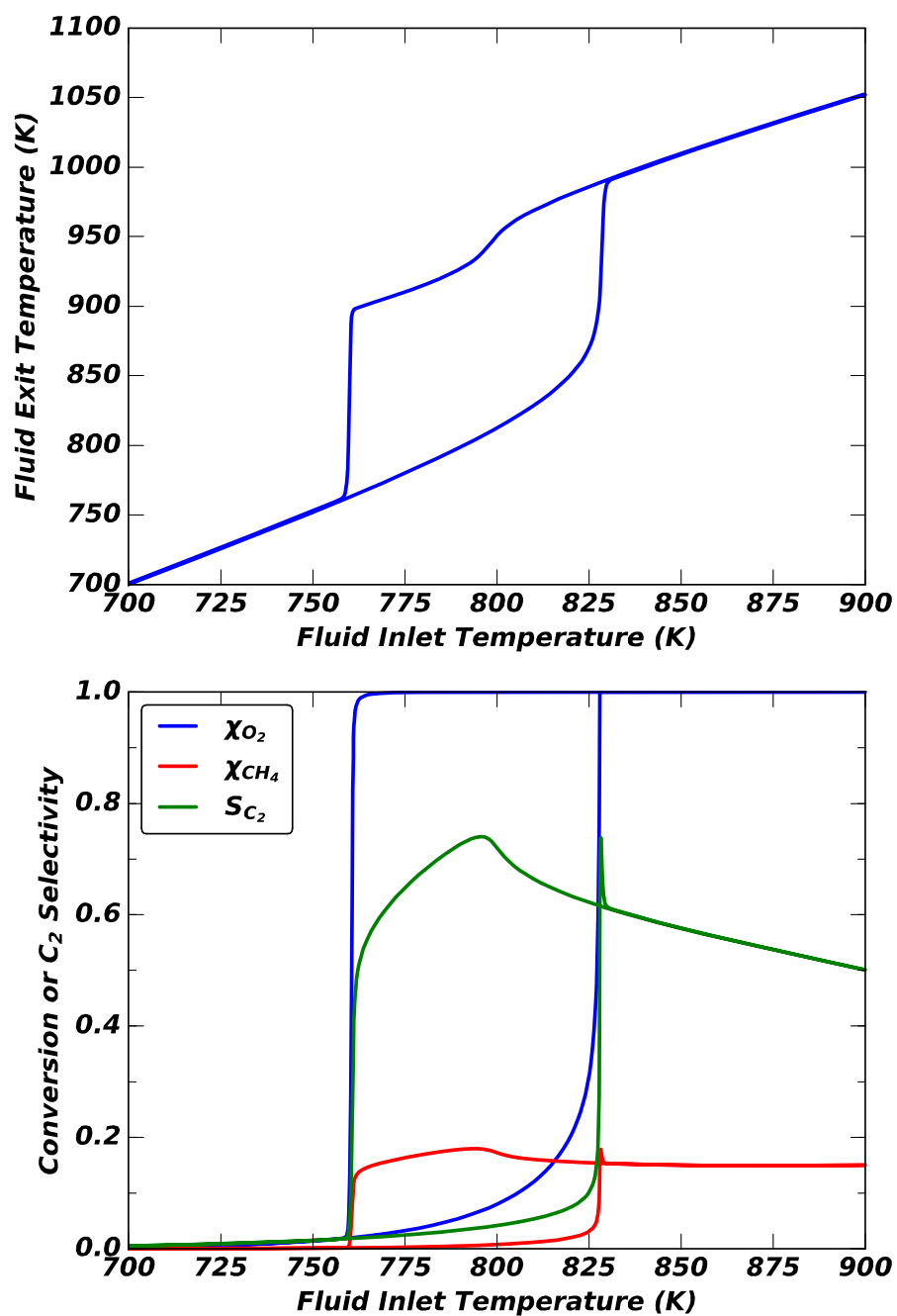


Figure 5.14: Computed dynamic hysteresis plots of exit fluid temperature (top), CH_4 conversion, O_2 conversion and C_2 selectivity (bottom) versus feed temperature in presence of heat loss.

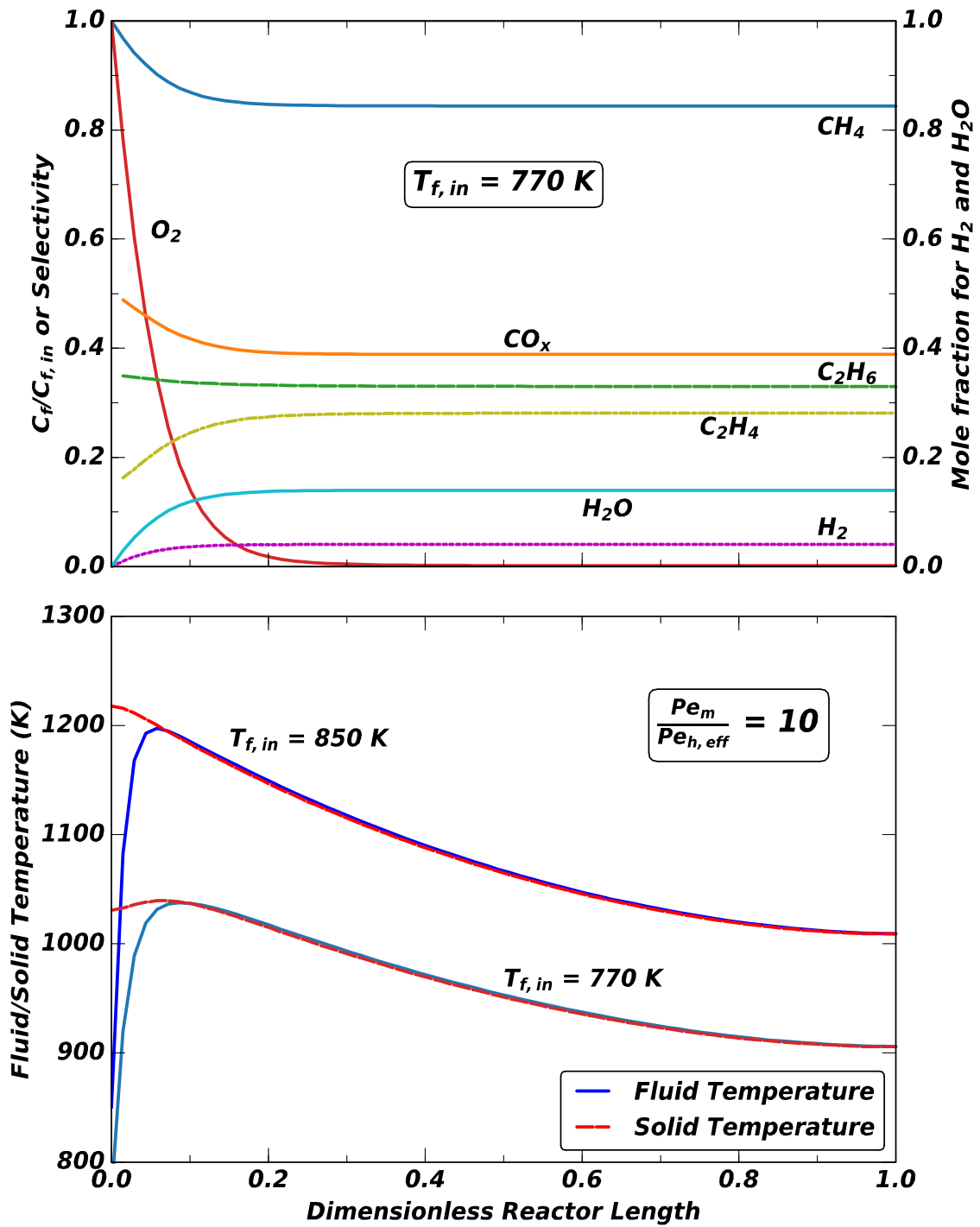


Figure 5.15: Concentration (top) and temperature (bottom) profiles along the dimensionless reactor length for $L = 10\text{ mm}$, $\kappa_w = 1.5\text{ W/m.K}$ and $\tau = 50\text{ ms}$ in presence of external heat loss.

5.6 Summary

In this chapter, we have presented a comprehensive bifurcation (ignition-extinction) analysis of the oxidative coupling of methane in monolith, gauze and wire-mesh type reactors. For this analysis, we have used a global kinetic model that is validated for a typical OCM catalyst such as La_2O_3/CaO along with gas phase reaction kinetics from the literature. Our analysis shows that autothermal operation (on the ignited branch) of OCM in these reactors is feasible for space times of the order of 10 to 100 ms, feed temperatures in the range 450 to 600 K, methane to oxygen ratios in the range 6 to 8 and pressure within 1 to 5 bar. Further, the C_2 selectivity (on the ignited branch) goes through a maximum around an operating temperature of about 1100 K, and is in the 75 to 85% range (with the actual value attained depending on other parameters), while the per pass methane conversion is in the range 16 to 25%. Moreover, for the specific OCM kinetics used in this study, short and/or high conductivity monoliths lead to better selectivity and a wider region of autothermal operation. Autothermal operation is also feasible using monoliths with larger hydraulic diameter but requires much larger space times compared to the homogeneous limit (smaller hydraulic diameter). The presence of washcoat diffusional effects reduces the C_2 selectivity as well as the width of the hysteresis region. The use of longer monoliths and proportionately higher velocities (so that space time is constant) could lead to higher productivity but shrinks the operability window, especially if the substrate conductivity is not high. The productivity and/or operability window can be enhanced with high conductivity substrates (so that the effective bed scale heat Peclet number is below unity).

Also, we have lumped the short monolith, gauze and wire-mesh reactors into a single category (from a bifurcation analysis point of view) as the form of the model (or governing equations) is the same for all cases, the main difference being in the local heat and mass transfer correlations [99]. Thus, we expect the ignition-extinction behavior of these systems to be qualitatively similar. Further, the analysis presented here can also be extended to other catalytic partial oxidation systems and/or reactors with structured substrates such as open-cell foams which offer enhanced mass and heat transfer rates ([100]-[101]). However, the case of long monoliths with ceramic substrates or packed-bed reactors is very different because of thermal backmixing being different and strongly influencing the autothermal boundary (or extinction point). In the case of a packed-bed reactor, as discussed in recent work [102], local ignition of catalyst particles could occur and an ignited state could exist even with zero thermal backmixing in the reactor. Further, lower thermal conductivity in a packed bed reactor shrinks the region of suitable operating window by increasing the fluid inlet temperature, which eventually leads to lower C_2 selectivities. High heat transfer coefficients can be achieved by increasing flow velocities, which in turn will reduce the contact times and can again lead to poorer selectivity and conversion in addition to increasing pressure drop. The behavior of a long monolith reactor with a very low substrate conductivity can approach that of a packed-bed of particles. Additionally, low cell density monoliths with high voidage can also be advantageous in enhancing the ratio of CH_4/O_2 at the fluid-washcoat interface, thereby increasing the selectivity to C_2 products. In our view, the main difference between these two reactor types is the flexibility of tuning the heat Peclet number and voidage in the monolith (and

hence the thermal backmixing as well as the ratio of axial heat and species Peclet numbers in the reactor) by proper selection of substrate properties (e.g., conductivity, effective wall thickness, hydraulic diameter, and so forth) that makes it a preferred choice for OCM as well as other such catalytic partial oxidations.

Chapter 6

Microkinetic modeling of oxidative coupling of methane

6.1 Introduction

As described in the previous chapter, comprehensive kinetic models are very useful in evaluating reactor performances due to their relative simplicity and inexpensive computation times. However, they often come with a limited range of validity beyond which the predictions may not be accurate or sufficient. Also, the global kinetic models are not fully capable of providing a richer insight into the fundamental chemistry of the reaction system. For example, in the case of OCM, the general consensus in literature is that methane is catalytically activated to form methyl radical which recombines in the gas phase to form ethane [73]. In global kinetic models, these steps are usually lumped together to be treated as a catalytic reaction [93]. Therefore, it is crucial to consider detailed microkinetics to have a deeper understanding of the underlying reaction mechanism. Typically, such detailed mechanisms may include hundreds of elementary steps with widely varying reaction time scales, thereby making the numerical computation of reactor models extremely stiff and expensive.

Another key challenge in this regard is the correct estimation of reaction parameters for all of the elementary steps. A good agreement between experimental and model data may not necessarily ensure the preservation of relevant thermodynamic constraints. Therefore, estimation of reaction parameters which can correctly explain the physics of the system, while maintaining the thermodynamic consistency is highly desirable from a practical standpoint.

In OCM, both homogeneous and heterogeneous reactions are in synergy. The gas-phase mechanisms are relatively well-developed due to the extensive research in the combustion field ([103], [104]). Reduced mechanism dedicated for OCM conditions has been developed by Zanthoff and Baerns [105] which consists of 164 reactions among 28 gas-phase species. Using an isothermal plug flow reactor model, Reyes et al. [106] validated a reaction network of 145 reversible reactions among 28 species. Chen et al. ([107], [108]) further reduced the number of elementary steps and proposed a network of 39 reactions among 23 species. Due to the compact size of the latter model, it is often combined with catalytic reactions for kinetic simulation of OCM reactors ([95], [98], [109]-[115]). There have been extensive efforts focused in the development of reaction mechanisms of OCM for various catalysts. Sun et al. [109] developed and validated a 14 step microkinetic model for Li/MgO and Sn/Li/MgO catalysts. They identified the major thermodynamic cycles of the gas-phase and surface species. By applying thermodynamic consistency in these cycles, the microkinetic model is expressed in terms of a few reaction enthalpies and sticking coefficients, which are denoted as catalyst descriptors. The activation energies of all the elementary steps are deduced from those reaction enthalpies using Evans-Polanyi principle. In a different

study, Ahari et al. [110] proposed a 11 step network for Mn/Na₂WO₄/SiO₂ catalyst, where only the dissociative adsorption-desorption of oxygen is taken as a reversible reaction. Sensitivity analysis is performed to identify the rate limiting steps and reduce the number of surface reactions. However, these two reaction networks only considered H-atom abstraction from methane, ethane and/or ethylene. Through experiments and kinetic modeling Sinev et al. [111] showed that other gas phase species like ethyl, methoxy and formyl radicals can also undergo similar H-atom abstraction steps. Based on these observations, the original 14 step network on Li/MgO catalyst is expanded to 17 [112] and then later to 26 steps by Kechagiopoulos et al. [113] using the robust approach of catalyst descriptors. Furthermore, implementing this same 26 step reaction network, the parameters for a library of catalysts such as Sr/La₂O₃, LaSr/CaO and Na-Mn-W/SiO₂ are also estimated ([114], [115]). Recently, Karakaya et al. [98] fitted the experimental data obtained for La₂O₃/CeO₂ nanofiber catalysts [74]. However, in this latter study, the kinetic parameters of both the gas phase and surface reactions are modified in order to match the spatially resolved experimental profiles. Rigorous optimization techniques or sensitivity analysis was not explicitly performed.

In this chapter, we take a few of the kinetic models mentioned above and perform isothermal simulations in monolith reactors. The main objectives of this work are to gain a deeper understanding of these proposed mechanisms and investigate the impact of various parameters on the reactor performance when microkinetic models are being used instead of comprehensive global kinetic models. The chapter is organized as follows. First we present the isothermal reduced order models for monolith

reactors. A brief description of the homogeneous and heterogeneous kinetic model is also provided. Next we analyze the kinetic model using the parameters proposed by Karakaya et al. [98]. Reaction path diagrams at various operating conditions are illustrated. Afterwards, we consider the kinetic parameters of Sun et. al [109] and Kechagiopoulos et al. [113] and determine the impact of inlet mole ratio, space time, channel hydraulic radius and pressure. Finally, we conclude by validating our results with some experimental data available in open literature.

6.2 Mathematical model

We use the transient version of the short monolith model given by eqns. (2.54-2.55) as our governing model. Since we are dealing with microkinetic reactions, in addition to the species balance equations in fluid and washcoat phases, we also need to consider the temporal variations of the surface adsorbed species and conservation of the total active sites to fully describe our model. It is needless to say that energy balance equations are not required as isothermal conditions are only investigated. With these considerations the model equations are given as:

$$\frac{\partial c_{f,j}}{\partial t} = \frac{c_{f,j}^{in} - c_{f,j}}{\tau} - \frac{j_{f_{wc},j}^*}{R_{\Omega_f}} + \sum_{i=1}^{Nh} \nu_{ij}^h r_i^h(\mathbf{c}_f, T_f^{in}), \quad (6.1)$$

$$\varepsilon_{wc} \frac{\partial c_{wc,j}}{\partial t} = \frac{j_{f_{wc},j}^*}{R_{\Omega_{wc}}} + a_c \sum_{i=1}^{Nc} \nu_{ij}^c r_i^c(\mathbf{c}_{wc}, \boldsymbol{\theta}, T_f^{in}), \quad (6.2)$$

$$\frac{\partial \theta_j}{\partial t} = \frac{1}{\Gamma} \sum_{i=1}^{Nc} \nu_{ij}^\theta r_i^\theta(\mathbf{c}_{wc}, \boldsymbol{\theta}, T_f^{in}), \quad (6.3)$$

$$\text{and } \theta_v + \sum_{j=1}^S \theta_j = 1. \quad (6.4)$$

The initial conditions of the above model are as follows:

$$c_{f,j}(t = 0) = c_{f,j}^0, \quad c_{wc,j}(t = 0) = c_{wc,j}^0, \quad (6.5)$$

$$\text{and } \theta_j(t = 0) = \theta_j^0. \quad (6.6)$$

Here, θ_j is the fractional surface coverage of surface species j and θ_v denotes the fractional coverage of the vacant sites. Γ and a_c are the respective catalyst surface site density and exposed active surface area per unit volume of washcoat. ν_{ij}^k with $k = h, c$ and θ denotes the stoichiometric coefficient of j^{th} species in i^{th} reaction. The superscripts h, c and θ are used to represent the respective gas-phase reactions, catalytic reactions of gas-phase species and surface reactions of surface adsorbed species. It is important to point out that the reaction term in eqn. 6.2 only represents the surface reactions of gas-phase species. However, within the washcoat interstitial pores, gas-phase homogeneous reactions can also take place. In that case, another reaction term, similar to the one in eqn. 6.1, is to be added in the right-hand-side. Evidently the contribution of these homogeneous reactions is insignificant, because the total pore volume is negligible in comparison to the total volume available for flow in a monolith type reactor.

The interfacial species flux vector $\mathbf{j}_{f_{wc,j}}^*$, where each element $j_{f_{wc,j}}^*$ represents the flux of the j^{th} gas-phase species, can be calculated from the overall mass transfer coefficient matrix $\mathbf{K}_o$ and the concentration difference between fluid and washcoat using the same approach outlined earlier. In this particular work we have further simplified the calculation of the Sherwood matrices by assuming asymptotic values.

Thereby, eqns. 2.65 and 2.66 can be simply written as

$$\mathbf{D}_{wc}^{-1} \mathbf{K}_i R_{\Omega_{wc}} = \mathbf{Sh}_i = Sh_{i,\infty} \mathbf{I} \quad (6.7)$$

$$\text{and } \mathbf{D}_f^{-1} \mathbf{K}_e R_{\Omega_f} = \mathbf{Sh}_e = Sh_{e,\infty} \mathbf{I}. \quad (6.8)$$

This assumption is inconsequential in context of our analysis, since the main purpose here is to gain a better understanding of the reaction chemistry and not to accurately predict conversion and selectivities. The values of the design and operating parameters used in our simulations are listed below.

Table 6.1: List of parameters for the transient, isothermal short monolith model

Parameter	Unit	Value
τ	ms	50, 100 or 200
P	atm	1, 5 or 10
R_{Ω_f}	μm	250
$R_{\Omega_{wc}}$	μm	50
a_c	m^2 / m^3 washcoat	10^6
Γ	mol/cm^2	9.84×10^{-10} or 1.33×10^{-10}
ε_{wc}	-	0.4
τ_c	-	10
$Sh_{e,\infty}, Sh_{i,\infty}$	-	3.0

6.3 Kinetic model

As mentioned earlier, in this study we have considered a few kinetic models available in the literature, specifically the ones proposed by Sun et al. [109] and Kechagiopoulos et al. [113] for Sn/Li/MgO catalyst, and Karakaya et al. [98] for

Table 6.2: Elementary steps in gas phase OCM

	Reaction	A	E_a
H1	$CH_4 + O_2 \rightleftharpoons CH_3^\bullet + HO_2^\bullet$	9.83×10^{12}	193.86
H2	$CH_4 + H^\bullet \rightleftharpoons CH_3^\bullet + H_2$	2.34×10^{14}	51.17
H3	$CH_4 + O^\bullet \rightleftharpoons CH_3^\bullet + OH^\bullet$	1.27×10^{15}	33.83
H4	$CH_4 + OH^\bullet \rightleftharpoons CH_3^\bullet + H_2O$	1.27×10^{14}	41.43
H5	$CH_4 + HO_2^\bullet \rightleftharpoons CH_3^\bullet + H_2O_2$	4.01×10^{13}	99.61
H6	$CH_3^\bullet + O_2 \rightleftharpoons CH_3O^\bullet + O^\bullet$	3.08×10^{14}	141.00
H7	$CH_3^\bullet + O_2 \rightleftharpoons CH_2O + OH^\bullet$	4.59×10^{13}	103.66
H8	$CH_3^\bullet + HO_2^\bullet \rightleftharpoons CH_2O^\bullet + OH^\bullet$	8.85×10^{13}	0.00
H9	$2CH_3^\bullet + M \rightleftharpoons C_2H_6 + M$	6.50×10^{19}	0.00
H10	$CH_3O^\bullet + M \rightleftharpoons CH_2O + H^\bullet + M$	6.50×10^{20}	115.00
H11	$CH_2O + OH^\bullet \rightleftharpoons CHO^\bullet + H_2O$	5.80×10^{14}	5.00
H12	$CH_2O + HO_2^\bullet \rightleftharpoons CHO^\bullet + H_2O_2$	4.17×10^{12}	40.12
H13	$CH_2O + CH_3^\bullet \rightleftharpoons CHO^\bullet + CH_4$	7.00×10^{13}	25.03
H14	$CHO^\bullet + M \rightleftharpoons CO^\bullet + H^\bullet + M$	2.80×10^{15}	64.36
H15	$CHO^\bullet + O_2 \rightleftharpoons CO + HO_2^\bullet$	1.71×10^{11}	0.00
H16	$CO + HO_2^\bullet \rightleftharpoons CO_2 + OH^\bullet$	3.08×10^{14}	107.34
H17	$C_2H_6 + H^\bullet \rightleftharpoons C_2H_5^\bullet + H_2$	9.10×10^{14}	51.70
H18	$C_2H_6 + OH^\bullet \rightleftharpoons C_2H_5^\bullet + H_2O$	5.45×10^{14}	17.16
H19	$C_2H_6 + CH_3^\bullet \rightleftharpoons C_2H_5^\bullet + CH_4$	2.39×10^{13}	64.73
H20	$C_2H_5^\bullet + HO_2^\bullet \rightleftharpoons CH_3^\bullet + CH_2O + OH^\bullet$	9.48×10^{12}	0.00
H21	$C_2H_5^\bullet + M \rightleftharpoons C_2H_4 + H^\bullet + M$	5.96×10^{19}	167.66
H22	$C_2H_5^\bullet + O_2 \rightleftharpoons C_2H_4 + HO_2^\bullet$	6.35×10^{12}	53.20
H23	$C_2H_4 + O_2 \rightleftharpoons C_2H_3^\bullet + HO_2^\bullet$	2.81×10^{12}	144.55
H24	$C_2H_4 + H^\bullet \rightleftharpoons C_2H_3^\bullet + H_2$	1.50×10^{14}	42.70
H25	$C_2H_4 + OH^\bullet \rightleftharpoons C_2H_3^\bullet + H_2O$	6.12×10^{13}	24.70
H26	$C_2H_4 + CH_3^\bullet \rightleftharpoons C_2H_3^\bullet + CH_4$	1.99×10^{11}	51.46
H27	$C_2H_4 + OH^\bullet \rightleftharpoons CH_3^\bullet + CH_2O$	2.72×10^{11}	0.00
H28	$C_2H_3^\bullet + M \rightleftharpoons C_2H_2 + H^\bullet + M$	1.21×10^{21}	176.44
H29	$C_2H_3^\bullet + O_2 \rightleftharpoons C_2H_2 + HO_2^\bullet$	5.00×10^{12}	0.00
H30	$C_2H_3^\bullet + O_2 \rightleftharpoons CH_2O + CHO^\bullet$	5.50×10^{12}	0.00
H31	$C_2H_5^\bullet + CH_3^\bullet \rightleftharpoons C_3H_8$	8.00×10^{12}	0.00
H32	$C_3H_8 + H^\bullet \rightleftharpoons C_3H_7^\bullet + H_2$	9.00×10^{14}	32.00
H33	$C_2H_4 + CH_3^\bullet \rightleftharpoons C_3H_7^\bullet$	3.00×10^{11}	29.00
H34	$C_3H_7^\bullet \rightleftharpoons C_3H_6 + H^\bullet$	1.50×10^{15}	156.00
H35	$O_2 + H^\bullet \rightleftharpoons OH^\bullet + O^\bullet$	2.20×10^{14}	70.30
H36	$O_2 + H^\bullet + M \rightleftharpoons HO_2^\bullet + M$	1.39×10^{17}	0.00
H37	$2HO_2^\bullet \rightleftharpoons O_2 + 2OH^\bullet$	2.00×10^{12}	0.00
H38	$H_2O_2 + M \rightleftharpoons 2OH^\bullet + M$	1.27×10^{17}	199.36
H39	$C_2H_6 \rightleftharpoons C_2H_5^\bullet + H^\bullet$	4.00×10^{16}	378.51
Unit of A is s^{-1} or $cm^3 mol^{-1} s^{-1}$ or $cm^6 mol^{-2} s^{-1}$ and E_a is kJ/mol.			

Table 6.3: Catalytic reaction mechanism of OCM

	Reaction	A^f or S_0	E_a^f	A^b or S_0	E_a^b
C1	$O_2 + 2* \rightleftharpoons 2O^*$	0.56	0.0	2.39×10^{19}	55.4
C2	$CH_4 + O^* \rightleftharpoons CH_3^\bullet + OH^*$	1.85×10^{13}	139.3	1.91×10^{13}	82.6
C3	$C_2H_4 + O^* \rightleftharpoons C_2H_3^\bullet + OH^*$	1.40×10^{13}	159.1	1.42×10^{13}	76.0
C4	$C_2H_6 + O^* \rightleftharpoons C_2H_5^\bullet + OH^*$	1.35×10^{13}	127.3	1.37×10^{13}	86.6
C5	$2OH^* \rightleftharpoons H_2O^* + O^*$	2.25×10^{19}	190.3	2.17×10^{19}	98.2
C6	$H_2O^* \rightleftharpoons H_2O + *$	2.10×10^{13}	34.8	0.0765	0.0
C7	$CH_3^\bullet + O^* \rightleftharpoons CH_3O^*$	6.23×10^{-5}	0.00	2.24×10^{13}	244.6
C8	$CH_3O^* + O^* \rightleftharpoons CH_2O^* + OH^*$	1.72×10^{19}	0.00	1.69×10^{19}	155.9
C9	$CH_2O^* + O^* \rightleftharpoons CHO^* + OH^*$	1.69×10^{19}	35.1	1.75×10^{20}	112.6
C10	$CHO^* + O^* \rightleftharpoons CO^* + OH^*$	1.75×10^{19}	14.7	1.81×10^{19}	133.9
C11	$CO^* + O^* \rightleftharpoons CO_2^* + *$	1.81×10^{19}	0.0	1.39×10^{19}	205.3
C12	$CO + * \rightleftharpoons CO^*$	5.66×10^{-5}	0.0	1.81×10^{13}	74.4
C13	$CO_2 + * \rightleftharpoons CO_2^*$	0.0154	0.0	1.07×10^{13}	87.0
C14	$C_2H_4 + O^* \rightleftharpoons C_2H_4O^*$	2.2×10^{12}	85.3	6.00×10^{11}	186.3
C15	$C_2H_4O^* + O^* \rightleftharpoons C_2H_3O^* + OH^*$	1.00×10^{21}	76.0	1.00×10^{21}	3.0
C16	$C_2H_3O^* + O^* \rightleftharpoons CH_2O^* + HCO^*$	1.00×10^{21}	69.0	1.00×10^{21}	186.5
C17	$C_2H_5^\bullet + O^* \rightleftharpoons C_2H_4 + OH^*$	1.00×10^{12}	183.5	8.00×10^{10}	70.9
C18	$CH_3O^\bullet + O^* \rightleftharpoons CH_2O^* + OH^*$	7.00×10^{11}	307.8	1.00×10^{11}	26.5
C19	$CH_2O + O^* \rightleftharpoons CHO^\bullet + OH^*$	1.00×10^{13}	109.9	1.00×10^{10}	39.3
C20	$CHO^\bullet + O^* \rightleftharpoons CO + OH^*$	1.00×10^{12}	88.1	1.00×10^{13}	89.7
C21	$H_2 + O^* \rightleftharpoons H^\bullet + OH^*$	8.00×10^{13}	400.0	1.00×10^{10}	0.0
C22	$H_2O_2 + O^* \rightleftharpoons HO_2^\bullet + OH^*$	1.00×10^{13}	344.0	1.00×10^{13}	13.8
C23	$OH^\bullet + O^* \rightleftharpoons O^\bullet + OH^*$	1.00×10^{11}	390.0	1.00×10^{11}	0.0
C24	$H_2O + O^* \rightleftharpoons OH^\bullet + OH^*$	1.00×10^{11}	460.0	1.00×10^{11}	0.0
C25	$HO_2^\bullet + O^* \rightleftharpoons O_2 + OH^*$	1.00×10^{13}	224.0	1.00×10^{10}	54.0
C26	$HO_2^\bullet + * \rightleftharpoons OH^\bullet + O^*$	1.00×10^{11}	0.0	1.99×10^{11}	30.0
Unit of A is s^{-1} or $cm^2mol^{-1}s^{-1}$ or $cm^3mol^{-1}s^{-1}$ and E_a is kJ/mol.					

La₂O₃/CeO₂ nanofiber catalysts. In all three of the kinetic models, the main framework of the homogeneous mechanism consists of 39 reversible reactions reported by Chen et al. [108]. In Table 6.2, we have listed these reactions and the associated parameters given in the original reference. The reaction network is constituted of 13 stable gas phase species (hydrogen, water, hydrogen peroxide, oxygen, methane, formaldehyde, carbon monoxide, carbon dioxide, ethane, ethylene, acetylene, propane and propylene) and 10 gas phase radicals ($H^\bullet$, $O^\bullet$, $OH^\bullet$, $HO_2^\bullet$, $CH_3O^\bullet$, $CHO^\bullet$, $CH_3^\bullet$, $C_2H_5^\bullet$, $C_2H_3^\bullet$, $C_3H_7^\bullet$). Pre-exponential factors and activation energies of the forward reactions are provided, while the reverse reaction rates and the corresponding parameters can be calculated from thermodynamics. In this context, it is noteworthy that even though Karakaya et al. [98] used this same reaction network, the pre-exponential factor and activation energy of some of these reactions are modified in their work in order to match the experimental results.

The catalytic reaction scheme comprises of 26 reversible reactions (52 if written as irreversible pairs) which are listed in Table 6.3. The reaction parameters are taken from the works of Sun et al. [109] and Kechagiopoulos et al. [113] for Sn/Li/MgO catalyst. The corresponding parameters for La₂O₃/CeO₂ catalyst are tabulated by Karakaya et al. [98]. All these mechanisms assume the catalyst as a single-phase surface and hence considers a single type of active site which is represented as $*$ in Table 6.3.

6.4 Isothermal simulations of short monolith model

In this section we present the reactor simulation results computed by time integration of eqns. (6.1-6.3) with the kinetic models described above. For a fixed set of operating conditions, the model is integrated to almost 50 times the space time to reach steady state. The chemical kinetic, thermodynamic and transport calculations are done using Cantera [116], while our governing equations are integrated using the stiff solver - VODE. In the following sections, first we have analyzed the kinetics proposed by Karakaya et al. [98]. The reaction mechanism and the results obtained through it are compared against the one presented by Kechagiopoulos et al. [113]. Afterwards, the impact of various parameters like inlet mole ratio, space time and pressure are demonstrated. We use the same definitions of reactant conversions and selectivity given by eqns. (5.2-5.4).

6.4.1 Homogeneous contribution in the coupled homo-/hetero system

Fig. 6.1 illustrates the exit C_2 ($C_2H_6 + C_2H_4$) selectivity, and CH_4 and O_2 conversions against feed temperature for inlet CH_4/O_2 mole ratio of 6, space time, $\tau = 100$ ms and channel hydraulic radius, $R_{\Omega_f} = 250 \mu m$. This particular case is computed using the kinetics reported by Karakaya et al. [98]. As expected, the inclusion of the catalytic reactions reduces the light-off temperature. However, it is interesting to note that there is only a minimal increase in C_2 selectivity when surface reactions are coupled with homogeneous reactions. In fact, as per their kinetics, 42% C_2 selectivity

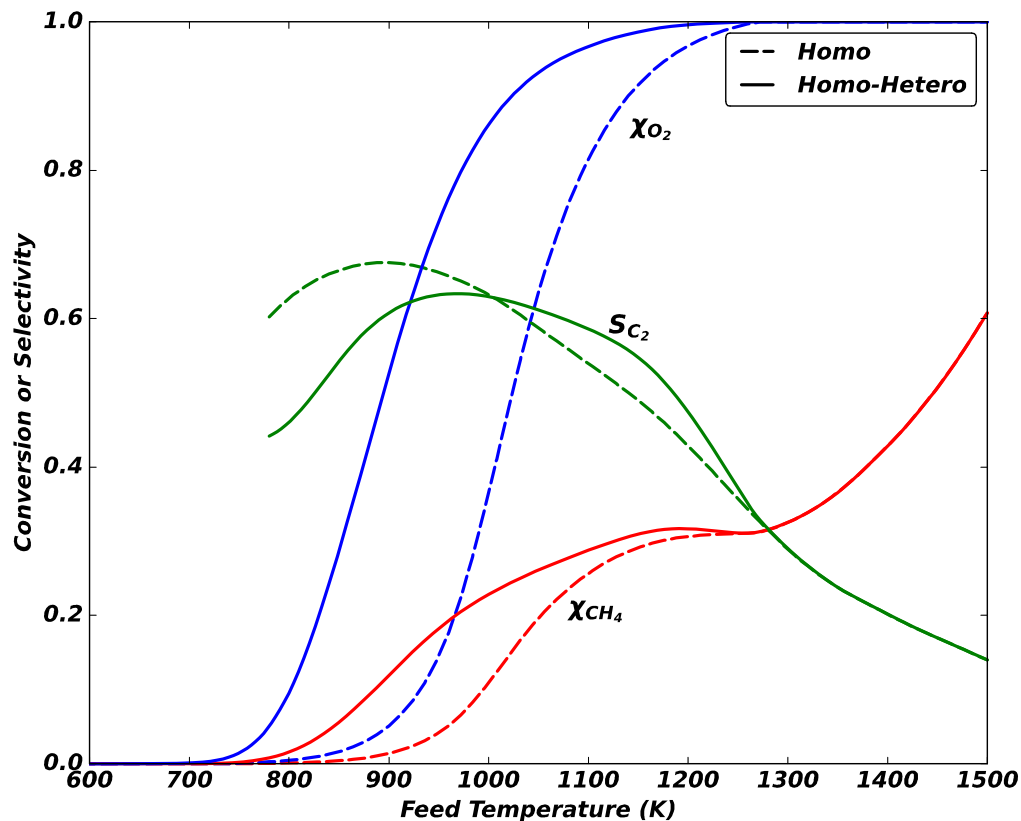


Figure 6.1: Exit conversions (χ) of CH_4 & O_2 and selectivities (S) of C_2 products ($C_2H_6 + C_2H_4$) against fluid inlet temperatures using the kinetic parameters proposed by Karakaya et al. [98].

can be obtained with 22% CH_4 conversion at a reactor temperature of 1100 K without the catalyst. This is in stark contrast to the experimental data available in the literature. This mismatch between the experimental and modeling results is solely due to the incorrect estimation of kinetic parameters. One easy way to detect such inconsistencies is through the visualization of reaction pathways which are shown in fig. 6.2 and 6.3.

Fig 6.2 shows the pathways of gas-phase carbon containing compounds through the homogeneous reactions routes at a reactor temperature of 1100 K, whereas fig.

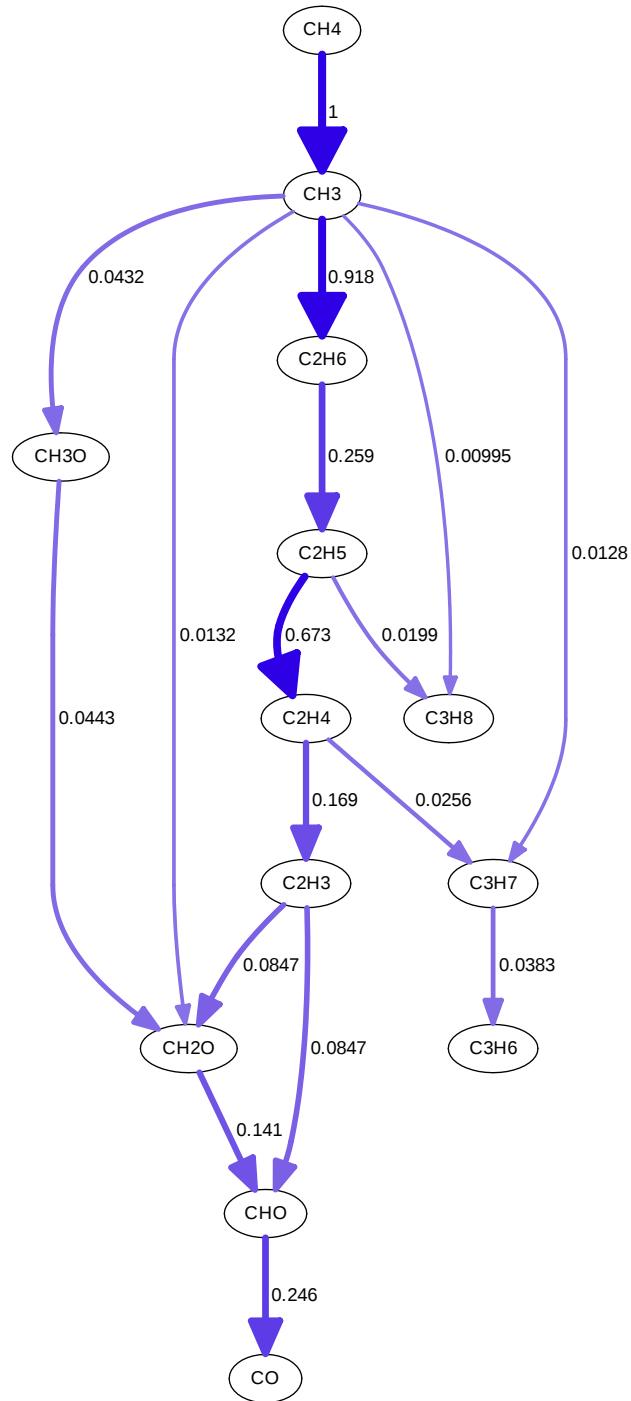


Figure 6.2: Homogeneous reaction pathways for carbon containing compounds at $T_{f,in} = 1100$ K and inlet mole ratio $CH_4/O_2 = 6$. The actual rate is scaled by a factor of 0.025.

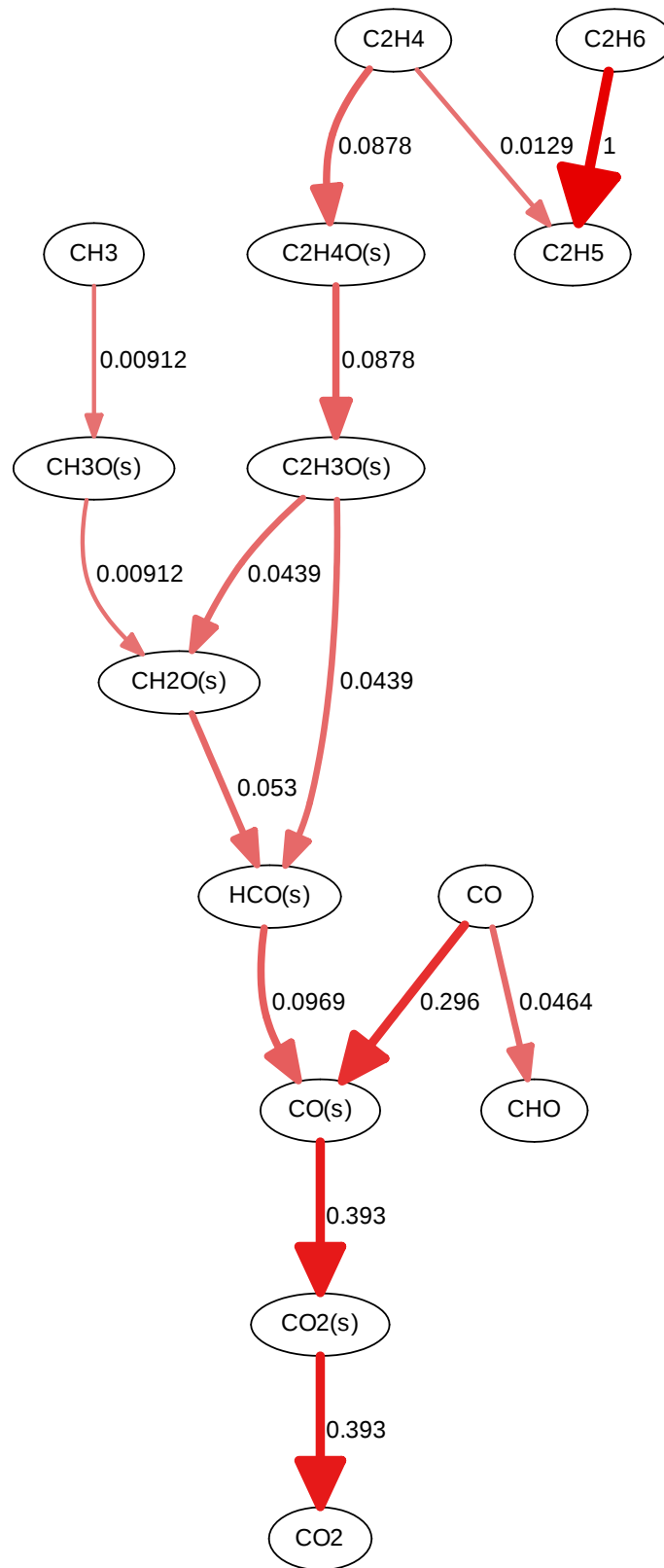


Figure 6.3: Catalytic reaction pathways of carbon containing compounds at $T_{f,in} = 1100$ K and inlet mole ratio $CH_4/O_2 = 6$. The actual rate is scaled by a factor of 5.4×10^{-8} .

6.3 shows the catalytic reaction pathways of both gas phase and surface adsorbed carbon containing species. Both homogeneous and catalytic reactions are taken into account while computing these reaction pathway diagrams. To put it differently, fig. 6.2 and 6.3 actually corresponds to 24% CH₄ conversion, 99% O₂ conversion and 60% C₂ selectivity as per the solid lines in fig. 6.1. The width and color saturation of the arrows are proportional to the net reaction rates. The largest net reaction rate, which is for the formation of methyl radical from methane in the homogeneous case, is scaled by a factor of 0.025 to make it 1 kmol/m³s. The numbers beside the arrows represent the net reaction rate between those species scaled by that same factor. From fig. 6.2, it is evident that the major reaction in the gas phase is the formation of methyl radical from methane (especially through reactions H2, H4 and H5) which recombines to form ethane (H9). Ethane forms ethyl radical in the gas phase (H19) which then can either get oxidized to form CO or form ethylene and C₃ products like propane and propylene.

Among the catalytic routes, unlike ethane and ethylene, methane is not at all activated by the catalyst to form methyl radical as shown in fig. 6.3. In OCM literature, catalytic activation of methane (C2) is considered to be the main purpose of an OCM catalyst. However, this particular reaction mechanism fails to explain it. This is because the activation energy of this reaction is chosen to be as high as 174.4 kJ/mol, while the respective values for ethylene and ethane activation are just 100.4 kJ/mol and 88.2 kJ/mol. Moreover, lower values of activation energies are considered for the reactions of methane to methyl radical (H2 and H5) in the homogeneous phase. All these reasons led to the substantial formation of C₂ products through the

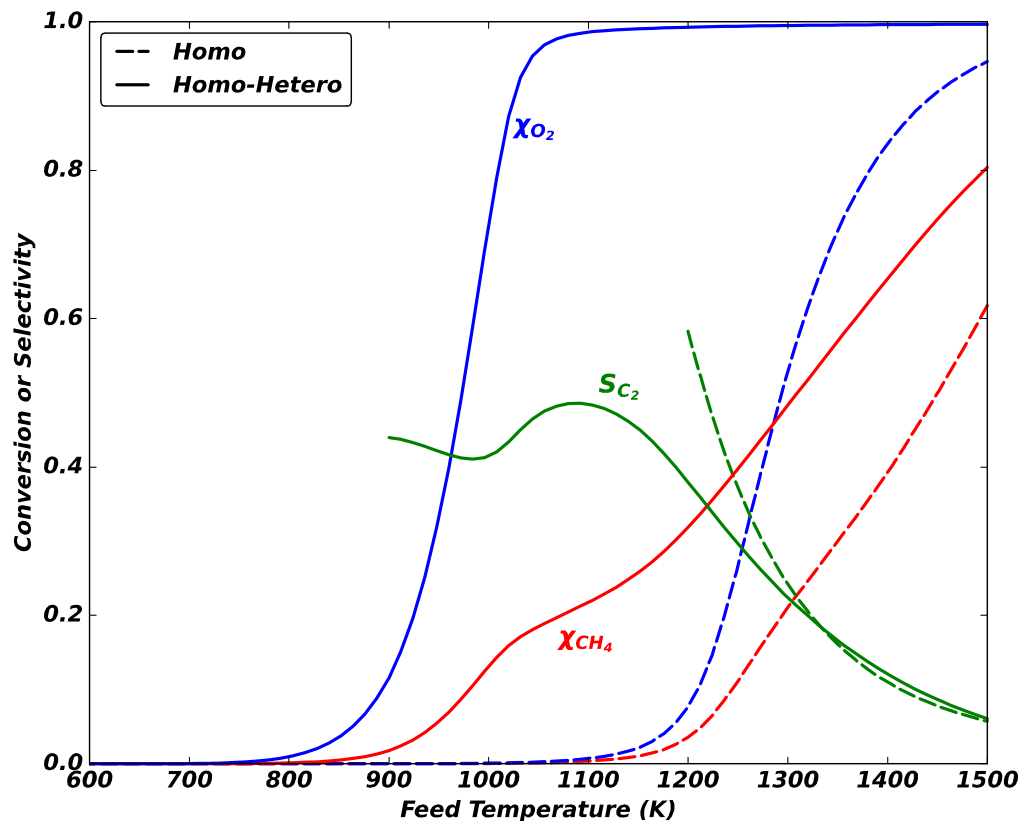


Figure 6.4: Exit conversions (χ) of CH_4 & O_2 and selectivities (S) of C_2 products ($C_2H_6 + C_2H_4$) against fluid inlet temperatures using the kinetic parameters proposed by Kechagiopoulos et al [113].

gas phase reactions and resulted in its insignificant increase in presence of catalytic reactions. Though this mechanism has been proven to fit the experimental data well, in our opinion it lacks a thorough sensitivity analysis and does not truly reflect the underlying chemistries. [In this context it is important to clarify that the net reaction rates of the surface reactions in fig. 6.3 are expressed in $\text{kmol}/\text{m}^2\text{s}$, while the scaling factor is 5.4×10^{-8} . Note that these reaction rates when multiplied by the catalyst active area, a_c , are comparable to the net volumetric homogeneous reaction rates.]

On the contrary, the original gas-phase kinetics of Chen et al. [107] and the

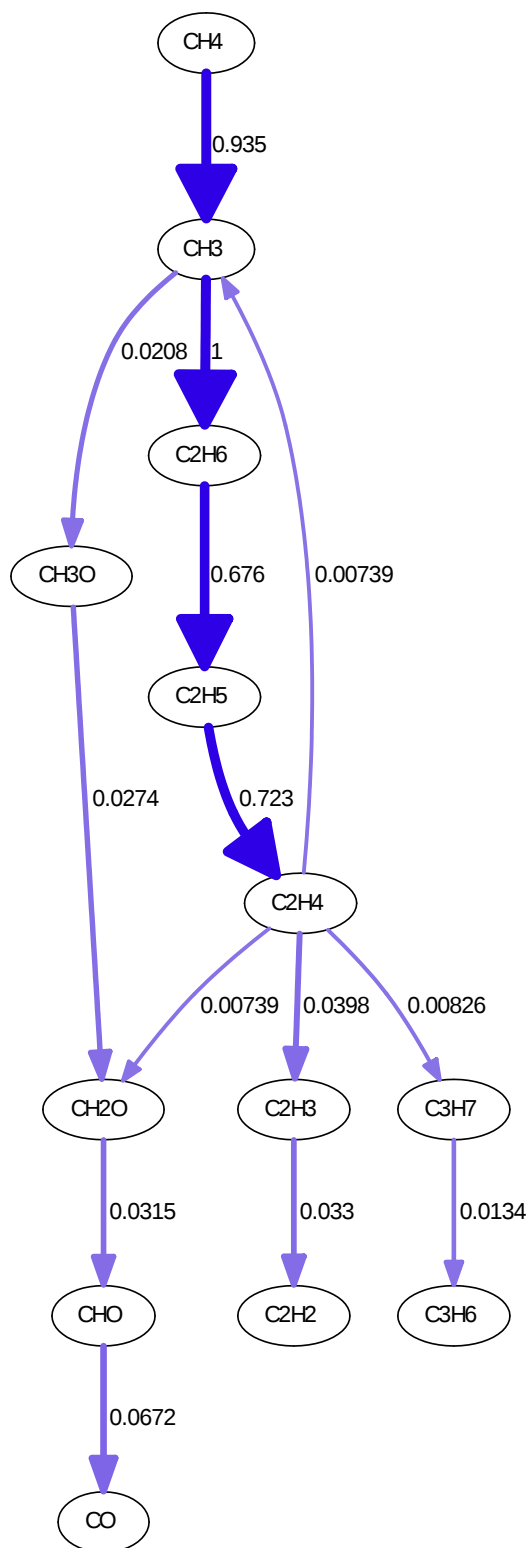


Figure 6.5: Homogeneous reaction pathways of carbon containing compounds at $T_{f,in} = 1100$ K and inlet mole ratio $\text{CH}_4/\text{O}_2 = 6$. The actual rate is scaled by a factor of 0.018.

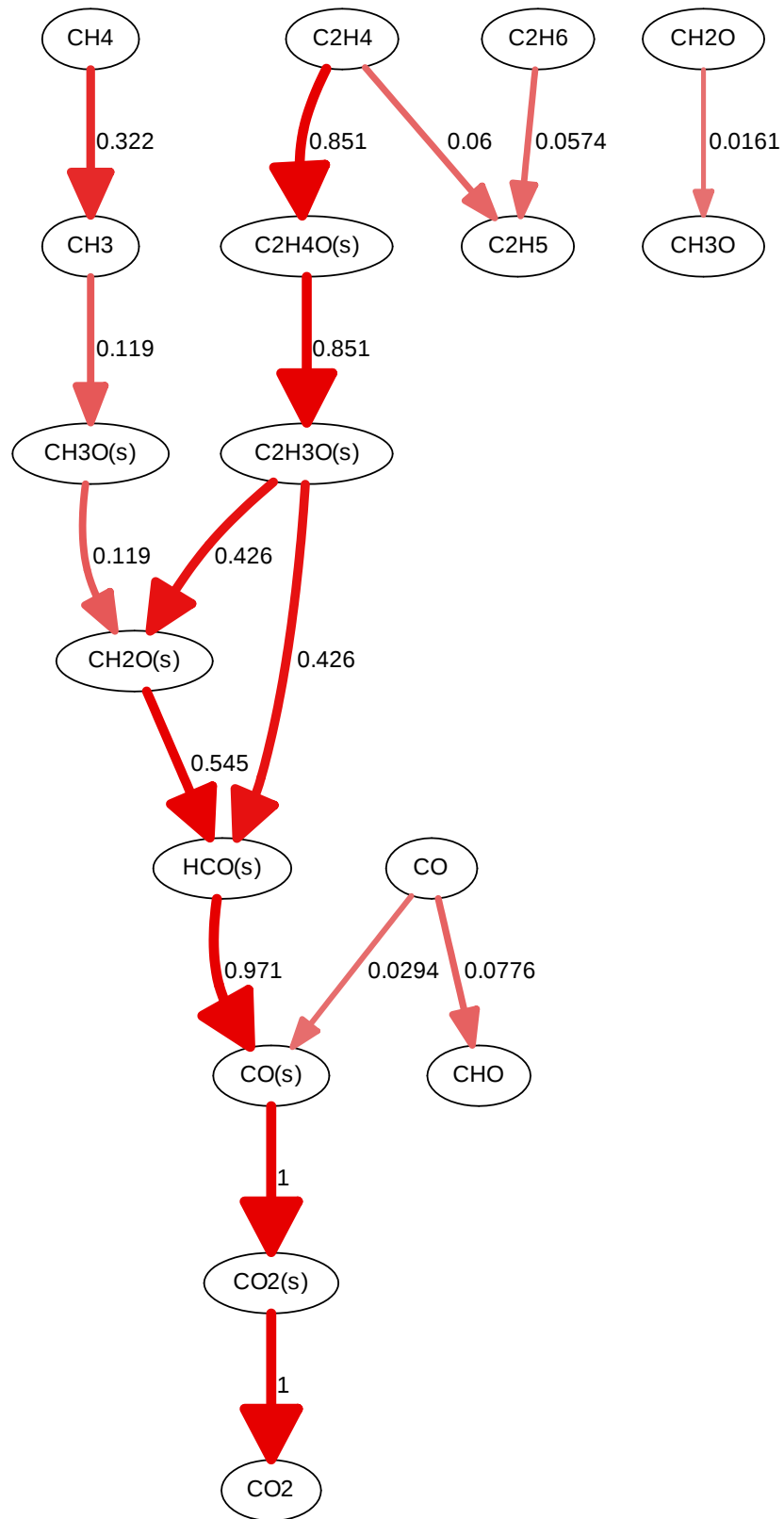


Figure 6.6: Catalytic reaction pathways of carbon containing compounds at $T_{f,in} = 1100$ K and inlet mole ratio $CH_4/O_2 = 6$. The actual rate is scaled by a factor of 3.6×10^{-8} .

catalytic mechanisms of Kechagiopoulos et al. [113] do not appear to possess the limitations described above. In fig. 6.4, a similar comparison of the homogeneous contribution against the coupled homo-hetero case is presented using their kinetic data. The design and operating conditions are kept same as before. As can be seen from this figure, high C_2 selectivity (50%) along with high CH_4 conversion (20%) can only be achieved in presence of the catalyst. Also, the light-off temperature significantly decreases by almost 400 K when catalytic reactions are considered. The C_2 selectivity goes through a maximum in between 1000 to 1200 K reaching a peak value around 1070 K. Similar to the prior case, we have shown the reaction pathway diagrams of both homogeneous and catalytic reactions at 1100 K in figs. 6.5 and 6.6.

The homogeneous reaction pathways are very similar to the one presented earlier. Methane forms methyl radical mainly through reactions H2 and H4. A smaller fraction is formed through reaction H5 as well. Methyl radical goes through the inactivated coupling reaction (H9) to form ethane. Unlike the previous mechanism, traces of acetylene is found to be formed from $C_2H_3^\bullet$ radical through reaction H29. The main difference lies in the catalytic reaction pathways. Here, methane is actually activated by surface adsorbed oxygen to form methyl radical. The reported activation energy for this reaction (C2) is 139.3 kJ/mol. This value is also consistent with other catalytic data. Evidently, this kinetic data is more accurate in approximating the true chemical phenomena. In what follows, we consider this mechanism and investigate the impact of various design and operating conditions on the reaction kinetics and reactor performance.

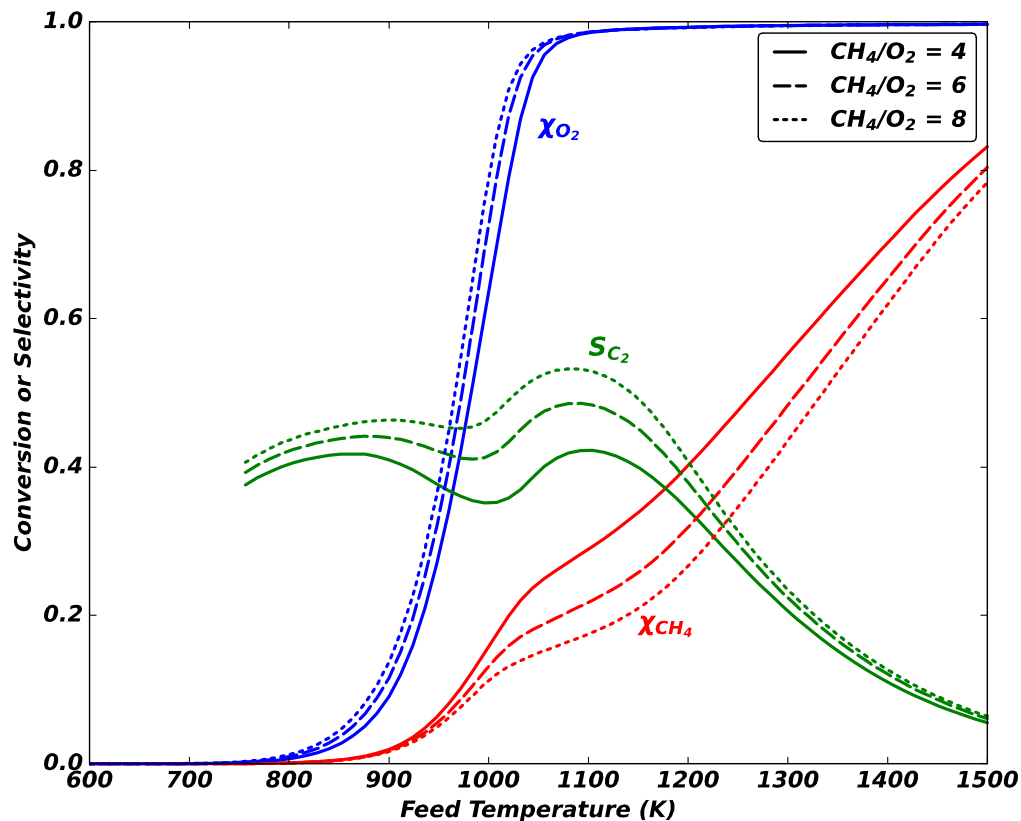


Figure 6.7: Exit conversions (χ) of CH_4 & O_2 and selectivities (S) of C_2 products ($C_2H_6 + C_2H_4$) against fluid inlet temperatures at different inlet CH_4/O_2 mole ratio.

6.4.2 Impact of design and operating parameters

The impact of inlet CH_4/O_2 mole ratio is illustrated in fig. 6.7. With the increase of inlet mole ratio from 4 to 8, the C_2 selectivity increases and CH_4 conversion decreases. In all the cases, oxygen almost reaches complete conversion. The qualitative trends of selectivity and conversion match with our earlier results obtained through the use of global kinetic model. With higher concentrations of CH_4 , the rate of methyl radical formation increases which eventually manifests in an increase of C_2 selectivity.

Fig. 6.8 demonstrates the impact of space time on reactant conversion and selectivity at a fixed inlet CH_4/O_2 mole ratio of 8 and reactor pressure $P_T = 1$ atm. With the increase of space time from 50 ms to 200 ms, methane and oxygen conversion are found to increase for a fixed feed temperature. The light-off temperature also shifts left towards lower values of feed temperatures with the increase of space time. The bifurcation diagrams obtained in the previous chapter can also capture this same trend. However, at higher feed temperature ($1100 < T_{f,in} < 1300$ K) C_2 selectivities decreases with the increase of feed temperature. This is somewhat opposite to what we have found using our global kinetic models. At higher space times, the undesirable secondary reactions of ethane and ethylene in both gas-phase and catalytic routes become dominant which leads to a lower C_2 selectivity. Further lowering the space time negatively impacts the reactor performance due to the external mass transfer limitations.

The impact of operating pressure at a constant inlet CH_4/O_2 mole ratio of 8 and space time, $\tau = 100$ ms is shown in fig. 6.9. The CH_4 conversion is not so sensitive to pressure at lower temperatures (1000 - 1200 K). At higher temperatures, CH_4 conversion decreases with the increase of pressure. On the other hand, oxygen conversion is found to decrease at higher pressure in the temperature range 1000 - 1200 K. There is also a slight decrease in light-off temperature at elevated pressures. Interestingly, higher C_2 selectivities at elevated pressures are achieved at lower temperatures (< 1100 K). Again at significantly higher temperatures (> 1300 K) C_2 selectivity is found to increase with increase of pressure. In between this temperature range (1100 - 1300 K), the selectivity trends are not so distinct and amount to similar values.

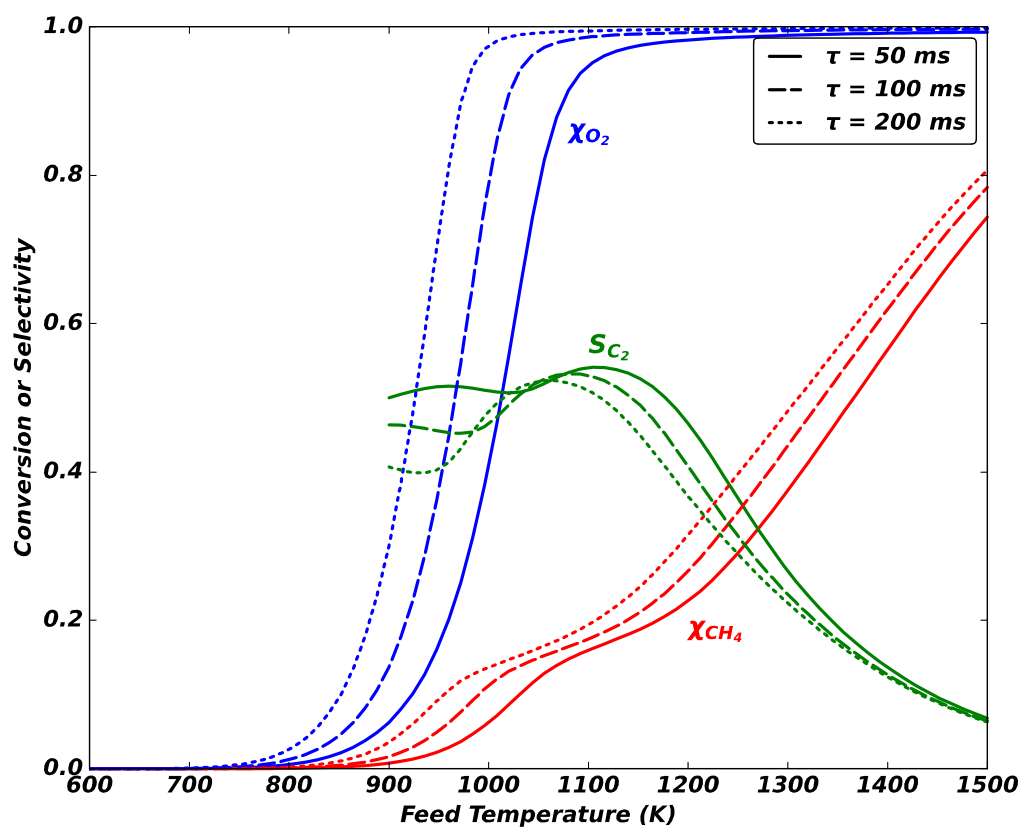


Figure 6.8: Exit conversions (χ) of CH_4 & O_2 and selectivities (S) of C_2 products ($C_2H_6 + C_2H_4$) against fluid inlet temperatures at different space times.

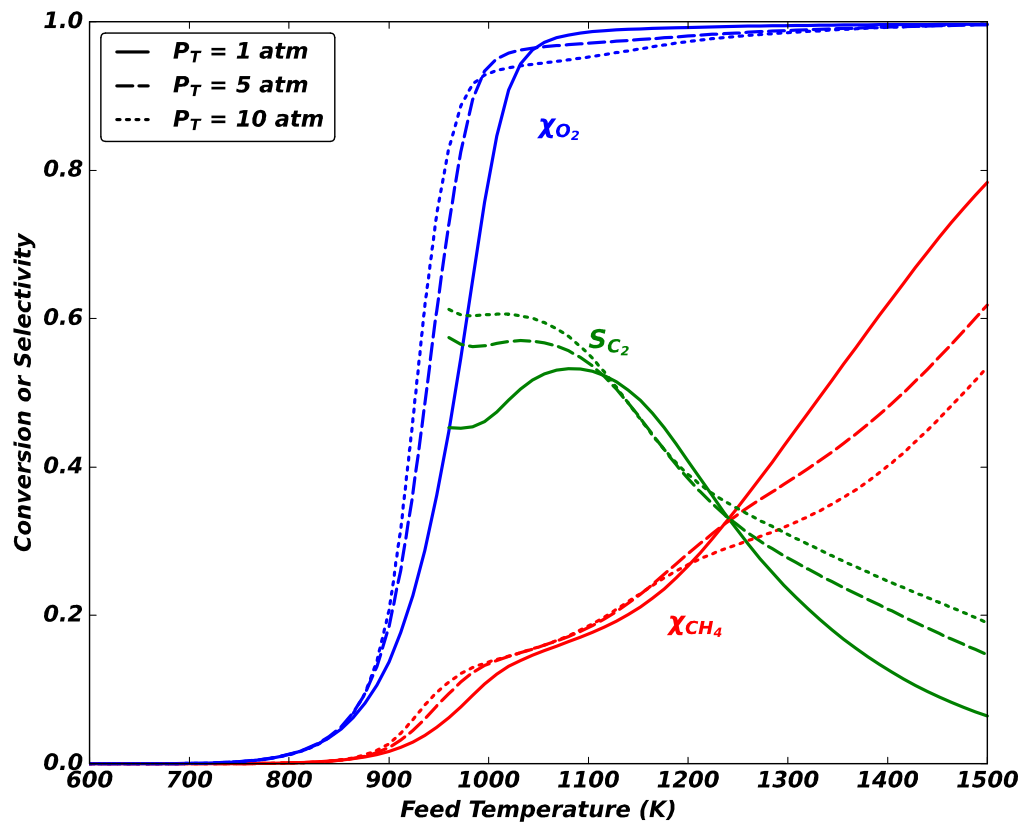


Figure 6.9: Exit conversions (χ) of CH_4 & O_2 and selectivities (S) of C_2 products ($C_2H_6 + C_2H_4$) against fluid inlet temperatures at different total pressure.

6.5 Summary

In this chapter, we have performed transient simulations of the short monolith model with microkinetic reaction mechanism of OCM and investigated the impact of various design and operating parameters such as inlet mole ratio, space time and pressure on the kinetics as well as reactor performance. 39 reversible homogeneous reactions coupled with 26 reversible surface reactions are considered. Kinetic parameters from two different independent studies are compared. Our analysis show that the data reported by Karakaya et al. [98] falls short in completely describing the actual chemistry. More specifically, the kinetic parameters are chosen in such a way, that methane is not at all activated by the catalyst, rather it forms methyl radical entirely through the homogeneous route. As a result, the mechanism predicts higher C_2 selectivity values even without a catalyst. Further inclusion of the catalytic reactions does not lead to any substantial increase in the selectivities. The parameters reported by Chen et al. ([107]-[108]) and Kechagiopoulos et al. [113] predict methane activation through the catalytic route and its subsequent recombination to form ethane. Using their kinetics, higher values of C_2 selectivity at high CH_4 conversion are only obtained in presence of a catalyst.

Our simulations reveal that higher C_2 selectivity can be attained at lower space times, provided there is no significant diffusional limitations. At higher space times, the secondary reactions of ethane and ethylene become dominant which finally lead to lower selectivity values. This is in contrast with what we have obtained from our global kinetic analysis discussed in the previous chapter. The effect of pressure is also

computed. It has been found that higher selectivity at elevated pressure is attainable when the reactor temperatures are lower.

Chapter 7

Conclusions and recommendations for future work

7.1 Conclusions

The main contribution of this thesis is the illustration of a detailed bifurcation analysis of coupled homogeneous-heterogeneous reactions in monolith, gauze and wire-mesh type reactors. We have presented the two most important limiting cases of the generalized multi-mode reduced order model for these reactor types. These simplified models are expressed in terms of various physically meaningful concentration and temperature modes (e.g., phase averaged or experimentally measurable cup-mixing concentrations/temperature). Local equations relate the various modes through transfer coefficients, which are local scale, flow and property dependent. We have illustrated the usefulness of the reduced order models with three simple examples - propane oxidation, hydrogen combustion and oxidative coupling of methane.

For propane oxidation, we have compared the phase diagrams computed by Alam et al. [17] assuming only surface or wall reaction against the case where washcoat diffusion is considered. As expected, the presence of washcoat diffusion shrinks the

region of multiplicity for the catalytic reaction. However, this suppression of catalytic pathway leads to the expansion of the hysteresis region for the homogeneous reaction. This effect is found to be more prominent at lower channel radii. Due to higher surface to volume ratio at lower channel hydraulic radius, the catalytic reaction usually dominates over the homogeneous counterpart at higher space times (> 1 ms). As a result the hysteresis region of the latter shrinks and moves further up towards higher inlet mole ratios and lower space times (< 1 ms). Under such lower space times, the internal diffusional resistance is greatest, because of which some fraction of reactants can no longer get converted through the catalytic pathway. Instead they go through the homogeneous route resulting in the expansion of its hysteresis region. Furthermore, the coupling between homogeneous and catalytic conversion is strongest when the effective axial heat and mass Peclet numbers are of order unity or smaller (or more precisely, the thermal coupling is strongest when the effective heat Peclet number approaches zero while the species coupling is also strong when the mass Peclet number is of order unity or smaller). In practice, Peclet values of order unity or smaller can be attained by either using shorter monoliths and/or substrates with high conductivity and/or low flow rates (or space velocities). This observation is extremely important as it can be used to control the extent of the coupling between homogeneous and catalytic chemistries and also remains valid in the other applications.

In the case of catalytically assisted lean hydrogen combustion, we have constructed phase diagrams in the plane of equivalence ratio versus feed temperature and equivalence ratio versus space time to classify the behaviors occurring and the extent of coupling between the homogeneous and catalytic conversion of the fuel. Using the

short monolith model, we have shown that the solid temperature can shoot-up to extremely high values exceeding the adiabatic limit, especially when the channel hydraulic radius is large. Since hydrogen is a diffusionally imbalanced fuel with a Lewis number less than unity, this is expected and has been widely discussed in the literature [31]. Additionally, we have also found the maximum fluid temperature in the channel to exceed the adiabatic value when catalytic ignition is followed by homogeneous ignition. This has been illustrated by computing both the axial and transverse temperature profiles inside the reactor using the two-mode long channel model. We have also included heat loss effects in our analysis and presented the existence of additional bifurcation features such as isola and mushroom.

Our analysis of OCM shows that autothermal operation (on the ignited branch) of OCM in short-monolith, gauze or wire-mesh type reactors is feasible for space times of the order of 10 to 100 ms, feed temperatures in the range 450 to 600K, methane to oxygen ratios in the range 6 to 8. The C_2 selectivity goes through a maximum around an operating temperature of about 1100K, and is in the 75 to 85% range, while the per pass methane conversion is in the range 16 to 25%. High conductivity (metallic or SiC) monoliths lead to better selectivity and a wider region of autothermal operation. The use of longer monoliths and proportionately higher velocities (so that space time is constant) could lead to higher productivity but shrinks the operability window, especially if the substrate conductivity is not high.

7.2 Recommendations for future work

We now discuss some limitations and extensions of the work presented here. First, we note that the reduced order model used to examine the ignition and extinction behavior is only applicable when the local gradients (across the channel) are small or finite. If this is not the case, we have to resort to models with higher number of modes or detailed partial differential equation models to determine the system behavior. It should be also pointed out that nonlinear diffusion-convection-reaction models can display extremely complex behavior, including spatio-temporal patterns at the smallest scales. While the reduced order models are useful to detect parameter regions in which such behavior could occur, we have to resort to the detailed CFD models to describe such patterned states.

Second, we have examined here only the steady-state behavior and not the transient behavior that could arise due to initial conditions or time varying inlet conditions (except for slow ramping of the inlet temperature). Proper start-up technique to reach the desired operating state (e.g., autothermal state) is also an important aspect of the design. The start-up procedure involves the determination of the correct initial conditions (e.g., initial reactor temperature) and how to vary the inlet reactant composition and temperature so that the monolith temperature remains nearly constant at the desired value until the system reaches the autothermal steady-state. This requires a detailed investigation of the transient (dynamic) behavior of the reactor. It can be pursued using the models presented in this work and is a topic for further investigation.

Finally, we have only considered global kinetic models for the bifurcation study. Although the qualitative bifurcation features are expected to remain same, use of detailed microkinetic reaction mechanisms in place of global kinetic models can push the extinction point to much lower feed temperatures, thereby resulting in a larger region of multiplicity [64]. The results obtained by our simple reaction kinetic models can be used to guide those computations with more detailed reaction mechanisms. This is another avenue which can be explored in future. Furthermore, the bifurcation analysis presented here can be extended to investigate hydrogen assisted oxidation of carbon monoxide and/or hydrocarbons. As reported in the literature, co-feeding hydrogen with CO or hydrocarbons can enhance the light-off behavior of the reactant mixture. Comprehensive analysis of such reaction systems is also a potential area to extend this work.

Bibliography

- [1] S. Chakraborty, V. Balakotaiah, "Spatially averaged multi-scale models for chemical reactors," *Adv. Chem. Eng.* 30 (2005), 205-297.
- [2] V. Balakotaiah, "On the relationship between Aris and Sherwood numbers and friction and effectiveness factors," *Chem. Eng. Sci.* 63 (2008) 5802-5812.
- [3] S. Y. Joshi, M. P. Harold, V. Balakotaiah, "Low-dimensional models for real time simulation of catalytic monoliths," *AIChE J.* 55 (2009) 1771-1783.
- [4] S. Y. Joshi, M. P. Harold, V. Balakotaiah, "On the use of internal mass transfer coefficient in modeling of diffusion and reaction in catalytic monoliths," *Chem. Eng. Sci.* 64 (2009) 4976-4991.
- [5] S. R. Gundlapally, V. Balakotaiah, "Heat and mass transfer correlations and bifurcation analysis of catalytic monoliths with developing flows," *Chem. Eng. Sci.* 66 (2011) 1879-1892.
- [6] E. J. Bissett, "An asymptotic solution for washcoat pore diffusion in catalytic monoliths," *Emission Control Sc. Tech.* 1 (2015) 3-16.
- [7] P. Kumar, I. Makki, J. Kerns, K. Grigoriadis, M. Francheck, V. Balakotaiah, "A low-dimensional model for describing the oxygen storage capacity and transient behavior of a three-way catalytic converter," *Chem. Eng. Sci.* 73 (2012) 373-387.

- [8] P. Kumar, T. Gu, M. Franchek, K. Grigoriadis, V. Balakotaiah, "Spatiotemporal dynamics of oxygen storage and release in three-way catalytic converters," *Chem. Eng. Sci.* 111 (2014) 180-190.
- [9] B. Mozaffari, S. Tischer, M. Votsmeier, O. Deutschmann, "A one-dimensional modeling approach for dual-layer monolithic catalysts," *Chem. Eng. Sci.* 139 (2016) 196-210.
- [10] J. Rink, B. Mozaffari, S. Tischer, O. Deutschmann, M. Votsmeier, "Real-time simulation of dual-layer catalytic converters based on the internal mass transfer coefficient approach," *Top. Catal.* 60 (2017) 225-229.
- [11] R. R. Ratnakar, M. Bhattacharya, V. Balakotaiah, "Reduced order models for describing dispersion and reaction in monoliths," *Chem. Eng. Sci.* 83 (2012) 77-92.
- [12] R. R. Ratnakar, V. Balakotaiah, "Reduced order multimode transient models for catalytic monoliths with micro-kinetics," *Chem. Eng. J.* 260 (2015) 557-572.
- [13] R. R. Ratnakar, V. Balakotaiah, "Reduced-order transient models for describing thermal gradients in catalytic monoliths," *Ind. Eng. Chem. Res.* 54 (2015) 10260-10274.
- [14] J. R. Picardo, S. Pushpavanam, "Low-dimensional modeling of transport and reactions in two-phase stratified flow," *Ind. Eng. Chem. Res.* 54 (2015) 10481-10496.

- [15] R. R. Ratnakar, R. K. Dadi, V. Balakotaiah, "Multi-scale reduced order models for transient simulation of multi-layered monolith reactors," *Chem. Eng. J.* 352 (2018) 293-305.
- [16] M. Tu, R. R. Ratnakar, V. Balakotaiah, "Reduced order models with local property dependent transfer coefficients for real time simulations of monolith reactors," *Chem. Eng. J.* 383 (2020) 123074.
- [17] I. Alam, D. H. West, V. Balakotaiah, "Bifurcation Analysis of thermally coupled homogeneous-heterogeneous combustion," *Chem. Eng. J.* 280 (2015) 293-315.
- [18] S. Sarsani, D. West, W. Liang, V. Balakotaiah, "Autothermal oxidative coupling of methane with ambient feed temperature," *Chem. Eng. J.* 328 (2017) 484-496.
- [19] V. Balakotaiah, N. Gupta, D. H. West, "A simplified model for analyzing catalytic reactions in short monoliths," *Chem. Eng. Sci.* 55 (2000) 5367-5383.
- [20] D. A. Hickman, L. D. Schmidt, "Modeling catalytic gauze reactors: ammonia oxidation," *Ind. Eng. Chem. Res.* 30 (1991) 50-55.
- [21] J. M. Pirie, "The manufacture of hydrocyanic acid by the Andrussov process," *Platin. Met. Rev.* 2 (1958) 7-11.
- [22] V. Balakotaiah, Z. Sun, D. H. West, "Autothermal reactor design for catalytic partial oxidations," *Chem. Eng. J.* 374 (2019) 1403-1419.

- [23] O. Sanz, E. D. Banús, A. Goya, H. Larumbe, J. J. Delgado, A. Monzón, M. Montes, "Stacked wire-mesh monoliths for VOCs combustion: effect of the mesh opening in the catalytic performance," *Catal. Today* 296 (2017) 76-83.
- [24] B. Sarkar, R. R. Ratnakar, V. Balakotaiah, "Multi-scale coarse-grained continuum model for bifurcation and transient analysis of coupled homogeneous-catalytic reactions in monoliths," *Chem. Eng. J.* 407 (2021) 126500.
- [25] V. Balakotaiah, I. Alam, D. H. West, "Heat and mass transfer coefficients and bifurcation analysis of coupled homogeneous-catalytic reactions," *Chem. Eng. J.* 321 (2017) 207-221.
- [26] R. H. Perry, D. W. Green, Perry's Chemical Engineers' Handbook, 7th ed., McGraw-Hill, New York, 1997.
- [27] B. J. McBride, S. Gordon, M. A. Reno, "Coefficients for calculating thermodynamic and transport properties of individual species," *NASA Report* TM-4513, 1993.
- [28] I. Alam, D. H. West, V. Balakotaiah, "Transport effects on pattern formation and maximum temperature in homogeneous-heterogeneous combustion," *Chem. Eng. J.* 288 (2016) 99-115.
- [29] M. Kubiček, "Algorithm 502: Dependence of solution of nonlinear systems on a parameter [C5]," *ACM Trans. Math. Software* 2 (1976) 98-107.
- [30] V. Balakotaiah, J. Khinast, Numerical bifurcation techniques for chemical reactor problems, pages 1-36, vol. 119, Springer, New York, 2000.

- [31] W. C. Pfefferle, L. D. Pfefferle, "Catalytically stabilized combustion," *Prog. Energy Combust. Sci.* 12 (1986) 25-41.
- [32] K. W. Beebe, K. D. Cairns, V. K. Pareek, S. G. Nickolas, J. C. Schlatter, T. Tsuchiya, "Development of catalytic combustion technology for single-digit emissions from industrial gas turbines," *Catal. Today* 59 (2000) 95-115.
- [33] W. C. Pfefferle, "Catalytically supported thermal combustion," *Belgian Patent No.* 814752 (1974).
- [34] R. Carroni, V. Schmidt, T. Griffin, "Catalytic combustion for power generation," *Catal. Today* 75 (2002) 287-295.
- [35] N. S. Kaisare, D. G. Vlachos, "A review on microcombustion: Fundamentals, devices and applications," *Prog. Energy Combust. Sci.* 38 (2012) 321-359.
- [36] J. Mantzaras, "Progress in non-intrusive laser based measurements of gas-phase thermoscalars and supporting modeling near catalytic interfaces," *Prog. Energy Combust. Sci.* 70 (2019) 169-211.
- [37] V. Balakotaiah, D. H. West, "Thermal effects and bifurcation in gas phase catalytic partial oxidations," *Curr. Opin. Chem. Eng.* 5 (2014) 68-77.
- [38] J. Chen, W. Song, X. Gao, D. Xu, "Hetero-/homogeneous combustion and flame stability of fuel-lean propane-air mixtures over platinum in catalytic micro-combustors," *Appl. Therm. Eng.* 100 (2016) 932-943.

- [39] V. R. Regatte, G. Selle, N. S. Kaisare, "The role of homogeneous chemistry during ignition of propane combustion in Pt-catalyzed microburners," *Int. J. Spray Combust. Dyn.* 4 (2012) 155-174.
- [40] M. Kommu, N. S. Kaisare, "Ignition of homo/hetero combustion of propane in a microreactor with catalyst segmentation," *Chem. Eng. Res. Des.* 138 (2018) 125-134.
- [41] S. Karagiannidis, J. Mantzaras, R. Bombach, S. Schenker, K. Boulouchos, "Experimental and numerical investigation of the hetero-/homogeneous combustion of lean propane/air mixtures over platinum," *Proc. Combust. Inst.* 32 (2009) 1947-1955.
- [42] C. K. Westbrook, F. L. Dryer, "Simplified reaction mechanisms for the oxidation of hydrocarbon fuels in flames," *Combust. Sci. Tech.* 27 (1981) 31-43.
- [43] L. Hiam, H. Wise, S. Chaikin, "Catalytic oxidation of hydrocarbons on platinum," *J. Catal.* 10 (1968) 272.
- [44] R. K. Dadi, D. Luss, V. Balakotaiah, "Dynamic hysteresis in monolith reactors and hysteresis effects during co-oxidation of CO and C₂H₆," *Chem. Eng. J.* 297 (2016) 325-340.
- [45] W. R. Williams, M. T. Stenzel, X. Song, L. D. Schmidt, "Bifurcation behavior in homogeneous-heterogeneous combustion: I. Experimental results over platinum," *Combust. Flame* 84 (1991) 277-291.

- [46] X. Song, W. R. Williams, L. D. Schmidt, R. Aris, "Bifurcation behavior in homogeneous-heterogeneous combustion: II. Computations for stagnation-point flow," *Combust. Flame* 84 (1991) 292-311.
- [47] D. G. Vlachos, "The interplay of transport, kinetics and thermal interactions in the stability of premixed hydrogen/air flames near surfaces," *Combust. Flame* 103 (1995) 59-75.
- [48] D. G. Vlachos, P. -A. Bui, "Catalytic ignition and extinction of hydrogen: comparison of simulations and experiments," *Surf. Sci.* 64 (1996) L625-L630.
- [49] P. -A. Bui, D. G. Vlachos, P. R. Westmoreland, "Homogeneous mixtures of hydrogen-air mixtures over platinum," *Proc. Combust. Inst.* 26 (1996) 1763-1770.
- [50] G. Russo, A. Di Benedetto, F. S. Marra, "Bifurcation analysis of lean premixed combustion of hydrogen/propane mixtures," *Combust. Sci. Technol.* 177 (2005) 413-434.
- [51] D. G. Norton, D. G. Vlachos, "Hydrogen assisted self-ignition of propane/air mixtures in catalytic microburners," *Proc. Combust. Inst.* 30 (2005) 2473-2480.
- [52] J. Pan, N. Miao, Z. Lu, Q. Lu, W. Yang, Z. Pan, Y. Zhang, "Experimental and numerical study on the transition conditions and influencing factors of heterogeneous/homogeneous reaction for H₂/Air mixture in micro-catalytic combustor," *Appl. Therm. Eng.* 154 (2019) 120-130.

- [53] C. Appel, J. Mantzaras, R. Schaeren, R. Bombach, A. Inauen, "Catalytic combustion of hydrogen-air mixtures over platinum: validation of hetero/homogeneous chemical reaction schemes," *Clean Air* 5 (2004) 21-44.
- [54] G. D. Stefanidis, D. G. Vlachos, "Controlling homogeneous chemistry in homogeneous-heterogeneous reactors: application to propane combustion," *Ind. Eng. Chem. Res.* 48 (2009) 5962-5968.
- [55] V. R. Regatte, N. S. Kaisare, "Numerical analysis of fractal catalyst structuring in microreactors," *Ind. Eng. Chem. Res.* 50 (2011) 12925-12932.
- [56] S. Karagiannidis, J. Mantzaras, K. Boulouchos, "Stability of hetero-/homogeneous combustion in propane- and methane-fueled catalytic microreactors: channel confinement and molecular transport effects," *Proc. Combust. Inst.* 33 (2011) 3241-3249.
- [57] G. B. Chen, C.P. Chen, C.Y. Wu, Y. C. Chao, "Effects of catalytic walls on hydrogen/air combustion inside a micro-tube," *Appl. Catal. A: Gen.* 332 (1) (2007) 89-97.
- [58] U. Dogwiler, P. Benz, J. Mantzaras, "Two-dimensional modelling for catalytically stabilized combustion of a lean methane-air mixture with elementary homogeneous and heterogeneous chemical reactions," *Combust. Flame* 116 (1999) 243-258.

- [59] O. Deutschmann, L. I. Maier, U. Riedel, A. H. Stroemann, R. W. Dibble, "Hydrogen assisted catalytic combustion of methane on platinum," *Catal. Today* 59 (2000) 141-150.
- [60] S. Specchia, S. Tacchino, V. Specchia, "Facing the catalytic combustion of CH_4/H_2 mixtures into monoliths," *Chem. Eng. J.* 167 (2011) 622-633.
- [61] N. M. Marinov, C. K. Westbrook, W. J. Pitz, "Detailed and global chemical kinetics model for Hydrogen," *8th Int'l. Symp. on Transport Properties* (1995) San Francisco, CA.
- [62] R. W. Schefer, "Catalyzed combustion of H_2 /Air mixtures in a flat plate boundary layer: II. Numerical model," *Combust. Flame* 45 (1982) 171-190.
- [63] S. Y. Joshi, Y. Ren, M. P. Harold, V. Balakotaiah, "Determination of kinetics and controlling regimes for H_2 oxidation on $\text{Pt}/\text{Al}_2\text{O}_3$ monolithic catalyst using high space velocity experiments," *Appl. Cat. B* 102 (2011) 484-495.
- [64] D. Bhatia, M. P. Harold, V. Balakotaiah, "Kinetic and bifurcation analysis of the cooxidation of CO and H_2 in catalytic monolith reactors," *Chem. Eng. Sci.* 64 (2009) 1544-1558.
- [65] L. B. Younis, "Modeling of hydrogen oxidation within catalytic packed bed reactor," *J. Energy Inst.* 79:4 (2006) 222-227.
- [66] V. N. Nguyen, R. Deja, R. Peters, L. Blum, D. Stolten, "Study of the catalytic combustion of lean hydrogen-air mixtures in a monolith reactor," *Int. J. Hydrog. Energy* 43 (2018) 17520-17530.

- [67] A. Basavaraju, A. B. Ramesh, D. Jajcevic, F. Heitmeir, "Experimental parametric investigation of platinum catalysts using hydrogen fuel," *Int. J. Hydrog. Energy* 43 (2018) 21307-21321.
- [68] R. R. Ratnakar, V. Balakotaiah, "Bifurcation analysis of index infinity DAE parabolic models describing reactors and reacting flows," *AIChE J.* 63 (2017) 295-305.
- [69] J. B. Powell, "Natural gas utilization: Current status and opportunities," *Catal. Today* 356 (2020) 27-36.
- [70] J. H. Lunsford, "Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century," *Catal. Today* 63 (2000) 165-174.
- [71] A. Holmen, "Direct conversion of methane to fuels and chemicals," *Catal. Today* 142 (2009) 2-8.
- [72] M. C. Alvarez-Galven, N. Mota, M. Ojeda, S. Rojas, R. M. Navarro, J. L. G. Fierro, "Direct methane conversion routes to chemicals and fuels," *Catal. Today* 171 (2011) 15-23.
- [73] K. D. Campbell, E. Morales, J. H. Lunsford, "Gas phase coupling of methyl radicals during the catalytic partial oxidation of methane," *J. Am. Chem. Soc.* 109 (1987) 7900-7901.
- [74] B. Zohour, D. Noon, S. Senkan, "New Insights into the oxidative coupling of methane from spatially resolved concentration and temperature profiles," *ChemCatChem* 5 (2013) 2809-2812.

- [75] J. H. Lunsford, "The catalytic oxidative coupling of methane," *Angew. Chem. Int. Ed.* 34 (1995) 970-980.
- [76] G. E. Keller, M. M. Bhasin, "Synthesis of ethylene via oxidative coupling of methane," *J. Catal.* 73 (1982) 9-19.
- [77] J. A. Sofranko, J. J. Leonard, C. A. Jones, "The oxidative conversion of methane to higher hydrocarbons," *J. Catal.* 103 (1987) 302-310.
- [78] A. Galadima, O. Muraza, "Revisiting the oxidative coupling of methane to ethylene in the golden period of shale gas: a review," *J. Ind. Eng. Chem* 37 (2016) 1-13.
- [79] U. Zavyalova, M. Holena, R. Schlögl, M. Baerns, "Statistical analysis of past catalytic data on oxidative methane coupling for new insights into the composition of high-performance catalysts," *ChemCatChem* 3 (2011) 1935-1947.
- [80] A. V. Annapragada, E. Gulari, "Fe-P-O catalysts for methane utilization - catalyst development and identification," *J. Catal.* 123 (1990) 130-146.
- [81] J. Y. Lee, W. Jeon, J. Choi, Y. Suh, J. Ha, D. J. Suh, Y. Park, "Scaled-up production of C_2 hydrocarbons by the oxidative coupling of methane over pelletized $Na_2WO_4/Mn/SiO_2$ catalysts: observing hot spots for the selective process," *Fuel* 106 (2013) 851-857.
- [82] D. Noon, A. Seusbai, S. Senkan, "Oxidative coupling of methane by nanofiber catalysts," *ChemCatChem* 5 (2013) 146-149.

- [83] A. Aseem, G. G. Jeba, M. T. Conato, J. D. Rimer, M. P. Harold, "Oxidative coupling of methane over mixed metal oxide catalysts: steady state multiplicity and catalyst durability," *Chem. Eng. J.* 331 (2018) 132-143.
- [84] Z. Sun, A. Kota, S. Sarsani, D. H. West, V. Balakotaiah, "Bifurcation analysis of methane oxidative coupling without catalyst," *Chem. Eng. J.* 343 (2018) 770-788.
- [85] D. H. West, "Progress and challenges in the autothermal oxidative coupling of methane," NASCRE-4 meeting, March 10-13, 2019, Houston, Texas
- [86] I. Lengyel, D. H. West, "Numerical bifurcation analysis of large-scale detailed kinetic mechanisms," *Curr. Opin. Chem. Eng.* 21 (2018) 41-47.
- [87] L. A. Vandewalle, I. Lengyel, D. H. West, K. M. Van Geem, G. B. Marin, "Catalyst ignition and extinction: a microkinetics-based bifurcation study of adiabatic reactors for oxidative coupling of methane," *Chem. Eng. Sci.* 199 (2019) 635-651.
- [88] L. A. Vandewalle, R. V. D. Vijver, K. M. Van Geem, G. B. Marin, "The role of mass and heat transfer in the design of novel reactors for oxidative coupling of methane," *Chem. Eng. Sci.* 198 (2019) 268-289.
- [89] J. M. Aigler, J. H. Lunsford, "Oxidative dimerization of methane over MgO and Li^+/MgO monoliths," *Appl. Catal.* 70 (1991) 29-42.

- [90] H. Liu, D. Yang, R. Gao, L. Chen, S. Zhang, X. Wang, "A novel Na_2WO_4 - Mn/SiC monolithic foam catalyst with improved thermal properties for the oxidative coupling of methane," *Catal. Commun.* 9 (2008) 1302-1306.
- [91] B. M. Sollier, L. E. Gómez, A. V. Boix, E. E. Miró, "Oxidative coupling of methane on cordierite monoliths coated with Sr/La_2O_3 catalysts. Influence of honeycomb structure and catalyst-cordierite interactions on the catalytic behavior," *Appl. Catal. A: Gen.* 550 (2018) 113-121.
- [92] D. Merino, O. Sanz, M. Montes, "Effect of the thermal conductivity and catalyst layer thickness on the Fischer-Tropsch synthesis selectivity using structured catalysts," *Chem. Eng. J.* 327 (2017) 1033-1042.
- [93] Z. Stansch, L. Mleczko, M. Baerns, "Comprehensive kinetics of oxidative coupling of methane over the La_2O_3/CaO catalyst," *Ind. Eng. Chem. Res.* 36 (1997) 2568-2579.
- [94] M. Daneshpaye, A. Khodadadi, N. Mostoufi, Y. Mortazavi, R. S. Gharebagh, A. Talebizadeh, "Kinetic modeling of oxidative coupling of methane over $Mn/Na_2WO_4/SiO_2$ catalyst," *Fuel Process Technol.* 90 (2009) 403-410.
- [95] V. I. Alexiadis, T. Serres, G. B. Marin, C. Mirodatos, J. W. Thybaut, Y. Schuurman, "Analysis of volume-to-surface ratio effects on methane oxidative coupling using microkinetic modeling," *AIChE J.* 64 (2018) 2603-2611.

- [96] Y. Liu, C. Yu, X. Liu, B. Zhang, S. Shen, "The effect of pressure on the surface structure of $MgO/BaCO_3$ catalyst for oxidative coupling of methane," *Chem. Lett.* 25 (1996) 1127-1128.
- [97] L. Chou, Y. Cai, B. Zhang, J. Niu, S. Ji, S. Li, "Oxidative coupling of methane over $Na-Mn-W/SiO_2$ catalyst at higher pressure," *React. Kinet. Catal. Lett.* 76 (2002) 311-315.
- [98] C. Karakaya, H. Zhu, B. Zohour, S. Senkan, R. J. Kee, "Detailed reaction mechanisms for the oxidative coupling of methane over La_2O_3/CeO_2 nanofiber fabric catalyst," *ChemCatChem* 9 (2017) 4538-4551.
- [99] Z. Jiang, K. S. Chung, G. R. Kim, J. S. Chung, "Mass transfer characteristics of wire-mesh honeycomb reactors," *Chem. Eng. Sci.* 58 (2003) 1103-1111.
- [100] F. Donsì, T. Caputo, G. Russo, A. Di Benedetto, R. Pirone, "Modeling ethane oxy-dehydrogenation over monolithic combustion catalysts," *AIChE J.* 50 (2004) 2233-2245.
- [101] L. Giani, G. Groppi, E. Tronconi, "Mass-transfer characterization of metallic foams as supports for structured catalysts," *Ind. Eng. Chem. Res.* 44 (2005) 4993-5002.
- [102] Z. Sun, D. H. West, P. Gautam, V. Balakotaiah, "Scale-up analysis of autothermal operation of methane oxidative coupling with La_2O_3/CaO catalyst," *AIChE J.* 66 (2020) e16949.

- [103] G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, W. C. Gardiner Jr., V. V. Lissianski, Z. Qin, GRI Mechanism Version 3.0, 1999.
- [104] W. K. Metcalfe, S. M. Burke, S. S. Ahmed, H. J. Curran, "A Hierarchical and comparative kinetic modeling study of C₁-C₂ hydrocarbon and oxygenated fuels," *Int. J. Chem. Kinet.* 45 (2013) 638-675.
- [105] H. Zanthoff, M. Baerns, "Oxidative coupling of methane in the gas phase. Kinetic simulation and experimental verification," *Ind. Eng. Chem. Res.* 29 (1990) 2-10.
- [106] S. C. Reyes, E. Iglesia, C. P. Kelkar, "Kinetic-transport models of bimodal reaction sequences-I. Homogeneous and heterogeneous pathways in oxidative coupling of methane," *Chem. Eng. Sci.* 48 (1993) 2643-2661.
- [107] Q. Chen, P. M. Couwenberg, G. B. Marin, "Effect of pressure on the oxidative coupling of methane in the absence of catalyst," *AIChE J.* 40 (1994) 521-535.
- [108] Q. Chen, P.M. Couwenberg, G. B. Marin, "The oxidative coupling of methane with cofeeding of ethane," *Catal. Today* 21 (1994) 309-319.
- [109] J. Sun, J. W. Thybaut, G. B. Marin, "Microkinetics of methane oxidative coupling," *Catal. Today* 137 (2008) 90-102.
- [110] J. S. Ahari, S. Zarrinpashne, M. T. Sadeghi, "Micro-kinetic modeling of OCM reactions over Mn/Na₂WO₄/SiO₂ catalyst," *Fuel Process. Technol.* 115 (2013) 79-87.

- [111] M. Y. Sinev, Z. T. Fattakhova, V. I. Lomonosov, Y. A. Gordienko, "Kinetics of oxidative coupling of methane: Bridging the gap between comprehension and description," *J. Nat. Gas Chem.* 18 (2009) 273-287.
- [112] J. W. Thybaut, J. Sun, L. Olivier, A. C. Van Veen, C. Mirodatos, G. B. Marin, "Catalyst design based on microkinetic models: Oxidative coupling of methane," *Catal. Today* 159 (2011) 29-36.
- [113] P. N. Kechagiopoulos, J. W. Thybaut, G. B. Marin, "Oxidative coupling of methane: a microkinetic model accounting for intraparticle surface-intermediates concentration profiles," *Ind. Eng. Chem. Res.* 53 (2014) 1825-1840.
- [114] V. I. Alexiadis, J. W. Thybaut, P. N. Kechagiopoulos, M. Chaar, A. C. Van Veen, M. Muhler, G. B. Marin, "Oxidative coupling of methane: catalytic behaviour assessment via comprehensive microkinetic modelling," *Appl. Catal. B Environ.* 150-151 (2014) 496-505.
- [115] V. I. Alexiadis, M. Chaar, A. Van Veen, M. Muhler, J. W. Thybaut, G. B. Marin, "Quantitative screening of an extended oxidative coupling of methane catalyst library," *Appl. Catal. B Environ.* 199 (2016) 252-259.
- [116] D. G. Goodwin, H. K. Moffat, R. L. Speth, Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes. <http://www.cantera.org>, 2017, Version 2.5.1.