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Modeling and Bifurcation Analysis of

Oxidative Coupling of Methane

A Dissertation

Presented to

the Faculty of the Department of Chemical and Biomolecular Engineering University of Houston

> In Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in Chemical Engineering

> > by Zhe Sun August 2019

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Oxidative Coupling of Methane

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Dedicated to my family, friends and teachers

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Abstract

In the first part, we present a detailed ignition-extinction analysis of Oxidative Coupling of Methane (OCM) in the gas phase using a global kinetic model for the various oxidation, reforming and dehydrogenation reactions. The kinetic model satisfies the thermodynamic constraints and is validated with literature data as well as new data obtained under near isothermal conditions. It is shown that the type of reactor used has profound influence on the width of the region of multiplicity. Further, the best C_2 yield may be obtained on the ignited branch close to the extinction point where exothermic chemistry dominates or at higher space times or feed temperatures where endothermic chemistry dominates. The extinction locus, which forms the boundary of the region of autothermal operation, is determined as a function of various design and operating variables.

In the second part, ignition-extinction analysis of laboratory scale catalytic reactors with heat exchange with the furnace is provided. It is shown that the same volume or mass of catalyst packed in tubes of different diameter and/or with different lengths of inert sections could lead to different types of ignition-extinction behavior as well as product distribution. The impact of tube diameter, heat exchange time, length of inert sections and catalyst dilution on the ignition-extinction behavior is analyzed. Simulations on the impact of heat loss, kinetics and heat/mass dispersion on the region of autothermal operation of lab-scale reactors are also presented.

In the third part, ignition-extinction behavior of catalytic OCM with La_2O_3/CaO catalyst in large scale adiabatic reactors is analyzed using a global kinetic model. It is shown that in the homogeneous limit (small particles), the best selectivity of the C_2 products is obtained in the limit of very thin bed (with effective heat and mass Peclet numbers approaching zero). When inter and intra-phase heat and mass transfer gradients are significant (larger particles) so that particle level igni-

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tion could occur, selectivity to C_2 product can be enhanced. The impact of catalyst particle properties, inter and intra-particle gradients on conversion and C_2 product selectivity on the ignited branch is analyzed. Finally, some potential autothermal reactor designs for OCM with catalysts of different activity are proposed.

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Nomenclature

Roman letters

 $a_v =$ heat (mass) transfer area per unit volume (m⁻¹) $\langle C_p \rangle$ = average molar specific heat $(J \cdot mol^{-1} \cdot K^{-1})$ $C_p =$ specific heat $(J \cdot kg^{-1} \cdot K^{-1})$ $C_{pv} =$ volumetric specific heat $(J \cdot m^{-3} \cdot K^{-1})$ d = diameter (m)D = mass diffusion/dispersion coefficient ($m^2 \cdot s^{-1}$) E = reaction activation energy $(J \cdot mol^{-1})$ F =mole flow rate (mol \cdot s⁻¹)Gr =Grashof number $\Delta H =$ enthalpy of reaction $(J \cdot mol^{-1})$ h = heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$) $h_i =$ heat transfer coefficient inside the wall ($W \cdot m^{-2} \cdot K^{-1}$) $h_o =$ heat transfer coefficient outside the wall ($W \cdot m^{-2} \cdot K^{-1}$) $h_{fc} =$ heat transfer coefficient of free convection ($\mathrm{W} \cdot \mathrm{m}^{-2} \cdot \mathrm{K}^{-1}$) h_r = heat transfer coefficient of radiation (W · m⁻² · K⁻¹) $k_{air} = air \text{ conductivity} (W \cdot m^{-1} \cdot K^{-1})$ $k_c = mass transfer coefficient (m \cdot s^{-1})$ $k_{eff} =$ effective conductivity across the bed $(\,\mathrm{W}\cdot\,\mathrm{m}^{-1}\cdot\,\mathrm{K}^{-1})$ $k_f =$ fluid phase conductivity (W · m⁻¹ · K⁻¹) $k_s =$ quartz chip conductivity (W · m⁻¹ · K⁻¹) $k_v =$ rate constant for first-order reaction (s⁻¹) $k_w =$ reactor wall conductivity (W · m⁻¹ · K⁻¹) L =reactor length (m)

Nu =Nussult number

P =transverse Peclet number

 $Pe_h = axial heat Peclet number$

 $Pe_m = axial mass Peclet number$

 $\Pr = \text{Prandtl number}$

 $\hat{r} =$ modified reaction rate (s⁻¹)

r =reaction rate $(mol \cdot m^{-3} \cdot s^{-1}$ or $mol \cdot kg^{-3} \cdot s^{-1})$

 R_{Ω} = hydraulic radius of flow channel (m)

 $R = gas constant (J \cdot mol^{-1} \cdot K^{-1})$

t = time (s)

T = absolute temperature (K) or celsius temperature (°C)

 ΔT_{ad} = adiabatic temperature rise (K)

 $\langle u \rangle =$ average velocity (m · s⁻¹)

U= overall heat transfer coefficient between reactor wall and coolant ($\mathrm{W}\cdot\mathrm{m}^{-2}\cdot$

 $K^{-1})$

x = spatial co-ordinate along the length of channel (dimensional)

y = mole fraction or dimensionless reactant concentration

z =coordinate along the length of the reactor (dimensionless)

Greek letters

 $\alpha =$ thermal diffusion coefficient (m² · s⁻¹)

 $\epsilon^* = {\rm capacitance}$ ratio of solid to fluid

 $\varepsilon = \text{emissivity}$

 $\tau =$ reactor contact time (s)

 τ_g = heat generation time (s)

 τ_h = heat loss time (s)

 τ_{hf} = fluid phase heat dispersion time (s)

 $\tau_{hi} = \text{inter-phase heat transfer time (s)}$

- $\tau_{hs} =$ solid phase heat conduction time (s)
- $\tau_{ip} = \text{intra-particle mass diffusion time (s)}$
- $\tau_{mf} =$ fluid phase mass dispersion time (s)
- $\tau_{mi} =$ inter-phase mass transfer time (s)
- τ_M = homogeneous mass dispersion time (s)
- τ_H = homogeneous heat dispersion time (s)

 $\chi =$ conversion

v =stoichiometric coefficient

 $\nu_f =$ kinematic viscosity (m² · s⁻¹)

 $\eta = {\rm effectiveness}$ factor

 $\phi =$ Thiele modulus

 $\sigma =$ Stefan-Boltzmann constant

 $\sigma^* = {\rm thermal}$ capacitance ratio of solid to fluid

 $\delta_p = \text{effective intra-particle diffusion length (m)}$

 $\delta_w =$ reactor wall thickness (m)

 $\xi =$ dimensionless radial distance in particle

 $\rho = \text{density} (\text{kg} \cdot \text{m}^{-3})$

Subscripts

c = coolant

eff = effective

f =fluid phase

$$fnc =$$
furnace

h = heat loss

- i = index number of reaction
- j = index number of species

p = particle

R = reaction

- s =solid phase
- t = reactor tube
- $T = \mathsf{total}$
- $v = \mathsf{volumetric}$
- $w = \mathsf{wall}$

Superscript

- 0 = standard condition $(1 \operatorname{bar}, 298.15 \operatorname{K})$
- exit = exit condition
- E = equilibrium
- in = inlet or feed condition

Chapter 1 Introduction

1.1 Preamble

Natural gas is a fossil energy source that contains many different compounds. The largest component (by volume) of natural gas is methane, but it may also contain small amounts of other hydrocarbons (such as ethane, propane, isobutane, etc.) and nonhydrocarbon gases (such as carbon dioxide, helium, hydrogen sulfide, etc.). U.S. proved reserves of natural gas increased nearly every year since 2000. In 2018, U.S. total natural gas proved reserves are estimated to be around 464 trillion cubic feet (Tcf). The abundant proved natural gas (and shale gas) reserves provides the basic chemical industry a huge amount of inexpensive raw material.

Currently, most of the produced natural gas is used for industrial, residential and commercial heating and generation of electric power. Natural gas is considered to be an environmentally friendly clean fuel. Combustion of natural gas produces fewer emissions of nearly all types of air pollutants (sulfur dioxide, nitrous oxide, etc.) and carbon dioxide compared to the combustion of other fossil fuels (coal and petroleum products). Natural gas also produces the largest heat of combustion relative to the amount of CO_2 formed compared to other hydrocarbons. All these properties of natural gas contribute to a global shift from conventional fossil fuels to natural gas fuel.

Alternatively, methane is also served as feedstock to produce chemicals, fertilizers and hydrogen. The generation of syngas and hydrogen from methane has already been commercialized successfully, however, the production of other hydrocarbons has not been fully applied. The utilization of methane to produce hydrocarbon chemicals can be categorized into two routes: indirect conversion of

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Figure 1.1: Indirect and direct routes for methane utilization

methane and direct conversion of methane, as shown in Fig.1.1. Choosing the way of methane utilization depends on various factors such as location, methane price, market demands for products and product price. For example, ethylene is largely demanded as feedstock in chemical industry to produce important chemicals such as polyethylene, ethylene oxide and olefins. Due to this reason, direct conversion of methane to C_2 products (ethane and ethylene) by oxidative coupling of methane (OCM) is one of the most attractive way of methane utilization. The modeling and analysis of OCM reactors is the main focus of this thesis. Before going into details, we present a brief review of different methods of methane utilization, including both indirect and direct routes. A brief history of oxidative coupling of methane is also provided.

1.2 Literature Review

1.2.1 Methane Utilization

Indirect conversion of methane

The indirect methods of methane conversion involve the production of CO and H_2 , which are main components of syngas, as an initial step. The syngas generated by methane can be subsequently converted to hydrocarbons by Fischer-Tropsch synthesis or to methanol by methanol synthesis. The Fischer-Tropsch synthesis is a well-established catalytic chemical process producing hydrocarbons and higher alcohols. The process is originally developed by Franz Fischer and Hans Tropsch in early 1920s (Fischer & Tropsch, 1926), and is the key component of gas to liquid technology. The methanol can be utilized to produce alternative fuels by various of routes, such as methanol to dimethyl ether (DME), methanol-to-gasoline (MTG) and methanol-to-olefin (MTO) process.

Syngas production Syngas is produced through three principal processes:

1) Steam reforming of methane (SRM):

$$CH_4 + H_2 O \rightleftharpoons CO + 3H_2 \tag{r.1.1}$$

2) Carbon dioxide methane reforming or dry reforming of methane (DMR):

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$
 (r.1.2)

3) Partial oxidation of methane (POM):

$$CH_4 + 0.5O_2 \rightleftharpoons CO + 2H_2 \tag{r.1.3}$$

These three processes produce syngas with H_2/CO ratio of 1:3,1:1 and 1:2.

The first two reactions are highly endothermic and the partial oxidation reaction is slightly exothermic. The reforming process maybe followed by the exothermic water-gas shift reaction to adjust H_2/CO ratio:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
. (r.1.4)

The oxidation reaction and reforming reaction may be combined into a single process called autothermal reforming (ATR). In ATR, the exothermic oxidation reaction provides heat to the endothermic reforming process.

Steam reforming is a mature industry process and was first described by Tessie du Motay and Marechal in 1868 (Adris, Pruden, Lim, & Grace, 1996). High temperature (900 – 1200 K) and pressures (5 – 25 bar) is required to overcome thermodynamic limitation of the reaction and to achieve high methane conversion (Simpson & Lutz, 2007). Nickel-based catalyst is the most widely used SMR catalyst in industrial applications because of its abundance, low cost and high activity (Bharadwaj & Schmidt, 1995). However, Nickel-based catalyst also promotes the formation of coke and leads to quick deactivation of catalyst and reactor plugging. On an industrial scale, excess amount of steam is added to the feedstock to suppress carbon formation (Trimm, 1997). New problems then arise in practice: extra energy is required to provide heat for steam generation and the increase in H_2/CO ratio is not desired for the downstream process.

Comparing to the steam reforming process, the dry reforming process is also energy intensive and suffers long conversion time due to its endothermic feature. However, DMR has its own advantages: *i*) it consumes two greenhouse gases $(CH_4 \text{ and } CO_2)$ in to valuable syngas (Bradford & Vannice, 1999; Usman, Daud, & Abbas, 2015); *ii*) it provides an effective way to utilize low grade natural gas resource with high CO_2 content (Tang, Zhu, Wu, & Ma, 2014); *iii*) it provides a H_2/CO ratio of approximately unity, which can be used for the synthesis of long chain hydrocarbons or oxygenate chemicals (Arora & Prasad, 2016; Jang, Shim, Kim, Yoo, & Roh, 2019). The DRM is first thoroughly studied by Fisher and Tropsch in 1928 (Fischer & Tropsch, 1928) over *Ni* and *Co* catalyst and is found to have severe carbon formation. Although the DRM has been studied intensively in the past decades, it is not regarded as an industrially mature process. Coke deposition and sintering of the active metal quickly deactivates the catalysts (Rostrupnielsen & Hansen,1993; Muraza & Galadima, 2015).

Partial oxidation of methane to syngas process was first investigated in 1930's and 1940's (Liander, 1929; Prettre, 1946; Tsang, Claridge, & Green, 1995). POM is the only exothermic process converting methane to syngas and thus has thermodynamic and economic advantages over the SRM and DRM reaction (Bharadwaj & Schmidt, 1995; Balachandran et al., 1995). Large amount of expensive superheated stream is not required for POM reaction. Further, as shown in reaction (r.1.3), POM produces a H_2/CO ratio of 2 by stoichiometry, which is ideal for downstream processes, in particular methanol synthesis. However, downstream processing requirements cannot tolerate nitrogen (recycling with cryogenic separations is required), pure oxygen is therefore required (York, Xiao, & Green, 2003). When nearly pure oxygen is used, the reaction releases large amount of heat and hot-spot may occur in catalyst bed.

Other than these three principle syngas production processes, methane reforming with combinations of different processes are also studied: combined reforming of methane (DRM + SRM) (Gangadharan, Kanchi, & Lou, 2012), auto-thermal reforming of methane (SRM +POM) (Ayabe et al., 2003) and a combination of all three processes called tri-reforming of methane (TRM) (Song & Pan, 2004). These combined processes are developed to deal with different problems in industrial methane reforming process, such as the carbon formation, the H_2/CO and the greenhouse gas emission.

5

Direct conversion of methane

In the indirect methods of methane conversion, the production of syngas accounts for more than 60% of the capital cost and most of the energy consumption. Direct methods of methane conversion circumvent this expensive intermediate step and should have a distinct economic advantage over indirect methods (Holmen, 2009; Ma, Guo, Zhao, Scott, & Bao, 2013). Due to this reason, direct conversion of methane attracted enormous interest in both catalysis and reaction engineering areas. However, despite the extensive research efforts over the last decades, direct conversion of methane still requires improvements to be commercially successful.

The main challenge of direct utilization of methane comes from the methane activation step. Methane is a very stable molecule with perfect symmetry and poor coordinative ability. It contains no functional group, magnetic moment or polar distribution to facilitate chemical reactions. Methane is also the least reactive among all hydrocarbons, with very high C - H bond energies of 438.8 kJ/mol (Hammond, Conrad, & Hermans, 2012; Horn & Schlögl, 2015). Activation of methane by cleaving C - H bonds either requires high temperature or the presence of oxygen (or the combination of both). Although various of approaches are developed and proven, they all face several significant challenges:

1) thermodynamically limited conversion;

2) catalyst selectivity to desired products;

3) catalyst deactivation via carbon deposits (Karakaya & Kee, 2016).

Additionally, separation processes are still required in direct conversion of methane and will greatly increase the technical complexity and capital cost. The most important ones may be the downstream separation of useful products and the separation of oxygen from air for upstream processes (Fierro, 2011).
Non-oxidative conversion of methane When oxygen (oxidant) is absent, the activation of methane requires high temperature. Thermodynamically, the reactant methane is more stable than the other hydrocarbon products up to 1303 K but is less stable than carbon and hydrogen with temperature from 803 K (Guéret, Daroux, & 1997 Billaud). The conversion of methane is limited for temperature below 1473 K. Thermodynamic calculations also indicate that it is possible to produce ethylene, acetylene and benzene via methane cracking at high temperatures. Several approaches have been proposed and proven to achieve high selectivity towards different target products.

The decomposition of methane is an attractive way to produce CO_x free hydrogen. This process provides high quality hydrogen with simple gas product separation. The reaction is moderately endothermic, the energy required per mole of H_2 produced (+37.8 kJ/mol H_2) is much lower than that required by steam reforming (+63.3 kJ/mol H_2) (Navarro, Pena, & Fierro, 2007). However, this process produces a lower yield of hydrogen per carbon than SMR:

$$CH_4 \rightleftharpoons 2H_2 + C, \Delta H_B^0 = +75.6 \,\mathrm{kJ/mol}CH_4.$$
 (r.1.5)

Holmen et al. (Holmen, Rokstad, & Solbakken, 1976) revealed that the methane decomposition can produce acetylene as main product if the reaction can be stopped before carbon is formed. The carbon formation is avoided by using short reaction times and low partial pressure of methane (diluted by hydrogen). The formation of acetylene is favored (with yield > 85%) at extremely high temperature (2000 K) and reaction times of 10^{-2} s. While methane decomposition at high temperature involves complex gas phase radical reactions, the global reaction scheme may be described as follow (Olsvik & Billaud, 1994; Holmen, Olsvik, & Rokstad, 1995):

$$2CH_4 \rightleftharpoons C_2H_6 + H_2 \rightleftharpoons C_2H_4 + 2H_2 \rightleftharpoons C_2H_2 + 3H_2 \rightleftharpoons 2C + 4H_2.$$
 (r.1.6)

An alternative way to convert methane to C_2 hydrocarbons under nonoxidative condition is the two-step methane homologation. This process involves methane decomposition in the first step followed by hydrogenation of the surface carbonaceous species in the second step to obtain C_2 hydrocarbons. The process can be operated at much lower temperature with the presence of catalyst. Van Santen and co-workers (Koert & van Santen, 1991; Koerts, Deelen, & Van Santen, 1992) operated the process at two different temperatures. Methane was dissociatively adsorbed on silica-supported Group VIII transition-metal catalysts (Ru, Rh, Co) at 700 K followed by hydrogenation of the surfaces species at lower temperatures (373 K). A maximum yield of 13% towards C_2 products is obtained on a Ru catalyst. A parallel study was carried out by Amariglio and coworkers under isothermal conditions (Belgued, Pareja, A. Amariglio, & H. Amariglio, 1991). In the experiments, pure methane was flowing through a platinum catalyst at 523 K, then the adsorbed species were hydrogenated by a flow of H_2 at 523 K. In subsequent research, they obtained a maximum yield of 36.9% (on basis of adsorbed CH_4) towards C_2 products on Ru catalyst at 433 K (Belgued, H. Amariglio, Pareja, A. Amariglio, & Saint-Just, 1992).

Other than olefins, methane can also be converted to a mixture of aromatics like benzene, naphthalene, toluene etc. This process is referred to as methane aromatization (MA) or methane dehydroaromatization (DMA). The main reaction in DMA, the direct conversion of methane to benzene reaction is as

$$6CH_4 \rightleftharpoons C_6H_6 + 9H_2, \Delta H_B^0 = +531 \,\text{kJ/mol.}$$
 (r.1.7)

Similar to the high temperature methane pyrolysis, the methane dehydroaromatization under non-oxidative condition is thermodynamically unfavorable (Spivey & Hutchings, 2014). However, the reaction take places at much lower temperature compared to the thermal pyrolysis reaction and noticeable amounts of benzene can be formed at 973 - 1173 K (Mamonov et al., 2013). In 1993, Wang et al. (1993) pioneered the study of MDA reaction on ZSM-5 based catalyst. They reported a methane conversion of 7 - 8% and 100% selectivity to benzene with Mo modified ZSM-5 catalyst. A bifunctional mechanism of MDA over Mo/ZSM-5 catalysts is generally accepted for this reaction. In this mechanism, methane is activated at the transition metal ions forming a C_2H_x intermediate which is subsequently aromatized at the Brønstedt acid sites of the zeolite (Solymosi, Cserényi, Szöke, Bánsági, & Oszko, 1997; Wang, Lunsford, & Rosynek, 1997; Liu, Wang, Ohnishi, & Ichikawa, 1999). Many other bifunctional catalysts consisting of narrow pore zeolites and a metal oxide phase are studied since then (Xu, Bao, & Lin, 2003; Ma, Guo, Zhao, Scott, & Bao, 2013; Guo et al., 2014). Nowadays, the MDA processes is still attracting extensive research efforts. However, the studies are mainly at the laboratory level and the commercial process has not been implemented.

Oxidative conversion of methane Compared to the non-oxidative direct conversion of methane, oxidative conversion of methane eliminates thermodynamic limitation and should have distinct economic advantages. However, the product yields are generally small in a single-pass mode, due to the fast oxidation of the desired intermediate products. A large number of research studies have contributed to this route of methane utilization, including the development of suitable catalyst and new methods. Among all oxidative direct methane conversion processes, the oxidative coupling of methane and the partial oxidation of methane into oxygenates such as methanol and formaldehyde are the most attractive routes.

Partial oxidation of methane to methanol and formaldehyde may be represented as

$$CH_4 + 0.5O_2 \to CH_3OH(HCHO).$$
 (r.1.8)

The methane to methanol process can be carried out at high temperature and high pressure in the absence of a catalyst. Most results indicate a selectivity of 30 - 40% at a conversion 5 - 10% under the best conditions, i.e. temperatures of 723 - 773 K and pressures of 30 - 60 bar (Otsuka & Wang, 2001). High pressure plays an important role in providing the necessary conditions for chain branching. When oxygen is completely depleted, it has been shown that by increasing the pressure the formation of *CO* decreases and the selectivity of methanol increases (Holmen, 2009). *Fig.*1.2 shows typical *C*1-oxygenate selectivity – methane conversion plot (Tabata et al., 2002) for partial oxidation of methane in gas phase. The figure clearly shows that the selectivity to desired products cannot be viewed separated without examining the dependence on conversion levels. Any improvement in the direct conversion of methane to methanol must come from the enhancement of selectivity without reducing the conversion.

The presence of a solid catalyst seems to have no positive effect when the gasphase chain radical reactions are dominant at high pressures (Walker, Lapszewicz, & Foulds, 1994). However, the catalyst plays important role in obtaining yields by direct partial oxidation of methane at low pressures. Numerous studies have been reported to develop active and selective catalyst for this process (Spencer, 1988; Hargreaves, Hutchings, & Joyner, 1990; Berndt et al., 2000). In most of these studies, the reactions were carried out at temperature greater than 773 K and *HCHO* was the only oxidation product with a few percent yield. The studies on the direct partial oxidation of methane to methanol over solid catalysts have so far not been successful. The intermediate product CH_3OH would be quickly



Figure 1.2: Gas-phase partial oxidation of CH_4 from several studies (Tabata et al., 2002).

decomposed and oxidized into HCHO and CO_x by the active surface oxygen and at high temperatures. Thus, low temperature activation of methane is essential for direct conversion of methane into methanol.

Investigations on low temperature partial oxidation of methane to methanol can be dated back to 1970s, Shilov showed that the methane could be converted to methanol by Pt(II) and (IV) complexes (Holmen, 2009; Alvarez-Galvan et al., 2011). These complexes selectively oxidize methane to methanol but do not oxidize methanol to CO_x . After this pioneering work, Periana et al. (1993; 1998) further developed the process with Hg(II) catalyst (also with Pt(II) and Pt(IV)) and concentrated sulfuric acid to convert CH_4 to methyl bisulfate. The methyl bisulfate can be easily hydrolyzed to methanol. The complete cycle also requires the reoxidation of SO_2 to sulfuric acid:

$$CH_4 + 2H_2SO_4 \rightarrow CH_3OSO_3H + 2H_2O + SO_2,$$
 (r.1.9)

$$CH_3OSO_3H + H_2O \rightarrow CH_3OH + H_2SO_4$$
 and (r.1.10)

$$SO_2 + 0.5O_2 + H_2O \rightarrow H_2SO_4.$$
 (r.1.11)

These three reactions can be summed up to reaction (r.1.8). With Hg(II) complex, the selectivity to CH_3OSO_3H reached 85% with methane conversion of 50%, the reaction was carried out at 453 K and CH_4 pressure of 34.5 bar. With Pt(II) complex, the selectivity and conversion could be even higher with a slight increase in temperature. The main problem of this process comes from the use of H_2SO_4 . Separation of methanol from sulfuric acid, storage and regeneration of sulfuric acid will largely increase the cost of the process. Another attractive way of direct methane partial oxidation at low temperature is the methane monooxygenase catalysis. The methane monooxygenase (MMO) enzyme converts methane to methanol under ambient condition (Labinger, 2004). Several complexes have been proposed to mimic the chemistry of these enzymes (Otsuka & Wang, 2001).

1.2.2 Oxidative Coupling of Methane

Oxidative coupling of methane (OCM) is one of the most challenging but rewarding route of direct conversion of methane. The oxidative coupling of methane involves coupled heterogeneous and homogeneous reactions and converts methane mainly into C_2 (C_2H_4 , C_2H_6) hydrocarbon products. As discussed previously, activation of gas phase methane typically requires very high temperature even with the presence of a catalyst. Depending on the type of catalyst, oxidative coupling of methane generally take place at temperature from 950 K to 1200 K. Furthermore, by adding oxidant agent, the process eliminates the thermodynamic constraints

but becomes highly exothermic. These factors lead to several main drawbacks of OCM reaction: i) the yield towards C_2 products is low due to the nonselective oxidation of hydrocarbons; ii) the large amount of heat released at high temperatures results in significant difficulties in heat management, temperature control and process scale up; iii) the process would suffer severe mass transfer limitation and undesired nonoxidative reactions (pyrolysis and reforming of hydrocarbons).

The earliest systematic study of oxidative coupling of methane was reported by Keller and Bhasin in 1982 (Keller & Bhasin, 1982). They screened more than 20 metal oxides, supported on an α -alumina support under atmospheric pressure and temperatures of 773 K-1273 K. With sequential feeding of methane, nitrogen and oxygen, they found the oxides of Sn, Pb, Bi, Tl, Cd and Mn to be active and selective to formation of the C_2 products. In later studies, Hinsen and Baerns (Lee & Oyama, 1988) obtained high selectivity to C_2 hydrocarbons on similar metal oxides but with co-feed of methane and air. Ito and Lunsford (1985) demonstrated that lithium-doped magnesia(Li/MgO) was an active and selective catalyst for oxidative coupling of methane. They found that the Li^+O^- centres on MgO were active for formation of $\cdot CH_3$ radicals and reported a maximum yield of 19.4% to C_2 products. Other studies showed that the unprompted alkaline earth metal oxides are effective catalysts for oxidative dimerization of methane, they can be improved in their activity and selectivity when they are doped with alkali (Aika, Moriyama, Takasaki, & Iwamatsu, 1986; Moriyama, Takasaki, Iwamatsu, & Aika, 1986; Ito, Tashiro, Watanabe, Toi, & Ikemoto, 1987). Fang and Yeh (1981) first reported the formation of higher hydrocarbons by passing methane over a rare earth oxide (ThO_2/SiO_2) . Otsuka et al. then made systematic comparison of methane oxidative coupling over rare earth oxides (Otsuka, Jinno, & Morikawa, 1985). Lin et al. reported lanthanum oxide is very effective in the generation of gas-phase CH_3 radicals. The lanthanum oxide thus provides reasonable selectivity to C_2 products

under oxygen-limiting conditions. However, the catalyst also catalyzes complete oxidation of C_2H_6 (Lin, Campbell, Wang, & Lunsford, 1986). The transition metal oxides were also demonstrated to be effective for methane oxidative coupling, their performance can be significantly improved when promoted with alkali metal halides (Otsuka, Liu, Hatano, & Morikawa, 1986; Otsuka & Komatsu, 1987).

After these pioneering works, extensive investigations have been reported with catalyst screening for oxidative coupling of methane. The reported effective catalysts involve various types of catalytic materials and/or combinations of these materials (Hutchings, Scurrell, & Woodhouse, 1989; Amenomiya, Birss, Goledzinowski, Galuszka, & Sanger, 1990). Most of them may be grouped into the following categories: *i*) highly basic pure oxides, of which the early members of the lanthanide oxide series (excluding *CeO*) are the best; *ii*) Group *IA* or *IIA* ions supported on basic oxides (for example, Li/MgO, Ba/MgO and Sr/La_2O_3); *ii*) monophasic oxides; *iv*) a few transition metal oxides that contain Group IA ions; and *v*) any of these materials that are promoted with chloride ions (Lunsford, 1995). *Fig.*1.3 shows the reported catalyst with yield to C_2 products higher than 25%. After decades of study, the upper bound of C_2 product yield is still around 30%. Only a few types of catalysts are close to the target for industrial application of the OCM process: single pass conversions of methane of at least 30% and C_2 product selectivity of 80% (Zavyalova, Holena, Schlögl, & Baerns, 2011).

Other than the catalyst, the loss of C_2 selectivity is also due to the high oxygen concentration in gas phase. Low concentration of gas phase oxygen limits the conversion of methane but provides high C_2 selectivity. High concentration of gas phase oxygen is required to obtain a respectable level of methane conversion but leads to significant drop in C_2 selectivity. The desired intermediate products are more active than the deep oxygenates and thus subsequently oxidized by the extra oxygen. Furthermore, as mentioned previously, the large amount of heat released



Figure 1.3: Elemental compositions of OCM catalysts with $Y(C_2)25\%$ reported in the literature. All the catalysts were tested in a fixed-bed reactor in the co-feed mode under atmospheric pressure at temperatures from 943 to 1223 K, $p(CH_4)/p(O_2) = 1.7 - 9.0$, and contact times from 0.2 to 5.5 s (Zavyalova et al., 2011).

at high temperature is also a great challenge for the practical application of the OCM process. Due to these reasons, the catalyst design alone may not be able to yield the successful commercialization of OCM reaction. The catalyst development should be complemented by new concepts on the reactor and process design for suppressing the detrimental effect of high oxygen concentration. Most of laboratory experiments of OCM reaction were done in fixed bed reactors and with co-feed of methane and oxygen (or air). In the conventional fixed bed reactor, steep axial and radial temperature gradients could occur due to the strong exothermic feature

of the OCM reaction. In order to achieve isothermal condition, both the catalyst bed and the feed gas have to be largely diluted by inert materials. However, such dilutions are detrimental to economics (Mleczko & Baerns, 1995). Dautzenberg et al. (Dautzenberg, Schlatter, Fox, Rostrup-Nielsen, & Christiansen, 1992) suggested that both muti-tubular reactors and fluid bed reactors are technically feasible for OCM reaction depending on the target methane conversion and C_2 selectivity. However, large number of tubes is required in muti-tubular reactors and the catalysts must have stringent mechanical properties to scale-up the process with fluid bed reactors. All these drawbacks could greatly increase the capital cost of the OCM process. The performance of the fluid bed reactor was studied extensively with different catalysts (Edwards, Tyler, & White, 1990; Mleczko, Pannek, Niemi, & Hiltunen, 1996; Mleczko & Marschall, 1997). Most of these studies showed yield to C_2 product lower than 19.4% and the agglomeration of the catalysts was observed.

An alternative reactor concept which attracted increasing attention is the membrane reactor. In the conventional packed-bed reactor, methane and oxygen are provided either in cyclic mode or in co-feed mode. Whereas in the membrane reactors, CH_4 and O_2 are fed separately and the O_2 permeates through the membrane. The O_2 can be delivered along the length of the bed. According to the means of oxygen transport through the membrane to the methane reaction compartment, three different types of membrane reactors can be realized: oxygen molecule transport in pores, oxygen lattice diffusion, and oxygen ion conduction. The former uses porous membranes, whereas the latter two employ the dense solid oxide membranes (Liu, Tan, Li, & Hughes, 2001). By controlling the oxygen supply, the deep oxidation of the C_2 product can be suppressed. Theoretically, the dense solid oxide membrane reactors could provide high C_2 selectivity by avoiding the direct presence of gas phase oxygen (Wang & Lin, 1995; Kao, Lei, & Lin, 1997). The dense solid oxide membranes have received much more attention among the various

membranes (Liu et al., 2001; Karakaya & Kee, 2016). The study of membrane reactor, especially its application to the OCM reaction is still challenging. To achieve the theoretical high yield to C_2 hydrocarbons, the selected material has to satisfy several properties: *i*) enough oxygen permeation flux under the OCM conditions; *ii*) excellent phase structural stability, chemical stability and mechanical stability; *iii*) attractive catalytic performance for OCM (Wei, Yang, Caro, & Wang, 2013).

1.3 Objectives of thesis

As discussed in the introduction, the oxidative coupling of methane is a highly exothermic reaction occurring at high temperatures. Commercialization of OCM requires both catalyst development and investigations dealing with reaction engineering aspects. When the temperature is not high enough, the gas phase methane can hardly be activated and the reaction will yield low conversion. On the other hand, when the temperature is too high, the undesired deep oxidation reactions and other side reactions like reforming and water gas shift reaction become significant. All these factors could result in the loss of C_2 product selectivity. The OCM reaction is thus very sensitive to the reaction temperature range. Temperature control and heat management issues are very challenging for the OCM process. Further, the OCM reaction is also sensitive to the space time. The undesired endothermic reactions such as pyrolysis and reforming of hydrocarbons can dominate at high space times.

The exothermic nature of OCM also leads to strong bifurcation or ignitionextinction behavior of the system. Fig.1.4 shows one of the experimentally observed ignition-extinction behavior of catalytic OCM reaction on La - Ce catalyst (Sarsani, West, Liang, & Balakotaiah, 2017). As the furnace temperature is gradually increased, the reacting system suddenly jumps to an ignited branch with high conversion and selectivity at the ignition point. When the furnace temperature is gradually decreased from high values, this ignited branch can be largely extended to low furnace temperatures with the other operating conditions remaining unchanged. The system will be quenched at the extinction point. In the region between the ignition and the extinction points, two stable steady state branches (and an unstable middle branch) coexist at the same furnace temperature. In this region of multiple steady state (or region of multiplicity), we can obtain high C_2 selectivity and reactant conversion with low furnace temperature and/or low space time. This idea provides us an alternative way to operate the OCM reaction in the conventional packed-bed reactors, that is, control the catalyst temperature by the high velocity, low temperature feed. The complex and expensive external heat manage system is thus not required. This type of operation mode is called autothermal operation. The concept of autothermal operation has already been applied successfully in my industrial processes. A detail discussion of autothermal operation is provided in chapter 5.

Obviously, the key point of autothermal operation is to identify the region of multiplicity or the location of the ignition and extinction points. Therefore, the main objective of this thesis is to present a comprehensive bifurcation analysis of gas phase and catalytic OCM reaction by numerical modeling of the OCM reaction in various reactor types. The impact of operating parameters (space time, feed temperature and composition, heat exchange to the environment) and catalyst bed design parameters (bed aspect ratio, heat and mass dispersion, inert section, catalyst activity, inter-phase heat and mass transfer, internal or pore diffusion and so on) on the ignition-extinction behavior and C_2 product selectivity are studied systematically. In the next chapter, we present an analysis of thermodynamic aspect of OCM reaction, including the equilibrium constraints under isothermal and adiabatic conditions and the adiabatic temperature rise of various reactions in the OCM. In chapter 3, we develop and validate a global kinetic model with minimum number of



Figure 1.4: Ignition and extinction behavior of La - Ce oxide powder catalyst (10 mg) in a 4 mm i.d. reactor; with 1 mm catalyst bed height, 14 ms space time, $CH_4/O_2 = 4$. (a) Oxygen conversion (b) C_2 product selectivity (Sarsani et al., 2017).

reactions for gas phase OCM. The kinetic model is then used to analyze ignitionextinction behavior of gas phase OCM in different types of ideal reactor models. In chapter 4, we analyze the ignition-extinction behavior of general catalytic partial oxidation reactions in laboratory scale packed bed reactors. The impact of heat loss, catalyst properties and bed aspect ratio on the region of autothermal operation is also studied. In chapter 5, we present ignition-extinction analysis of catalytic OCM, with emphasis on the product distribution and scale-up issues. In the last chapter, we summarize the main conclusions of this thesis and recommend some topics for future work.

Chapter 2

Thermodynamic Aspects of Oxidative Coupling of Methane

2.1 Thermodynamics of Dehydrogenation, Water-Gas Shift and Reforming Reactions

It is of interest to note some thermodynamic aspects of the reversible dehydrogenation and shift reactions, specifically the temperature above which these reactions are favored, i.e. the temperature at which the Gibbs free energy changes from positive to negative. While reactions with negative Gibbs free energy changes are are still limited by the kinetics, those with positive Gibbs free energy changes are unlikely to occur to any appreciable extent. The transition temperature is listed in *Table* 2.1 for various dehydrogenation/pyrolysis and reforming reactions [The reactions marked in bold font are those included in the kinetic scheme while others are reactions of interest but are not independent]. The following observations can be made from the numbers in *Table* 2.1: (*i*) steam reforming of C_2 hydrocarbons is favored at much lower temperatures than that of methane, (*ii*) steam reforming of methane is favored at temperature above 894 K, (*iii*) ethane cracking (ethylene formation) is favored in the temperature range 1066 - 1393 K, and (*iv*) acetylene formation is favored at temperatures above 1393 K.

2.2 Adiabatic Temperature Rise for Oxidation Reactions

The adiabatic temperature rise is an important factor in the design and scaleup of large scale OCM reactors. For a single step oxidation in which oxygen is the limiting reagent (and nearly constant or using average physical properties), the adiabatic temperature rise may be expressed as

$$\Delta T_{ad} = \frac{(-\Delta H_R^0) y^{in}}{\langle C_p \rangle (-\nu_i)}.$$
(2.1)

r					
Pyrolysis/Dehydrogenation Reactions					
$2CH_4 \leftrightarrow C_2H_6 + H_2$	1488K				
$2CH_4 \leftrightarrow C_2H_4 + 2H_2$	1570K				
$\mathbf{2CH}_4 \!\! \leftrightarrow \mathbf{C}_2\mathbf{H}_2 \!+\! \mathbf{3H}_2$	1483K				
$\mathbf{C}_{2}\mathbf{H}_{4}\!\!\leftrightarrow\mathbf{C}_{2}\mathbf{H}_{2}\!+\!\mathbf{H}_{2}$	1393K				
$\mathbf{C}_{2}\mathbf{H}_{6}\!\!\leftrightarrow\mathbf{C}_{2}\mathbf{H}_{4}\!+\!\mathbf{H}_{2}$	1066K				
Hydrocarbon Reforming Reactions					
$\mathbf{CH}_4 + \mathbf{H}_2\mathbf{O} \leftrightarrow \mathbf{CO} + \mathbf{3H}_2$	894K				
$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	916K				
$C_2H_6 + 2H_2O \leftrightarrow 2CO + 5H_2$	751K				
$C_2H_4 + 2H_2O \leftrightarrow 2CO + 4H_2$	632K				
$C_2H_2 + 2H_2O \leftrightarrow 2CO + 3H_2$	165K				
Water-Gas Shift Reaction					
$\mathbf{CO} + \mathbf{H}_2\mathbf{O} \leftrightarrow \mathbf{H}_2 + \mathbf{CO}_2$	1084K				

Table 2.1: Temperature at which Gibbs free energy of reversible reactions changes sign

where ΔH^0_R is the heat of reaction per mole of extent, y^{in} is mole fraction of the limiting reactant (oxygen) in the feed, $\langle C_p \rangle$ is the average molar specific heat of the reaction mixture and ν_i is the stoichiometric coefficient of the limiting reactant. For the more general case of single or multiple reactions with varying physical properties, ΔT_{ad} can be calculated using standard methods. Assuming that the feed contains only methane and oxygen (and no inert diluent), Table 2.2 shows ΔT_{ad} at three different feed temperatures (T^{in}) for selected oxidation reactions and also the coupled system at equilibrium. The following may be observed from this table: (i)for a fixed CH_4/O_2 ratio, the adiabatic temperature rise decreases with increase in the feed temperature, which implies that thermal effects are moderated at higher feed temperatures (i.e. the temperature sensitivity of the process is reduced at higher feed temperatures). This is due to the fact that gas heat capacities increase with temperature (*ii*) the equilibrium adiabatic temperature rise (ΔT_{ad}^E) is much smaller compared to that when oxidation chemistry dominates. This result implies that in an open flow reactor, the temperature rise at intermediate space times could be much higher than that at equilibrium (or at large space times) (iii) for low feed

	System							
$(1)CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$								
$(2)CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$								
$(3)CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O$								
$(E)CH_4 + xO_2 \rightarrow CO, CO_2, H_2O, H_2, C_2H_6, C_2H_4, C_2H_2$								
$T^{in}(K)$	CH_4/O_2	2	3	4	5	6	8	12
300	$\Delta T^1_{ad}(K)$	2075	1585	1305	1120	988	808	604
	$\Delta T^2_{ad}(K)$	1925	1446	1186	1015	892	726	539
	$\Delta T^3_{ad}(K)$	1077	1132	1152	1045	892	729	544
	$\Delta T^E_{ad}(K)$	728	644	603	574	550	511	452
900	$\Delta T^3_{ad}(K)$	933	867	870	782	670	523	366
	$\Delta T^E_{ad}(K)$	301	193	152	126	107	82	55
1200	$\Delta T^3_{ad}(K)$	750	774	772	720	618	476	328
	$\Delta T^E_{ad}(K)$	243	133	85	57	37	9	-22

Table 2.2: Adiabatic temperature rise for selected oxidation reactions and coupled system

temperatures (300 K), the dimensionless activation energy $\gamma = E/RT^{in} \sim 90$ while the dimensionless adiabatic temperature rise $\beta = \Delta T_{ad}/T^{in}$ is in the range 1 to 7 and hence the Zeldovich number, $B = \gamma \beta/(1 + \beta)$ is very high (> 40), which indicates a wide hysteresis region (or large region of multiple solutions). For higher feed temperatures and methane to oxygen ratio, the Zeldovich number is lower (and could even be negative) and the hysteresis region may be narrow or may not exist. Thus, the magnitude of *B*, which depends both on the methane to oxygen ratio and the feed temperature, is very important in determining the bifurcation behavior.

2.3 Equilibrium Compositions

While autocatalytic reaction systems, such as the present one, display complex bifurcation behavior (ignition, extinction and various types of spatio-temporal patterns) when operated far from equilibrium, their behavior approaches the so called *flow branch* for space time $\tau \rightarrow 0$ and the *thermodynamic branch* for $\tau \rightarrow \infty$. The flow branch simply corresponds to the exit conditions that are not substantially different from the inlet conditions while the thermodynamic branch corresponds to text conditions that are not substantially different from that are not substantially different from equilibrium values. Thus, it

is of interest to know the equilibrium composition for various methane to oxygen ratios under isothermal as well as adiabatic conditions. The isothermal equilibrium conditions are useful in interpreting the laboratory scale data while the adiabatic conditions are of interest in the simulation of large scale reactors.

The fraction conversion of methane or oxygen are given by:

$$\begin{split} \chi_{_{CH_4}} &= \ \frac{F_{CH_4}^{in} - F_{CH_4}^{exit}}{F_{CH_4}^{in}} \\ \chi_{_{O_2}} &= \ \frac{F_{O_2}^{in} - F_{O_2}^{exit}}{F_{O_2}^{in}}. \end{split}$$

The selectivity and yield for product j are based on methane and are defined by following equations, n_j and m_j are number of carbon and hydrogen atoms in product *j*.

For hydrocarbon products, *CO* and *CO*₂:

$$S_{j,CH_4} = \frac{n_j (F_j^{exit} - F_j^{in})}{F_{CH_4}^{exit} - F_{CH_4}^{in}}$$
$$Y_{j,CH_4} = S_{j,CH_4} \cdot \chi_{CH_4}$$

For H_2 and H_2O

$$S_{j,CH_4} = \frac{m_j(F_j^{exit} - F_j^{in})}{4(F_{CH_4}^{exit} - F_{CH_4}^{in})}.$$

Fig.2.1 shows the isothermal equilibrium calculations for molar ratio $CH_4/O_2 =$ 4 and P = 1 bar (These calculations as well the adiabatic calculations described below were made using the code of McBride and Gordon (1996)). In these calculations, the C_3 and other hydrocarbon products are not included because their yields are very small at P = 1 bar and the temperature range of interest (since O_2 is the limiting reactant, its equilibrium fraction is zero). From the results in Fig.2.1, it may be observed that the oxidation chemistry dominates the path to equilibrium for $T <\sim 1200$ K while the reforming and dehydrogenation chemistries dominate at higher temperatures (as can be expected intuitively). Also, for T < 1200 K, the primary products are those of partial and deep oxidation (CO, CO_2 and H_2O), while at much higher temperatures (T > 1800 K) the products are those of partial oxidation and pyrolysis (CO and C_2H_2). It is also of interest to note that the equilibrium yield of ethylene goes through a maximum at an intermediate temperature. The selectivity towards C_2 products increases while the CH_4 conversion decreases as CH_4/O_2 ratio increases, as shown in Fig.2.2. A maximum ethylene selectivity around 19% is obtained at 1300 K with CH_4/O_2 ratio of 8 under isothermal equilibrium condition. The products at high temperatures (T > 1800 K) are still those of partial oxidation and pyrolysis (CO and C_2H_2), but the the selectivity towards C_2H_2 is much higher comparing to the case with lower CH_4/O_2 ratios.

*Fig.*2.3 and 2.4 show the adiabatic equilibrium temperature and composition for two different methane to oxygen feed molar ratios (2 and 4) as a function of initial/feed temperature. First, we note that for $CH_4/O_2 = 2$, the adiabatic temperature rise is always positive for all inlet temperatures that are in the range of interest (300 to 2000 K). Second, the highest adiabatic temperature rise (~ 728 K) occurs at the lowest feed temperature of 300 K (which is the specific heat effect mentioned earlier) and the equilibrium adiabatic temperature rise reaches a nearly constant value (in this case about 240 K) at higher feed/inlet temperatures. Third, the equilibrium methane conversion increases monotonically with the feed temperature and reaches near 100% at about 1200 K with the main equilibrium products being *CO* and *H*₂. Fourth, no significant amount of *C*₂ products are predicted at equilibrium for the entire range of feed temperatures considered. Thus, the observation of any *C*₂ products will be purely a kinetic effect. [Remark: It may be



Figure 2.1: Equilibrium CH_4 conversion (dotted lines), selectivity to various products (solid lines) for isothermal operation at 1 *bar* (carbon/graphite formation excluded), $CH_4 : O_2 = 4$.

shown that exothermic effects dominate and the behavior shown in Fig.2.3, where the isothermal and adiabatic lines never intersect, persists for any $CH_4/O_2 < 2.3$.]

When $CH_4/O_2 = 4$, the equilibrium adiabatic temperature rise can be either positive or negative depending on the feed temperature (*Fig.2.4*). In this case, the adiabatic temperature line may be divided into three segments. In the first segment (which spans the inlet temperature range 300 to ~ 900 K), exothermic effects dominate and the equilibrium products are primarily those of oxidation. In the second segment, which spans from 900 K to the crossover point of the isothermal and adiabatic lines at $T^{in} \approx 1350$ K, exothermic effects still dominate but pyrolysis and



Figure 2.2: Equilibrium CH_4 conversion (dotted lines), selectivity to various products (solid lines) for isothermal operation at 1 *bar* (carbon/graphite formation excluded), $CH_4 : O_2 = 8$.

reforming reactions also occur so that the equilibrium adiabatic temperature rise is small. In the third segment ($T^{in} > 1350$ K), only endothermic pyrolysis and reforming reactions dominate and the adiabatic temperature rise is negative. It may be shown that this qualitative behavior of the equilibrium compositions persists for all higher methane to oxygen ratios. When CH_4/O_2 ratio further increases from 4 to 8, the crossover point of the isothermal and adiabatic lines moves to lower feed temperature ($T^{in} \approx 1218$ K), as shown in Fig.2.5. This is due to the smaller equilibrium adiabatic temperature rise at higher CH_4/O_2 ratios (also shown in Table 2.2). Sim-



Figure 2.3: Equilibrium CH_4 conversion (dotted lines), temperature (dashed lines) and selectivity to various products (solid lines) for adiabatic operation at 1 bar (carbon/graphite formation excluded), $CH_4 : O_2 = 2$.

ilar to the cases under equilibrium isothermal condition, the selectivity towards C_2 products also increases with increasing CH_4/O_2 ratio under equilibrium adiabatic condition. However, high selectivity towards C_2 products can hardly be obtained under equilibrium condition. High selectivity towards acetylene together with high methane conversion may be obtained from the endothermic pyrolysis reactions at extremely high temperatures (> 1900 K) with high CH_4/O_2 ratio.



Figure 2.4: Equilibrium CH_4 conversion (dotted lines), temperature (dashed lines) and selectivity to various products (solid lines) for adiabatic operation at 1 bar (carbon/graphite formation excluded), $CH_4 : O_2 = 4$.



Figure 2.5: Equilibrium CH_4 conversion (dotted lines), temperature (dashed lines) and selectivity to various products (solid lines) for adiabatic operation at 1 *bar* (carbon/graphite formation excluded), $CH_4 : O_2 = 8$.

Chapter 3 Analysis of Oxidative Coupling of Methane without Catalyst

3.1 Preamble

In this chapter, we present a detailed bifurcation analysis of methane oxidative coupling in the gas phase using a global kinetic model for the various oxidation, reforming and dehydrogenation reactions. The kinetic model satisfies the thermodynamic constraints and is validated with literature data as well as new data obtained under near isothermal conditions. It is used to determine the methane conversion and C_2 products selectivity under various feed and operating conditions in large scale ideal adiabatic reactors. It is found that at higher CH_4/O_2 ratios (e.g. > 4), ignition and extinction points exist only at either high feed temperatures and/or space times, which may not be of practical interest. Autothermal operation on the ignited branch with feed at near ambient conditions (~ 300 K and 1 bar) is feasible for practical range of space times (1 ms to 1 s) only for low CH_4/O_2 ratios (e.g. 1.7 to 2.5), which includes the flammability range. Further, the best ethylene yields are obtained on the ignited branch close to the extinction point while best C_2 yields may be obtained at higher space times or feed temperatures. Feeds with a high CH_4/O_2 ratio lead to higher selectivity of C_2H_4 but lower methane conversion and require higher inlet temperatures. The ratio C_2H_4/C_2H_2 decreases as the methane conversion increases or CH_4/O_2 ratio decreases. While oxidation (exothermic) chemistry dominates on the ignited branch near the extinction point, the dehydrogenation and reforming (endothermic) chemistries dominate as the space time or feed temperature is increased. It is shown that the highest yield of intermediate products and largest region of autothermal operation is obtained for an ideal reactor with perfect thermal back-mixing and zero species back-mixing

(lumped thermal reactor model).

This chapter is organized as follows. In the next section, we outline our approach and briefly discuss the works in kinetic modeling and reactor simulation of the OCM process. In section 3.3, we present a global kinetic model for OCM that includes various oxidation, dehydrogenation and reforming reactions. We also validate the kinetic model with literature data as well as new data obtained under near isothermal conditions. In section 3.4, we consider various ideal adiabatic homogeneous reactor models CSTR, PFR and lumped thermal reactor (LTR) and present a detailed bifurcation analysis. The main goal of our analysis is to determine the methane conversion and yields of various C_2 products (ethane, ethylene and acetylene) and how these vary with the feed composition, operating conditions (inlet temperature and space time) and the reactor type. The results of our investigations are summarized in the last section.

3.2 Global and Micro-kinetic Models

Direct conversion of methane to C_2 hydrocarbon products, especially ethylene or acetylene, has been investigated extensively in the past both experimentally and theoretically through kinetic modeling and reactor simulations. As discussed in the first chapter, one such process is by pyrolysis (non-oxidative thermal coupling) of methane. This approach, however, has the requirement of heat supply at high temperature to drive the highly endothermic pyrolysis reactions (Holmen et al., 1995), as demonstrated in the previous section. Another process, which received considerable attention, is the thermal oxidative coupling of methane (OCM). Early efforts indicated that partial oxidation of methane to C_2 products requires high operating temperatures and suffers from low yield to useful products. Efforts were then made to overcome these limitations by a variety of catalyst designs (Keller et al., 1982; Ito et al., 1985; Aika et al., 1986; Sofranko, Leonard, & Jones, 1987). Meanwhile, investigations were also conducted focusing on the role of pure gas phase reactions in OCM chemistry. Lunsford and co-workers proposed that a homogeneous coupling of methyl radicals occurs (Driscoll, Martir, Wang, & Lunsford, 1985) and confirmed that at least 40% to 45% of ethane produced can be accounted for by this gas phase reaction (Campbell, Morales, & Lunsford, 1987). Nelson and co-workers then suggested that ethylene is produced dominantly by gas phase conversion of ethane (Nelson, Lukey, & Cant, 1988) while the deep oxidation of C_2 products is an important source of carbon oxides for temperatures above 1013 K (Nelson & Cant, 1990). They used a series of isotopic studies based on MIESR (matrix isolation electron spin resonance). Based on these early studies, it was clear that gas phase reactions play an important role in the formation of main carbon products in partial oxidation of methane. In related studies, Lane and Wolf (1988) reported significant gas phase oxidative coupling with pure homogeneous reactions only by adjusting the operating conditions. Fujimoto et al. were able to enhance the yield to C_2 hydrocarbon products in gas phase by varying pressure and temperature as well as an oxidizing agent (Asami, Omata, Fujimoto, & Tominaga, 1988). These achievements also suggested that a detailed study of gas phase OCM reactions, and subsequently on reactor design can be utilized to improve methane oxidative coupling process.

Parallel studies were done for kinetic modeling and reactor simulations, most of which were based on micro-kinetic models with hundreds of elementary reactions. Zanthoff and Baerns (1990) first proposed a simplified kinetic reaction scheme with 164 steps and 28 species, Chen et al. were then able to reduce the number of elementary reactions to 33 (Chen, Hoebink, & Marin, 1991). Other proposed kinetic schemes, Geerts et al. (Geerts, Chen, Van Kasteren, & Van Der Wiele, 1990) and Mackie et al. (Mackie, Smith, Nelson, & Tyler, 1990) included similar number of reactions. Recently, Metcalfe et al. (Metcalfe, Burke, Ahmed, & Curran, 2013) further developed and validated the micro-kinetic models for gas phase hy-

drocarbon combustion. There are two main advantages of a correctly developed micro-kinetic model: (i) thermodynamic consistency is built into the model, by regarding all reactions as reversible and then specifying rate constants in only one direction; (ii) the kinetic parameters can be estimated from theory. We have chosen a different approach. We have developed the smallest possible global reaction mechanism that is consistent with the limited experimental data. We have built consistency with thermodynamics in the same manner as used in micro-kinetic modeling. We have then fitted the kinetic parameters in one direction only using published and our own experimental data. We have limited the complexity of our model in order to focus our attention on the bifurcation analysis (ignition, extinction, and hysteresis behavior) and the potential for autothermal operation under adiabatic conditions. With this approach we have obtained the advantage of built-in thermodynamic consistency, while also achieving kinetic time scales that are consistent with the experimental kinetic data. It should also be pointed out that most of the earlier studies dealing with gas phase chemistry were restricted to reactor simulations for isothermal operation. Very few prior studies presented a complete bifurcation analysis (ignition, extinction and hysteresis behavior) of the gas phase OCM process, especially in large scale reactors, whose operation may be close to adiabatic conditions.

It is generally accepted that gas phase reactions may become significant in OCM when the temperature exceeds about 700 °C (973 K) but certainly important and may be even dominant for temperatures above 900 °C (1173 K). Since the oxidation reactions occurring in OCM are highly exothermic leading to adiabatic temperature rise of 300 to 1500 K (depending on the methane to oxygen ratio in the feed and dilution), a detailed understanding of the catalytic OCM also requires an understanding of the contribution of the gas phase chemistry to the overall process. These reasons, i.e. lack of prior literature on the bifurcation behavior of

gas phase OCM and this understanding being the pre-requisite for catalytic OCM, are the main motivations for this chapter of thesis.

3.3 Validation of Kinetic Model

In this section, we describe briefly the kinetic model used, the laboratory scale experimental conditions and data, validation of the model and the various characteristic times.

3.3.1 Reaction Scheme

As stated in the introduction, while detailed models consisting of many molecular as well as free radical species and several hundred reaction steps have been proposed for gas phase OCM, such models are not used here due to lack of data for validation. Here, we assume that the feed to the reactor consists of only methane and oxygen and limit the product stream to only C_2 species and oxidation products, i.e. we consider only the nine gas phase molecular species $(CH_4, O_2, CO, CO_2, C_2H_6, C_2H_4, C_2H_2, H_2, H_2O)$. Limiting to only steady-state and equilibrium calculations, a minimum of six independent global reactions need to be considered among these 9 species. We use a global reaction/kinetic scheme consisting of three groups of reactions as follows:

(*i*) Parallel oxidation reactions

$$2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O, \Delta H_R^0 = -42.26 \text{ kcal/mol},$$
 (r.3.1)

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O, \ \triangle H_R^0 = -67.38 \text{ kcal/mol}, \quad (r.3.2)$$

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O, \ \triangle H_R^0 = -124.1 \text{ kcal/mol and}$$
 (r.3.3)

$$CO + 0.5O_2 \rightarrow CO_2, \ \triangle H^0_R = -67.64 \text{ kcal/mol.}$$
 (r.3.4)

(ii) Dehydrogenation/Pyrolysis reactions

$$2CH_4 \implies C_2H_2 + 3H_2, \ \triangle H_R^0 = 89.94 \text{ kcal/mol},$$
 (r.3.5)

$$C_2H_6 \implies C_2H_4 + H_2, \ \triangle H_R^0 = 41.69 \ \text{kcal/mol and}$$
 (r.3.6)

$$C_2H_4 \rightleftharpoons C_2H_2 + H_2, \ \Delta H_R^0 = 32.77 \text{ kcal/mol.}$$
 (r.3.7)

(iii) Reforming /Shift reactions

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2, \Delta H_R^0 = 49.37 \text{ kcal/mol and}$$
 (r.3.8)

$$H_2 + CO_2 \rightleftharpoons CO + H_2O, \Delta H_R^0 = 9.84 \text{ kcal/mol.}$$
 (r.3.9)

We note that the last six of these reactions form an independent set and are sufficient to describe the observed equilibrium (and steady-state) compositions. However, we have included the three competing parallel primary oxidation reactions (r.3.1 to r.3.3) so that there is some flexibility in predicting the product selectivities, especially at short space times when oxidation chemistry dominates. [Remarks:(a) As we show in the next section, reaction r.3.2 may be dropped without impacting any of the results qualitatively as its rate is negligible compared to the two primary competing paths/oxidations leading to C_2H_6 and CO (b) We have neglected the carbon/graphite forming reactions which limits the range of applicability of the model to lower values of methane to oxygen ratio and lower temperatures].

The form of the global rate equations used for the last five (reversible reactions) is selected so that the thermodynamic constraints are satisfied. The form of the rate equations and kinetic constants for the oxidation reactions were taken from the combustion literature (Westbrook & Dryer, 1981, 1984) and minor adjustments were made based on experimental data on carbon selectivity at low methane and oxygen conversions. A similar approach was followed for dehydrogenation (pyrol-ysis) and shift (reforming) reactions.

Reaction	Frequency	Activation	Kinetic
#	factor $k_0(s^{-1})$	energy E_i/R	expressions
<i>r</i> .1	1.3×10^{9}	25740K	$k_1 \cdot y_{CH_4}^{1.5} \cdot y_{O_2}^{0.75}$
r.2	2.5×10^8	33900K	$k_2 \cdot y_{CH_4}^{1.5} \cdot y_{O_2}^{1.5}$
r.3	7×10^8	24385K	$k_3 \cdot y_{CH_4}^{-0.3} \cdot y_{O_2}^{1.3}$
r.4	2.1×10^9	25500K	$k_4 \cdot y_{CO} \cdot y_{O_2}^{0.5}$
r.5	1.5×10^{13}	44022K	$k_5 \cdot (y_{CH_4}^2 - y_{C_2H_2} \cdot y_{H_2}^3 / K_{eq}^5)$
<i>r</i> .6	4.65×10^{12}	32800K	$k_6 \cdot (y_{C_2H_6} - y_{C_2H_4} \cdot y_{H_2}/K_{eq}^6)$
<i>r</i> .7	1.8×10^{13}	38249K	$k_7 \cdot (y_{C_2H_4} - y_{C_2H_2} \cdot y_{H_2}/K_{eq}^7)$
<i>r</i> .8	7.5×10^8	24056K	$k_8 \cdot (y_{CH_4} \cdot y_{H_2O} - y_{CO} \cdot y_{H_2}^3 / \tilde{K}_{eq}^8)$
<i>r</i> .9	4.5×10^8	29830K	$k_9 \cdot (y_{CO_2} \cdot y_{H_2} - y_{CO} \cdot y_{H_2O} / K_{eq}^9)$

Table 3.1: Values of kinetic parameters and rate expressions used in the nine reactions global kinetic model

3.3.2 Kinetic Model

Since the data reported here as well as most of the literature kinetic data were limited to a pressure of 1 bar, the kinetic model (as well as all other calculations presented) will be limited to P = 1 bar. For convenience, we choose to use mole fractions (which are equivalent to partial pressures at 1 bar) to express the reaction rates. As stated in the previous section, if the oxygen mole fraction at equilibrium is assumed to be zero, the last five reversible reactions describe the equilibrium composition. Thus, mass action kinetics that is consistent with equilibrium constraints is used to describe the kinetics of the dehydrogenation and reforming reactions, i.e. only the forward rate constants are fitted for these reactions. The rate expressions for the oxidation reactions are taken from the combustion literature, which were determined under fuel rich conditions. The initial values of various rate constants were taken from the combustion and pyrolysis literature and then were optimized to fit the laboratory scale data on OCM obtained in the literature as well as data obtained by us.

Table 3.1 lists the kinetic parameters for the nine reaction scheme. It should be noted that all the rate constants are assumed to be of Arrhenius form and having units of s^{-1} . The temperature dependence of the various equilibrium constants is

calculated using following equations:

$$\Delta H_R^i(T) = \Delta H_R^{i,0}(T) + \int_{298.15}^T \Delta C p_i dT$$

$$\Delta S_R^i(T) = \Delta S_R^{i,0}(T) + \int_{298.15}^T \frac{\Delta C p_i}{T} dT$$

$$\Delta G_R^i(T) = \Delta H_R^i(T) + T \Delta S_R^i(T)$$

$$K_{eq}^i = \exp(-\frac{\Delta G_R^i(T)}{RT}).$$

The calculated results are plotted in Fig.3.1. A few comments are in order. The rate expressions for the two-step methane combustion reactions r.3.3 and r.3.4 are taken from Westbrook and Dryer (1981) and the optimization procedure made only minor adjustments to the numerical values (1984). The reaction orders in the rate expressions for reactions r.3.1 and r.3.2 were assumed and optimized to fit the selectivity data at low oxygen conversions. The global rate expressions for reactions r.3.5, r.3.6 and r.3.7 predict with reasonable accuracy the methane pyrolysis data (in the temperature range 1200 to 1800 K) when there is no carbon/graphite formation (Olsvik, Rokstad, & Holmen, 1995; Sundaram & Froment, 1977; Robertson & Hanesian, 1975). The forward rate constants and activation energies of the reforming reactions r.3.8 and r.3.9 were also taken from the literature and only minor adjustments were made to fit the CO and CO_2 selectivities. Thus, the scheme of the Table 3.1 is the simplest consistent global kinetic model for gas phase OCM.

3.3.3 Experimental System

The experimental data are obtained with reactor set up as shown in Fig. 3.2(a). The reactor consists of a quartz (or alumina) tube with a small diameter (3 or 4 mm in most experiments). In some experiments, it is filled with quartz chips in the reaction zone, in order to enhance radial conductivity and minimize the radial temperature gradient. The length of reactor that is placed in the furnace is about



Figure 3.1: Equilibrium constant values for reversible reactions used in the simulation.

15 cm (6 in) with a similar length for the fore and after sections. The fore and after sections are heated to a lower temperature than the reaction section. A typical temperature profile of the entire section with furnace set at 750 °C is shown in *Fig.* 3.2(b). [Remark: All the experimental data reported here was obtained at SABIC Technology Center, Sugarland, Texas. This was a collaborative project between University of Houston and SABIC]

The reactor tube is heated to a desired temperature by flowing inert gas (Neon). Methane and oxygen are then co-fed into the reactor tube and the exit gases are routed through a genie membrane filter to condense and separate water before being analyzed by a Micro GC (Agilent). The temperature of the furnace is measured with a thermocouple placed at the middle of each zone. In most of our experiments, the reactor's temperature is in the range 1000 K to 1250 K and the space time is in the range 0.1 s to 0.8 s. The Reynolds number of gas mixture based on



Figure 3.2: Schematic diagram of experiment set up showing the fore, reactor and after section (a). Temperature profile along the tube with furnace temperature at $750^{\circ}C$ (b).

the empty tube diameter is of the order of 10, so the flow in the tube is laminar.

Under our experimental conditions, the characteristic heat removal (loss) time is estimated using the expression (Balakotaiah & West, 2014):

$$\tau_h = \frac{0.25d_t C_{pv}(T)}{U},$$
(3.1)

where d_t is the inside tube diameter. In computing τ_h , the specific heat of the methane is used as an approximation to the volumetric heat capacity of the reaction mixture $C_{pv}(T)$. The overall heat transfer coefficient U is calculated based on heat transfer inside the tube, wall conductivity and convective as well as radiative heat transfer from the tube exterior to the furnace (Sarsani et al., 2017):

$$\frac{1}{U} = \frac{1}{h_i} + \frac{d_t}{2k_w} Ln(1 + \frac{2\delta_w}{d_t}) + \frac{d_t}{(d_t + 2\delta_w)} \frac{1}{h_o},$$
(3.2)

where $\delta_w(k_w)$ is wall thickness (conductivity), $h_i(h_o)$ is the heat transfer coefficient

inside (outside) the wall. Heat transfer coefficient within the tube is calculated by equation 3.3 or 3.4 where d_p is the average quartz chip diameter. In these computations, the conductivity of methane (k_f) is used to approximate the heat conductivity of gas mixture. The Nusselt number in an empty tube (Nu_0^T) is estimated using asymptotic values in the literature (Gundlapally & Balakotaiah, 2011), while Nusselt number in a tube filled with quartz chips (Nu_0^p) is calculated using the correlation proposed by Wakao et al. (Wakao, Kaguei, & Funazkri, 1979), i.e.,

$$h_i = N u_0^T \frac{k_f(T)}{d_t}$$
 for empty tube and (3.3)

$$h_i = N u_0^p \frac{k_s}{d_p}$$
 for tube with quartz chips. (3.4)

Heat transfer outside the tube is calculated based on free convection heat transfer(h_{fc}) and radiation(h_r) by the following equations:

$$h_o = h_{fc} + h_r, \tag{3.5}$$

$$h_{fc} = C \frac{k_{air}(T_{fnc})}{L} (Gr \operatorname{Pr})^{0.25}$$
 and (3.6)

$$h_r = \varepsilon \sigma (T^2 + T_{fnc}^2) (T + T_{fnc}), \qquad (3.7)$$

where *L* is the height (length) of reaction zone, k_{air} is air conductivity, ε is the emissivity (assumed to be in the range 0.7 to 0.9), σ is the Stefan-Boltzmann constant, *T* is the reactor tube temperature and T_{fnc} is the furnace temperature. The constant *C* is correlated to the Prandtl number (Bird, Stewart , & Lightfoot, 2007).

It is well known that for exothermic reactions occurring in a tube with heat transfer at the wall, there could be an axial hot spot in the temperature (Balakotaiah,



Figure 3.3: Plot of axial hot spot criterion for different feed ratios (solid lines) and estimated heat loss time (dashed lines) for a tube with $d_t = 4 \text{ mm}$ and furnace temperature of $T_{fnc} = 1173 \text{ K}$.

1989; Balakotaiah & Luss, 1991). This hot spot does not exist and the operation is close to isothermal only if (Balakotaiah, Kodra, & Nguyen, 1995)

$$\frac{E}{RT_{fnc}}\frac{\Delta T_{ad}}{T_{fnc}}k(T_{fnc})\tau_h < 0.368.$$
(3.8)

Here, $k(T_f)$ is the first-order rate constant for the homogeneous oxidation reaction 3 (which is the fastest reaction as shown later in this section), and *E* is the corresponding activation energy. The adiabatic temperature rise corresponding to reaction *r*.3.3 was used in estimating the critical heat loss time in the above hot spot criterion. The calculated heat loss time for an empty reactor tube and tube
with quartz chips is plotted as a function of reactor temperature in Fig. 3.3. For comparison, the thermal runaway (hot spot) criterion is also provided in the same figure for various values of CH_4/O_2 ratio. It can be seen that the estimated values for the heat loss (transfer) time τ_h for the 4 mm reactor tube used in most of our experiments are in the range of 5 to 15 ms under typical OCM reaction temperatures ($T_{fnc} > 700$ K). Further, we note that these values are about an order of magnitude smaller than the space times used in our experiments (100 to 800 ms). Thus, the axial hot spot criterion is strictly satisfied when the reaction is taking place under methane rich conditions (relatively smaller ΔT_{ad}) but is likely to be violated when CH_4/O_2 ratio is smaller than 4. [It should be pointed out that the hot spot criterion given by Eq. 3.8 is not satisfied in many experiments reported in the literature but our experiments were designed to satisfy this condition, by choosing a higher CH_4/O_2 ratio, smaller tube diameter, or filling the tube with quartz chips so that τ_h is small under the temperature range of interest].

For the conditions of our experiments, the well known Mears criterion (Mears, 1971) for negligible radial gradients

$$\frac{E}{RT_{fnc}} \frac{\Delta T_{ad}}{T_{fnc}} \frac{k(T_{fnc})d_t^2}{[k_{eff}/C_{pv}(T)]} < 1$$
(3.9)

is also satisfied. Finally, because of the temperature profile shown in Fig. 3.2(b), only the middle 15 cm section of the tube is used to calculate the space time. [Remark: Since the temperature profile along the tube is smooth, the reaction zone is not clearly defined and there is some error in the estimation of space time. This point should be kept in mind in comparing the predictions of the kinetic model with laboratory scale results].

3.3.4 Experimental Results and Kinetic Model Validation

We show in *Table* 3.2 sample experimental results. The results in *Table* 3.2(a) are obtained using three different reactor types (empty quartz tube, quartz tube filled with quartz chips and an alumina tube) at the same furnace temperature, methane to oxygen ratio and space time. These results clearly indicate that within experimental error, the conversions and selectivities are the same, implying that there is no catalytic effect (e.g. quenching or generating of the free radicals by the quartz or alumina surfaces) and the reactant conversion is mainly due to homogeneous chemistry. We also note that at this temperature, the C_2 products are mainly ethane and ethylene and there is also a small amount of propylene formed. The results in *Table* 3.2(b) at different methane to oxygen ratios indicate that the methane conversion decreases while the selectivity to C_2 products increases as the CH_4/O_2 ratio increases. Additional experimental results and comparisons are presented in the kinetic model validation section below.

A comparison of the predictions of the kinetic model with the assumption of isothermal plug flow reactor and experimental data is shown in Fig. 3.4. Other similar comparisons with literature data (Chen et al., 1991) were also made to validate the kinetic model. At zero O_2 conversion, the selectivity to C_2H_6 is the highest among all species, followed by CO and then to C_2H_4 . Selectivity of CO_2 goes to zero at zero conversion of methane (i.e. CO_2 is not a primary product). As expected, with increase in space time, conversion of O_2 increases and the ratio of C_2H_4/C_2H_6 goes up as C_2H_6 dehydrogenation to other C_2 products (in this case primarily to C_2H_4 and H_2), results in increasing selectivity to C_2H_6 are the primary products generated by oxidation reactions, CO_2 is a secondary product formed after CO. Ethylene is formed mostly by dehydrogenation and only a very small amount by oxidative dehydrogenation. Within the range of our experiments (lim-

(a) Impact of reactor type on conversion and selectivity												
$(T = 1173 \text{ K}, \tau = 512 \text{ ms}, CH_4/O_2 = 8)$												
Reactor		Quartz chips in	tube	Quartz tube	Alumina tube							
		(4 mm i.d.))	(4 mm i.d.)	(3 mm i.d.)							
C	H_4 conversion (%)	5.6		6.4	6.8							
O_2 conversion (%)		31.4		32.7	34.6							
C_2H_4		35.0		35.7	36.3							
C_2H_6		22.9		23.0	22.0							
	C_3H_6	4.1		4.0	4.1							
		35.6		36.1	36.2							
CO_2		2.4		1.2	1.3							
H_2/CO		1.2		1.2	1.3							
	(b) Impact of CH_4/O_2 ratio on conversion and selectivity											
	(4 mm i.d.reactor with 18 - 35 quartz chips)											
	CH_4/O_2	4	8	12	16							
	CH_4 conversion (%	6) 17.0	7.6	6.9	6.3							
	O_2 conversion (%) 59.0	47.8	56.4	66.9							
	C_2H_4	30.2	34.2	38.8	40.7							
	C_2H_6	10.3	16.2	13.8	11.1							
	C_3H_6	2.7	4.5	5.2	5.6							

41.5

3.5

1.2

1173

768

40.3

1.9

1.6

1223

502

40.4

2.2

1.9

1248

491

52.8

4.0

0.8

1173

512

CO

 CO_2

 H_2/\bar{CO}

Temperature (K)

 $\tau (ms)$

Table 3.2: Sample Experimental results

ited to a maximum furnace temperature of 950 °C), very little C_2H_2 is formed and the kinetic model in the high temperature range was validated using literature data (Olsvik et al., 1995) on methane pyrolysis. A comparison of isothermal plug flow simulation results using the kinetic model with literature data (Olsvik et al., 1995) in the high temperature range (1450 to 1800 K) is shown in *Fig.* 3.5. As expected, the predicted methane conversion increases with feed temperature as well as space time. The yield to C_2H_4 and C_2H_2 also increases with increase in methane conversion, while the selectivity to C_2H_2 increases with increase in the feed temperature. The experiments as well as the model clearly indicate that C_2H_4 and C_2H_2 selectivities agree reasonably well with the experimental results.



Figure 3.4: Comparison of isothermal PFR simulation results with experimental data, $CH_4/O_2 = 8$, T = 1073 K (green), T = 1123 K (blue), T = 1173 K (red).

We note that the experimental data indicates a small amount of C_3 products (mostly propylene) formed but as our model cannot predict these, we have lumped these with the C_2 products in comparing the model predictions to experiments.

It should be pointed out that using the nine step global kinetic model, we were able to simulate our data as well as most other laboratory scale data reported in the literature with acceptable accuracy but with some small changes in the kinetic constants. As stated earlier, we attribute the small quantitative differences to either inaccuracy/inadequacy of the model and/or inaccuracy in the reported temperature (i.e., the experiment is not truly isothermal) or the space time is not known exactly. [These quantities are either not measured directly in the experiments or if measured, the accuracy is not quantified.]



Figure 3.5: Comparison of isothermal PFR simulation results with literature data (Olsvik et al., 1995) for high temperature pyrolysis, $CH_4/H_2 = 0.5$

The kinetic expressions and parameters used in the simulation are reported in Table 3.1. In order to gain insight on the characteristic times of the different reactions, we show in Fiq. 3.6 a plot of the rate constants of all the nine reactions as a function of temperature. We note that the oxidation reactions (r.3.3 & r.3.4)forming CO and CO_2 have very similar rate in the temperature range of interest and are slightly faster than the oxidative coupling reaction (r.3.1) forming ethane. The rate of oxidation of methane to form ethylene (r.3.2) is negligible compared to all the other reactions. Thus, ethylene is mainly formed by dehydrogenation of ethane (r.3.6) and this rate constant is the highest of all for temperatures exceeding 1000 K. The dehydrogenation of ethylene to acetylene (r.3.7) is slow at low temperatures but becomes important (and is the second highest rate) when the temperature exceeds 1450 K. As expected, the direct pyrolysis of methane to acetylene (r.3.5) becomes important only at very high temperatures (T > 1500K). The water-gas shift reaction (r.3.9) is slow in most of the temperature range of interest, and is important only when the space time is high enough for the system to reach equilibrium state. The steam reforming of methane reaction (r.3.8) is the fastest reaction before 1000 K, and remains important within the temperature range of interest.

As stated in the introduction, one objective of the present study is to determine the role of homogeneous chemistry in the catalytic oxidative coupling of methane. The above kinetic model may be used to make preliminary assessment of the role of homogeneous chemistry in catalytic OCM as follows. Suppose that the temperature range of interest in catalytic OCM is 750 to 950 °C (1023 - 1223 K) and the range of space times of interest is 0.01 to 0.1 second. Assuming that only those reactions having a Damköhler number (product of rate constant times space time) greater than 0.1 can be considered significant, based on the kinetic parameter values in *Table 3.1*, we note that the main homogeneous reaction of importance in the



Figure 3.6: Plot of the rate constants of global reactions as a function of temperature (Irreversibe reactions: solid lines, reversible reactions: dashed lines)

temperature and space time ranges indicated above is the ethane cracking reaction (r.3.6). The methane reforming (r.3.8) and deep oxidation reactions (r.3.3 andr.3.4) also start becoming important but only at the upper range of temperatures and space times. However, when the space time is increased to values of the order of a second, the homogeneous coupling (r.3.1) and the ethylene cracking (to acetylene, r.3.7) also become important. Finally, we note that for temperatures below $750 \, {\rm ^{\circ}C}$ and space times below about $10 \, {\rm ms}$, the contribution of the homogeneous chemistry can be neglected and this is an ideal range for laboratory experiments aimed at the determination of the kinetics of catalytic oxidative coupling. Our laboratory experiments have indeed confirmed these estimates. For example, in one experiment with a 2.3 mm ID tube, CH_4/O_2 ratio of 16, and with catalyst powder replaced by quartz particles, it was found that the methane conversion was below 0.1% and the oxygen conversion below 5% at 750 °C and a contact time of 10 ms. [Remark: This result may also be interpreted in terms of catalyst activity, i.e. any significant oxygen conversion and C_2 product formation for contact times below 10 ms and T < 750 °C is mainly due to catalytic effect and coupling between catalytic and homogeneous chemistries].

3.4 Ignition-Extinction Analysis of Ideal Adiabatic Reactor Models

In this section, we analyze the bifurcation (ignition/extinction) behavior of the nine step reaction scheme using three ideal adiabatic reactor models. The first model is that of an adiabatic plug flow reactor (PFR) which is obtained from the more general axial dispersion model when the heat and mass Peclet numbers are assumed to be infinity ($Pe_h \rightarrow \infty$, $Pe_m \rightarrow \infty$, or both species and thermal back mixing is assumed to be zero). The second model is that of an adiabatic continuous-flow stirred tank reactor (CSTR), which assumes perfect or complete backmixing for both species and energy ($Pe_h \rightarrow 0$, $Pe_m \rightarrow 0$). The third, which is

not considered or discussed as extensively in the literature but very important in the present context, is the lumped thermal reactor (LTR) model, which assumes zero back-mixing of species but complete backmixing of energy $(Pe_h \rightarrow 0, Pe_m \rightarrow \infty)$. As discussed in the literature in the context of a single exothermic reaction with first-order kinetics (Balakotaiah, 1995), the lumped thermal reactor model has the largest region of multiple solutions and can lead to autothermal operation on the ignited branch with lowest feed temperature and/or space time [Remark: In the literature, the lumped thermal model is also known as the bubble column reactor model]. It is not clear if this result extends to the case of multiple reactions, especially when some reactions are exothermic while others are endothermic. We determine the ignition and extinction loci (whenever they exist) as well as the yields to the desired C_2 products in all three ideal reactors in the following sections, in order to evaluate the impact of thermal and species backmixing on the gas phase OCM process.

3.4.1 Reactor Models

(a) PFR model:

The species balances for steady-state PFR model are given by

$$\frac{dF_j}{dz} = \tau F_T^{in} \sum_{i=1}^N v_{i,j} R_i(y_j, T), \quad j = 1, 2, ..., S;$$
(3.10)

while the energy balance may be expressed as

$$\left(\sum_{j=1}^{S} F_j C_{p,j}(T)\right) \frac{dT}{dz} = \tau F_T^{in} \sum_{i=1}^{N} [-\Delta H_R^i(T)] R_i(y_j, T),$$
(3.11)

with inlet (boundary) conditions:

$$F_j = F_j^{in}, \ T = T^{in}$$
 at $z = 0.$ (3.12)

Here, F_j is the molar flow rate of species j, F_j^{in} is inlet molar flow rate of species

j, F_T^{in} is the total inlet molar flow rate, z is the dimensionless position along the reactor tube, and τ is the space time, defined as reactor volume over volumetric flow rate at inlet conditions. [Note that the reaction rates R_i in the above balance equations have units of s^{-1} . Also, in the calculations, the number of species S = 9 and the number of reactions N = 9.]

(b) CSTR model:

The steady-state species and energy balances for a perfectly mixed or ideal CSTR are given by

$$F_j = F_j^{in} + \tau F_T^{in} \sum_{i=1}^N v_{i,j} R_i(y_j, T), \quad j = 1, 2, ..., S; \text{ and}$$
 (3.13)

$$\sum_{j=1}^{S} F_{j}^{in} \int_{T^{in}}^{T} C_{p,j}(T') dT' = \tau F_{T}^{in} \sum_{i=1}^{N} [-\Delta H_{R}^{i}(T)] R_{i}(y_{j},T).$$
(3.14)

(c) Lumped Thermal Reactor (LTR) model:

For the lumped thermal model, the species balances are given by

$$\frac{dF_j}{dz} = \tau F_T^{in} \sum_{i=1}^N v_{i,j} R_i(y_j, T), \quad j = 1, 2, ..., S;$$
(3.15)

while the energy balance is given by

$$\sum_{j=1}^{S} F_{j}^{exit} \int_{T^{in}}^{T} C_{p,j}(T') dT' = \tau F_{T}^{in} \sum_{i=1}^{N} [-\Delta H_{R}^{i}(T^{in})] \int_{0}^{1} R_{i}(y_{j},T)) dz,$$
(3.16)

with inlet conditions

$$F_j = F_j^{in}$$
, at $z = 0$. (3.17)

We note that the enthalpy/energy balance give by Eq.(3.16) may also be expressed

$$\sum_{j=1}^{S} F_{j}^{in} \int_{T^{in}}^{T} C_{p,j}(T') dT' = \tau F_{T}^{in} \sum_{i=1}^{N} [-\Delta H_{R}^{i}(T)] \int_{0}^{1} R_{i}(y_{j},T)) dz.$$
(3.18)

The above model equations are used to determine the bifurcation diagrams of reactor steady-states as a function of feed temperature for a fixed space time. The bifurcation diagrams are also determined with space time taken as the bifurcation variable and fixed inlet temperature. In both cases, the impact of the ratio (CH_4/O_2) in the feed is examined.

as

Before presenting the computed results, we review some generic features of open reacting systems with multiple reactions. As stated earlier, when the space time is taken as the bifurcation variable, irrespective of the reactor type, any diagram of reactor state variable (e.g., reactor exit temperature, conversion of CH_4 or O_2 , selectivity of a product, etc.) versus space time should approach the flow and thermodynamic (equilibrium) branches when the space time is sufficiently small and sufficiently large, respectively. The behavior at intermediate space times (and the existence of ignition/extinction points) is mainly due to reaction kinetics and species as well as thermal backmixing. Further, when the inlet temperature is low (e.g. $T^{in} = 300$ K), the ignition points as well as approach to equilibrium may occur at very high space times (e.g. $au > 10^6~{
m s}$) that are not of practical interest. Similarly, when the inlet temperature is sufficiently high, depending on the level of thermal mixing in the reactor, the extinction point could be located at very small space times (e.g. below 1 ms), which are difficult to attain at normal gas velocities. Thus, in the results presented below, we restrict the calculations to space times below 100 s (and in most cases below 50 s) and above 1 ms. We also note that for the plug flow model, ignition and extinction coincide at the point of parametric sensitivity (where the reactor temperature or conversion increases rapidly). Following literature terminology, we refer this point of parametric sensitivity as ignition.

When the space time is fixed and inlet temperature is taken as the bifurcation variable, the flow branch corresponds to the range in which $T - T^{in}$ approaches zero, while the thermodynamic branch corresponds to the region where $T - T^{in}$ approaches a value corresponding to the adiabatic temperature rise, which depends on the CH_4/O_2 ratio as well as T^{in} . Again, depending on the value of space time used, the approach to thermodynamic equilibrium may occur at very high feed and/or reactor temperatures. In such cases, we restrict the calculations for reactor temperatures T < 2000 K. [Remark: In addition to the validation of the kinetic model, a second reason for restricting the calculations to T < 2000 K is that our specific heat and other thermodynamic data may not be accurate beyond this temperature.]

3.4.2 PFR Model Simulation Results

Fig. 3.7 shows the computed results for a PFR with fixed feed temperature (900 K, 1000 K, 1100 K), CH_4/O_2 ratio of 4, with space time as the bifurcation variable (and restricted to the range of 0.01 to 50 s). The computed results for the same CH_4/O_2 ratio, with a fixed space time (0.1 s, 10 s) and inlet temperature as the bifurcation variable are shown in *Fig.* 3.8.

The following observations can be made from the results in Fig. 3.7: (*i*) the ignition point moves to lower space time while the maximum reactor temperature goes to higher values as the feed temperature increases although adiabatic temperature rise decreases (*ii*) the reactor temperature reaches a maximum value near ignition, together with full conversion of oxygen. As expected, the oxidation reactions are dominant before, during and just after ignition. However, a second (shallow) peak of reactor temperature may occur due to reversible dehydrogenation (hydrogenation) reactions (*iii*) the yields of different C_2 products are maximized near ignition but in sequential order. That is, C_2H_6 starts to form at ignition, followed by C_2H_4 , which goes through a maximum value as the space time is increased.



Figure 3.7: Adiabatic PFR simulation results with fixed feed temperature. Reactor exit temperature (a), conversion (b), product yield (c,d,e) and exit mole fraction (f) vs. space time. $CH_4/O_2 = 4, T^{in} = 900 \,\mathrm{K}$ (dotted lines), $1000 \,\mathrm{K}$ (dashed lines), $1100 \,\mathrm{K}$ (solid lines).



Figure 3.8: Adiabatic PFR simulation results with fixed space time. Reactor exit temperature (a), conversion (b), product yield (c,d,e) and exit mole fraction (f) vs. feed temperature. $CH_4/O_2 = 4$, $\tau = 0.1$ s (dotted lines), 10 s (solid lines).

The formation of C_2H_2 comes in the end among all C_2 products. An additional observation is that a second maximum of C_2 products, especially of C_2H_4 and C_2H_6 may exist due to pyrolysis reactions. The two yield peaks merge together at low feed temperatures and high space times, where the oxidation and pyrolysis reactions may occur in parallel (*iv*) the system approaches equilibrium state smoothly after ignition, the final temperature and product distribution values being consistent with the thermodynamic equilibrium calculations of the previous section. For this specific case, the main equilibrium products are CO and H_2 with only a very small amount of C_2 products (*Fig.* 2.4), but equilibrium is not yet reached in *Fig.* 3.7 within 50 s even for the highest inlet temperature.

When space time is fixed (*Fig.* 3.8), both feed temperature at ignition and maximum reactor temperature decreases as space time increases. Comparing with steady-state behavior with fixed feed temperature, the main difference here comes in the steady-state yield towards total C_2 products (and more specifically C_2H_2). With fixed space time, the yield of C_2 products (C_2H_2) keeps increasing as the feed temperature increases within the range of calculation shown. The methane conversion curves clearly indicate that after all the oxygen is consumed, the heat suppled in the form of higher feed temperature favors the pyrolysis and reforming reactions and the steady-state composition approaches that corresponding to the thermodynamic equilibrium (*Fig.* 2.4).

The above calculation results for an adiabatic PFR model as well as similar calculations for other values of CH_4/O_2 ratio clearly indicate the general features of the gas phase OCM process with only methane and oxygen in the feed. For example, the formation of C_2 products is favored at intermediate temperatures and space times (the actual values depending on the methane to oxygen ratio) and exothermic chemistry dominating until all oxygen is consumed. The temperature rise due to the oxidation reactions further increases the C_2 yields before reforming chemistry

takes over and the steady-state behavior approaches the thermodynamic branch.

3.4.3 CSTR Model Simulation Results

The steady-state bifurcation behavior of the CSTR model is expected to be different from that of PFR due to the backmixing in the reactor. As is well known, thermal backmixing leads to the existence of a region of multiple steady-state solutions, that is, the system can be either on the ignited branch or on the quenched branch for the same inlet temperature or space time. The start-up procedures (or the initial conditions) determine the actual steady-state that is attained.

Fig. 3.9 shows the computed bifurcation diagrams of reactor temperature, conversions and yields versus space time for the CSTR model with fixed feed temperature (700 K, 900 K, 1100 K) and CH_4/O_2 ratio of 4. The computed bifurcation behavior with feed temperature as the bifurcation variable for the same CH_4/O_2 ratio and fixed space time (0.1 s, 10 s) is shown in Fig. 3.10. The following observations can be made from the results shown in Fig. 3.9: (i) both ignition and extinction points move to lower space time as feed temperature increases, but the region of multiplicity shrinks (i.e. the range of space times over which three steady-states exist decreases with increasing inlet temperature and for sufficiently high inlet temperatures the ignition and extinction points may disappear. Also, note that the ignition point for $T_{in} = 700$ K is outside the range of the graph in Fig. 3.9. (*ii*) higher feed temperature results in higher reactor temperature but lower reactants conversion (both CH_4 and O_2) at extinction point (*iii*) the maximum yield to C_2H_6 may occur on the unstable branch. The maximum yield to C_2H_4 is obtained on the ignited branch close to extinction point while a second maximum may exist for the same reason as in PFR. The yield to C_2 products (C_2H_2) keeps increasing and reaches a maximum at much higher space time compared to that at ignition point (iv) the steady-state yield of CO behaves similar to that of C_2H_4 , a high yield towards CO is obtained on the ignited branch close to extinction point due to oxidation reactions, while a second maximum appears due to reforming/shift reactions. This can be seen more clearly from the exit mole fraction of H_2O which decreases monotonically after ignition.

When space time is fixed and the feed temperature is taken as the bifurcation variable (*Fig.* 3.10), the reactor temperature at ignition and extinction points decreases as the space time increases. Within the range of the calculations, the yield to C_2 products (C_2H_2) keeps increasing as the feed temperature increases.

Comparing the above results to those of the PFR, we note that the CSTR has similar ignition behavior and requires similar reactor conditions (reactor temperature and space time) to get C_2 products from partial oxidation reactions. However, the existence of a region of multiplicity (due to backmixing) makes the extinction behavior very different. For example, it provides a way to generate high reactor temperature (with proper start-up) and thus obtain high yield to C_2 products from oxidative coupling of methane with cold feed and short space times. A more detailed discussion of this is presented in the next section.

3.4.4 LTR Model Simulation Results

Although the CSTR provides lower maximum yields to C_2H_4 than PFR, the space time or feed temperature required is also much lower due to the ignitionextinction behavior. These features are important in design considerations of a gas phase OCM reactor with low feed temperature and short space time but leading to adequate yield of C_2 products. As discussed previously, a lumped thermal reactor model gives the largest region of multiplicity, which means that it has the lowest requirements on feed temperature or space time at the extinction point compared to other types of reactors. These features of the lumped thermal reactor make it the best reactor configuration for homogeneous OCM reaction. In *Fig.* 3.11 we show the computed steady-state bifurcation diagrams for lumped thermal reactor tor model, and also make comparisons with those of CSTR and PFR models. In



Figure 3.9: Adiabatic CSTR simulation results, bifurcation diagrams with fixed feed temperature. Exit temperature (a), conversion (b), product yield (c,d,e) and exit mole fraction (f) vs. space time. $CH_4/O_2 = 4, T^{in} = 700 \text{ K}$ (dotted lines), 900 K (dashed lines), 1100 K (solid lines).



Figure 3.10: Adiabatic CSTR simulation results, bifurcation diagrams with fixed space time. Exit temperature (a), conversion (b), product yield (c,d,e) and exit mole fraction (f) vs. feed temperature. $CH_4/O_2 = 4$, $\tau = 0.1$ s (dotted lines), 10 s (solid lines).

this calculations, the feed temperature is chosen as bifurcation variable and space time is fixed, in order to investigate system's behavior with short space time but different feed temperatures. Fiq. 3.11(a) clearly shows that lumped thermal model has lower feed as well as reactor temperature at the extinction point compared to CSTR, while the differences at ignition point are negligible. The reactor temperature overlaps with isothermal line in low feed temperature region and become much higher than isothermal temperature on the ignited branch, since the oxidation reactions are important at short space time and relatively low temperature. As the feed temperature keeps increasing, the adiabatic temperature line intersects the isothermal temperature line as dehydrogenation and reforming reactions that occur at high temperatures are endothermic. Fig. 3.11(b) shows that lumped thermal model not only provides lower extinction temperature, but also provides slightly higher conversion of both CH_4 and O_2 compared to CSTR. Fig. 3.11(c) shows the highest yield to C_2H_4 predicted by the lumped thermal model is almost two times higher than that of the CSTR model and close to that obtained in a PFR (but at a feed temperature that is higher by about 400 K). Fig. 3.11(d) shows that lumped thermal model provides slightly lower yield to C_2H_2 around the extinction point compared to the CSTR, due to the lower reactor temperature. However, the total C_2 yield at the extinction point in LTR is still higher than that in CSTR. Although the CSTR model predicts higher yield to total C_2 product yield than LTR in much higher feed temperature range, large amount of heat supply is required to achieve these high values of C_2 products yield. Fig. 3.11(e), (f) shows that lumped thermal reactor generates more syngas (both CO and H_2) than CSTR. Although lumped thermal reactor model predicts more H_2O around the extinction point than CSTR, the amount of H_2O and CO_2 formed is trivial compared to syngas.

The computed ignition-extinction loci (bifurcation sets) of the adiabatic lumped thermal as well as CSTR models for CH_4/O_2 feed ratios of 2, 3 and 4 are shown



Figure 3.11: Comparison of adiabatic lumped thermal model (solid lines), CSTR (dashed lines) and PFR (dotted lines) simulation results, bifurcation diagrams with fixed space time. Exit temperature(a), conversion(b), product yield (c,d,e) and exit mole fraction (f) vs. feed temperature. $CH_4/O_2 = 4, \tau = 1$ s.

in *Fig.*3.12. We note that the feed ratio and thermal/mass mixing have negligible impact on ignition locus of the system, but significantly impact the location of the extinction locus. As the feed ratio decreases, the extinction locus moves to a region with low feed temperature and/or low space time. Compared to CSTR, the lumped thermal model clearly requires much lower feed temperature (space time) when space time (feed temperature) is fixed. An ignited state with ambient feed temperature exists for CH_4/O_2 feed ratio smaller than 3 and space time shorter than 10 s for LTR and CSTR models. However, for feed temperatures below 800 K, ignition may not occur with space time up to tens of hours and hence the reactor operation has to be autothermal and special start-up procedure is needed.

3.4.5 Analysis at Low CH_4/O_2 Ratios

The calculations presented so far were limited to the non-flammability region, i.e. for inlet methane to oxygen ratios greater than about 2. In this section, we consider the case of lower ratios in the range 1.6 to 2.0, which are in the flammable region (and hence require special consideration with respect to safety related aspects of scale-up). Fig. 3.13 shows the computed steady-state bifurcation diagrams with CH_4/O_2 feed ratio of 1.8 for the CSTR model. Comparing this figure with Fig.3.9, the following observations can be made for low CH_4/O_2 feed ratios: (i) With same feed temperature, the maximum reactor temperature with low feed ratios ($CH_4/O_2 < 2$) is much larger than that with high feed ratios due to the high adiabatic temperature rise. (ii) Methane conversion after ignition is higher than that of the cases with high feed ratios, mainly due to the fact that methane pyrolysis and reforming reactions are activated by the high reactor temperature produced by low CH_4/O_2 feed ratio. (*iii*) The yield to C_2H_4 and C_2H_6 is low on the ignited branch and the maximum values are obtained on the unstable branch, C_2H_2 is thus the main C_2 product with low CH_4/O_2 feed ratios. For the specific case shown in Fig.3.13(d), the yield to C_2H_2 is greater than 20% at the extinction point and keeps



Figure 3.12: Computed ignition-extinction loci of adiabatic CSTR and lumped thermal reactor (LTR) models, in the feed temperature-space time plane for different high $CH_4/O_2 = 2,3$ and 4.

increasing as space time increases, the maximum value reaches 36% at space time around 10 ms. (*iv*) When the system approaches the thermodynamic equilibrium state, yield to C_2 product approaches zero. In this limit, the main carbon product is *CO* together with trivial amount of *CO*₂ while the main hydrogen product is H_2 with small amount of water (for example: 98.4% yield to *CO* and 1.6% yield to *CO*₂ when feed temperature is 1100 K).

Fig. 3.14 shows LTR model simulation result with fixed space time and low feed ratio, and also makes comparison with the simulation results of CSTR with same



Figure 3.13: Adiabatic CSTR simulation results, bifurcation diagrams with fixed feed temperature. Exit temperature (a), conversion (b), product yield (c,d,e) and exit mole fraction (f) vs. space time. $CH_4/O_2 = 1.8, T_{in} = 900 \text{ K}$ (dotted lines), 1100 K (solid lines).



Figure 3.14: Comparison of adiabatic lumped thermal model (solid lines) and CSTR (dotted lines) simulation results, bifurcation diagrams with fixed space time. Exit temperature(a), conversion(b), product yield (c,d,e) and exit mole fraction (f) vs. feed temperature. $CH_4/O_2 = 1.8, \tau = 0.01$ s.

feed conditions. The LTR model again provides higher reactant conversion than CSTR with lower reactor temperature (as in the case of high feed ratio). Furthermore, the LTR model provides higher yield to C_2 product and syngas within the range of our calculation (Again, calculations with reactor temperature higher than 2000 K are not included here as our kinetic model is not validated in this range).

Operating conditions				Product yields					
CH_4/O_2	Space time (s)	Temperature (K)	C_2H_6	C_2H_2	C_2H_4	CO	CO_2		
4	205(167)	967(1153)	8(1)	0(0)	5(7)	20(8)	4(21)		
3.5	34.6(41)	1041(1178)	5(1)	0(1)	9(9)	21(11)	5(21)		
3	4.3(8)	1147(1213)	2(1)	1(2)	14(9)	24(15)	6(19)		
2.5	0.4(1)	1282(1303)	1(0)	5(5)	12(7)	26(18)	8(18)		
2	0.041(0.096)	1470(1479)	0(0)	17(10)	4(3)	29(21)	11(20)		
1.8	0.013(0.031)	1594(1583)	0(0)	23(13)	2(1)	31(21)	14(22)		
1.6	0.004(0.009)	1744(1716)	0(0)	30(16)	1(1)	32(22)	16(24)		

Table 3.3: Simulation results of adiabatic LTR and CSTR (), for autothermal operation with ambient feed (300K). Space time, reactor temperature and product yields at extinction point

Fig. 3.15 shows ignition-extinction loci of adiabatic lumped thermal and CSTR models for CH_4/O_2 feed ratios of 1.6 and 1.8. Comparing the extinction points in *Fig.* 3.15 and 3.12, under the same feed temperature, the space time required by LTR model reduces by order of magnitude as inlet methane to oxygen ratio decreases through 2. With CH_4/O_2 feed ratio smaller than 2, a region of multiplicity always exists for both CSTR and LTR models as long as space time is greater than 1 ms. These observations clearly show that for lower CH_4/O_2 feed ratios, the region of autothermal operation expands and moves to ambient feed temperature and space times of the order of milliseconds. In order to compare the performance of adiabatic reactors with different feed ratios, we summarize the temperature, space time and the carbon product distribution under autothermal operation condition ($T_{in} = 300$ K) at extinction points in Table 3.3. Under autothermal operation, the yield to total C_2 products increases as CH_4/O_2 feed ratio decreases.

In summary, for CH_4/O_2 feed ratio smaller than 2: (*i*) high yield to C_2H_2 (29.8%) can be obtained with space time of millisecond at extinction point, while the yield to C_2H_4 is negligible (*ii*) high yield to syngas can be obtained simultaneously under the same condition (*iii*) for same feed ratio, LTR provides higher yield to useful carbon products and at lower space time.

For CH_4/O_2 feed ratio greater than 2, (i) the main C_2 product is C_2H_4 instead



Figure 3.15: Computed ignition-extinction loci of adiabatic CSTR and lumped thermal reactor (LTR) models in the feed temperature - space time plane for different low CH_4/O_2 ratios.

of C_2H_2 (*ii*) yield to syngas is still high in LTR but is not comparable to that with low feed ratios (*iii*) when inlet CH_4/O_2 ratio becomes greater than 3.5, LTR starts to loss its superiority over CSTR. The main reason is that high feed ratio requires very long space time even at extinction points, thus the impact of endothermic chemistry becomes significant and the reactor temperature is no longer favorable for oxidative coupling reactions in gas phase.

3.5 Conclusions and Discussion

We have presented a comprehensive bifurcation analysis of gas phase methane oxidative coupling using three ideal reactor models and a simplified reaction network with global kinetics for the various oxidation, pyrolysis, and reforming reactions. As the bifurcation features are mainly determined by the thermal and mixing effects, the approach followed here is more efficient compared to detailed computational fluid dynamic (CFD) models and/or detailed kinetic and reaction schemes involving hundreds of steps. The present approach has given a coarse map of the various C_2 products distribution (selectivity) as well as methane and oxygen conversions in the parameter region of interest (methane to oxygen ratio in feed, inlet temperature and space time) and serves as a guide for further investigation of the interesting regions using more detailed kinetic and fluid flow models.

The bifurcation analysis presented here was limited to the three ideal models (PFR, CSTR and LTR), which can be derived from the more general case of 1 - D axial dispersion model with finite heat and mass Peclet numbers. In the PFR model, conversion of both methane and oxygen as well as yield to an intermediate product such as ethylene is high due to zero mixing in the flow direction. However, there is no hysteresis (or the width of the hysteresis region is zero) in PFR for the same reason, and hence, high feed temperature and space time are required to reach the operating regime (whose width in space time or feed temperature is extremely narrow). In contrast, the highest yield of an intermediate product such as ethylene or acetylene in a CSTR is much lower than that in PFR while the operating regime (width of the hysteresis region and the region of autothermal operation) is much larger. When exothermic chemistry dominates, the lumped thermal model can further expand the region of autothermal operation while leading to higher selectivity for intermediate products. Our calculations indicate that in both CSTR and lumped thermal models, the best operating point to get high ethylene yield is on the ignited branch close to extinction point (sometimes at the extinction point depending on the methane to oxygen ratio). This observation is valid with either the residence time or the feed temperature as the bifurcation vari-

able. The calculations also indicate that with ambient feed temperature and space times of the order of a second, the best ethylene yields that can be obtained in a LTR are in the range 13 - 15% and for methane to oxygen ratios in the range 2.5 to 3.5. For higher CH_4/O_2 ratios, the temperature rise is not high enough to sustain autothermal operation (and activate pyrolysis of ethane to ethylene) with ambient feed and space times of practical interest. For lower CH_4/O_2 ratios, the temperature rise is high enough to favor formation of acetylene. Our calculations indicate that for autothermal operation with ambient feed and space times of the order of milliseconds, the best acetylene yields that can be obtained in a LTR are in the range 25 - 32% for methane to oxygen ratios in the range 1.6 to 2.0. In this regime, first the exothermic chemistry dominates (near extinction point), followed by the pyrolysis of methane, ethane and ethylene to acetylene (on ignited branch at intermediate space times), and finally the reforming chemistry at high space times leading to the thermodynamic branch. Thus, determination of the region of autothermal operation and identification of the optimal space times and the corresponding peak yields of C_2 products are the important results obtained from the bifurcation analysis. [Remark: For feed temperatures that are much higher than ambient, and space times of the order of milliseconds, we have observed that the acetylene yields can be much higher, in the 45 to 50% range (See Fig. 3.14)].

The bifurcation analysis in this work leads to the conclusion that a reactor with high thermal conductivity (or low effective heat Peclet number) and negligible species diffusion and strong convection (or high effective mass Peclet number) is optimal for gas phase oxidative coupling of methane (as well as other such partial oxidation reactions). In practice, such a reactor design can be approximated when the effective heat Peclet number is less than unity ($Pe_{h,eff} < 1$) and mass/species effective Peclet number larger than 10 ($Pe_{m,eff} > 10$). For example, a perforated (inert) metallic disk of high conductivity with appropriately selected thickness and

perforation diameter can lead to the desired range of Peclet numbers. We do not discuss here the practical aspects of construction of such a reactor as it is beyond the scope of this work.

The calculations presented here indicate that when exothermic effects are moderate or when the temperature rise due to combined exo and endothermic chemistries is moderate, reactors with intermediate levels of mixing may lead to higher yields of intermediate products.

Chapter 4

Ignition-Extinction Analysis of Catalytic Partial Oxidation Reaction in Lab-Scale Reactors

4.1 Preamble

The performance of many catalysts used in partial oxidation of hydrocarbons, oxidative dehydrogenations and other such applications is assessed by using a small quantity of catalyst (typically 10 mg to about 1 g) in powdered form (with particle size typically in the $0.1 \,\mathrm{mm}$ to $1 \,\mathrm{mm}$ range) in small diameter tubes placed in a temperature controlled furnace. In such laboratory scale tests, the experimental variables are the space time (or the mass or volume hourly space velocity measured at some reference condition such as STP), furnace temperature and the composition of the inlet stream. In these laboratory scale packed-bed reactors, the reactor tube diameter is usually in the range of 2 mm to 20 mm and the catalyst is often sandwiched between inert (quartz) particles. In an ideally designed experiment, the design and test conditions are selected so that isothermal or near isothermal conditions prevail and the test reactor behavior can approach that of an ideal reactor (which in most cases is an ideal PFR but in some cases could be an ideal CSTR and/or a differential mode of operation). However, in most practical cases, such ideal conditions for studying the catalytic kinetics are achieved only when the thermal effects are negligible (or the reactants and/or catalyst is diluted sufficiently), inter and intra-particle gradients are negligible (or catalyst particle size is sufficiently small) and heat transfer resistance between the reactor tube and furnace is negligible. Analytical and quantitative criteria for achieving such ideal conditions are well known in the literature (Weisz & Hicks, 1962; Mears, 1971a, 1971b; Doraiswamy & Tajbl, 1974; Kapteijn & Moulijn, 2008; Hickman, Degenstein, & Ribeiro, 2016) but it is extremely difficult to satisfy these criteria, especially for highly exothermic catalytic partial oxidation reactions. For example, in the case of oxidative coupling of methane, with an undiluted feed and methane to oxygen ratio of 4, the adiabatic temperature rise is about $1150 \,\mathrm{K}$ (Sarsani et al., 2017). To limit the maximum temperature rise to below $10 \,\mathrm{K}$, either the catalyst or the feed has to be diluted by about a factor 100, or the tube diameter has to be of the order of a few micrometers, all of which are not practical as they lead to other experimental difficulties.

In most laboratory catalytic packed-bed reactors used to test partial oxidations or oxidative dehydrogenations, thermal effects can be significant and the heat loss (gain) to (from) furnace can also be significant so that the reactor is neither isothermal nor adiabatic. Further, axial as well as radial temperature gradients may exist within the catalyst, especially when there is no dilution of the catalyst bed or the reactants. In such cases, it is known that depending on the catalyst activity, adiabatic temperature rise (inlet concentrations of reactants) and various other characteristic times, ignition and extinction (and hysteresis) phenomena could be observed in laboratory scale reactors of small diameter, when either the furnace temperature or the space time is varied. Further, due to existence of multiple steady-states, the product distribution may depend on the start-up conditions used to arrive at the steady-state (Pak & Lunsford, 1998; Lee et al., 2013; Zohour, Noon, & Senkan, 2013; Sarsani et al., 2017). In such cases, an understanding of the ignition and extinction behavior as well as the impact of heat exchange on the observed features is important in the interpretation of laboratory results, catalyst performance evaluation, kinetic parameter estimation and scale-up studies. The main goal of this chapter is to demonstrate some pathological (complex) behavior that could be observed, and provide a framework for such an understanding by applying the bifurcation theory techniques to partial oxidation reactions carried out in laboratory scale reactors.

While there exist many excellent reviews of laboratory scale catalytic reactors, we are not aware of any that focus on the ignition-extinction behavior that is related to heat exchange with furnace. Though the importance of thermal effects is recognized in the literature through many experimental publications, there have been very few systematic and comprehensive modeling studies on this topic. In an excellent combined modeling and experimental work, Kalthoff and Vortmeyer (1980) studied the ignition and extinction phenomena in a wall cooled reactor of diameter $50 \,\mathrm{mm}$ and total length $1000 \,\mathrm{mm}$ (with catalyst bed length of $72 \,\mathrm{mm}$) using complete combustion of ethane in a packed-bed reactor using $Pd/\gamma - Al_2O_3$ catalyst particles [Remark: This reactor may be classified as more of a pilot scale than a laboratory scale reactor used in testing of catalysts]. In addition to demonstrating the ignition-extinction and hot spot behavior, they compared the computed ignition-extinction locus using a two-dimensional pseudo-homogeneous model with the experimental data and found qualitative agreement. However, because of the limited range of flow rates used in their work (and relatively larger tube diameter), their conditions were closer to the adiabatic limit, and their study was not comprehensive. More recently, Mariani et al. (2012) examined the thermal behavior of laboratory scale catalytic reactors by approximating the heat generation rate as an exponential function of the position in the reaction zone (Mariani, Keegan, Martínez, & Barreto, 2012). The main limitation of this approach is that it does not show any ignition-extinction and hysteresis behavior. In the context of monolith reactors, Gu and Balakotaiah (2016) presented a rather comprehensive study on the impact of heat and mass dispersion and heat losses on the light-off behavior of laboratory and full scale monolith reactors. As stated above, in the context of catalytic partial oxidations carried out in packed-bed reactors, the adiabatic temperature rise is very high (typically 500 K to 1200 K) compared to monolith reactors used in catalytic after-treatment (typically $50 \,\mathrm{K}$ to $300 \,\mathrm{K}$) and the kinetics of the re-

actions studied is also different (transition metal oxide or perovskite based versus precious metal with the former much less active than the latter). While there are many experimental examples of ignition-extinction, hysteresis and hot spot observations in catalytic partial oxidations, it appears that there is no comprehensive modeling effort, which is the main focus of this work.

This chapter is organized as follows. In the next section, we review briefly the various established criteria for ideal behavior of laboratory scale reactors with focus on the heat exchange between furnace and reactor tube. In section 4.3, we present a mathematical model of a laboratory scale packed-bed reactor that can be used to determine the qualitative ignition-extinction behavior with varying furnace temperature or space time for the case of single and/or multiple reactions. In section 4.4, we present a comprehensive analysis of the ignition-extinction behavior and the impact of various parameters for the case of a single exothermic reaction under adiabatic condition. In section 4.5, we present the impact of heat exchange on the steady-state ignition-extinction behavior and examine the temperature and concentration profiles in a catalyst bed with inert materials. In section 4.6, we examine the impact of heat exchange on selectivity for competing oxidation reactions. In section 4.7, we determine the boundary of the region of autothermal operation for various heat exchange times and compare the model predictions with available experimental data. We also analyze the impact of catalyst activity, kinetics and catalyst bed aspect ratio on the region of autothermal operation. The last section summarizes the results of our investigation and provides some guidelines for the interpretation of data and estimation of kinetic parameters.

4.2 Review of diagnostic criteria

It is well established that the performance of a laboratory scale packed-bed reactor approaches that of an ideal isothermal one-dimensional pseudo-homogeneous reactor model if four distinct conditions are satisfied: (*i*) intra-particle concentration

and temperature gradients are negligible (ii) inter-particle or external concentration and temperature gradients are negligible (iii) radial (and azimuthal) temperature (and concentration) gradients are negligible and (iv) axial temperature gradient within the catalyst section is negligible, or equivalently, there is no axial hot spot. If only the first three criteria are satisfied, it may be shown that the reactor performance may still be described by a one-dimensional pseudo-homogeneous model but the operation is neither isothermal nor adiabatic. Further, when the first three criteria are satisfied and when the effective axial heat and mass Peclet numbers are sufficiently large, the behavior approaches that of an ideal plug flow reactor (PFR). Similarly, when the first three criteria are satisfied and when the axial heat and mass Peclet numbers are much smaller than unity, the reactor behavior approaches that of an ideal continuous-flow stirred tank reactor (CSTR), while for the case of sufficiently large mass Peclet number and small heat Peclet number, it approaches that of a lumped thermal reactor (LTR) model. It should be noted that the effective heat and mass Peclet numbers are functions of flow rate or space time (as well as many other variables such as particle size) and can vary over a wide range for laboratory scale reactors depending on the volume of catalyst, reactor tube diameter and the range of flow rates used. We provide in the Supplementary Material expressions for the effective Peclet numbers. Thus, even when the first three criteria are satisfied, the approach to one of the ideal reactor limits can be realized only in some range of flow rates. It should also be pointed out that in any given laboratory reactor setup, it is usually possible to vary the flow rate or space time only by about a factor 100 or less while interesting phenomena (e.g. hysteresis) may occur over a much wider range of space times, typically, one to five orders of magnitude, depending on kinetics and other design parameters.

Among the four criteria for ideal behavior, the first three are extensively investigated in the literature by the well established quantitative criteria (Weisz

& Hicks, 1962; Mears, 1971a, 1971b). In the context of catalytic partial oxidations, they can be satisfied in most cases by selecting sufficiently small (yet realistic/feasible) catalyst particle and tube diameters [Remarks: We note that among these three, the first one, namely the Weisz-Prater criterion, is the most useful one for testing intra-particle concentration gradients, as the assumption of negligible interior temperature gradient in catalyst powders used in lab scale reactors is valid in most practical cases. The second and third criteria, (also known as the Mears criteria) for testing external and radial gradients are based on linearization around the quenched state, and as already pointed out in the literature (Dommeti, Balakotaiah, & West, 1999; Chakraborty & Balakotaiah, 2004), may not be applicable under more general conditions such as when ignited states can coexist with quenched states]. However, as discussed in the recent literature (Sarsani et al., 2017; Sun, Kota, Sarsani, West, & Balakotaiah, 2018) and based on the example given above, it is extremely difficult to satisfy the fourth (axial hot spot) criterion. Our focus in this section will be on this criterion. For the case of a cooled (or heated) tubular reactor in which a single exothermic reaction occurs, and equal feed and furnace temperatures, the axial hot spot criterion (Balakotaiah, 1989) states the ratio of characteristic heat exchange time between the reactor tube and furnace to that of heat generation time has to be smaller than a critical value, i.e., an axial hot spot does not exist and the operation is close to isothermal only if

$$\frac{\tau_h}{\tau_g} < e^{-1} \text{ or } \frac{E}{RT_{fnc}} \frac{\Delta T_{ad}}{T_{fnc}} k(T_{fnc}) \tau_h < 0.368.$$
 (4.1)

Here, $k(T_{fnc})$ is the first-order rate constant and the quantity $\tau_g = 1/[\frac{E}{RT_{fnc}}\frac{\Delta T_{ad}}{T_{fnc}}k(T_{fnc})]$ is the characteristic heat generation time at the furnace (or coolant) temperature; E is the activation energy, ΔT_{ad} is the adiabatic temperature rise and T_{fnc} is the furnace temperature [Remark: In terms of the characteristic times, the hot spot
criterion simply states that the heat removal time should be below 0.368 times the heat generation time. When this condition is satisfied, there may still be a hot spot but the temperature rise is a small fraction of the adiabatic temperature rise. When the heat removal time is an order of magnitude smaller than that given by the criterion, the hot spot is practically eliminated and the reactor is practically isothermal].

The characteristic heat exchange (loss) time may be estimated using the expression (Balakotaiah & West, 2014; Sarsani et al., 2017; Sun et al., 2018):

$$\tau_h = \frac{0.25d_t C_{pv}(T)}{U},$$
(4.2)

where d_t is the reactor tube inside diameter, $C_{pv}(T)$ is the (volumetric) specific heat of the reaction mixture, and U is the overall heat transfer coefficient for heat exchange between catalyst and the furnace. It can be calculated based on heat transfer inside the tube, wall conductivity and convective as well as radiative heat transfer from the tube exterior to the furnace, for details see (Sarsani et al., 2017; Sun et al., 2018). An important point to note is τ_h is proportional to the tube diameter and decreases algebraically with increasing temperature, whereas the heat generation time, τ_g depends on the reaction kinetics (effective activation energy) and decreases exponentially with increasing temperature. This is the main reason for the difficulty in satisfying the hot spot criterion for highly exothermic and temperature sensitive (high E/R) reactions.

The actual heat loss time (Eq.4.2) and the required heat loss time (Eq.4.1) are estimated and compared in *Fig.*4.1 for a tube of 4 mm diameter, $\Delta T_{ad} = 900$ K (which is the typical value for oxidative coupling of methane with $CH_4/O_2 = 6$), and a first-order rate constant $k(T) = 4 \times 10^7 \exp(-10500/T) \text{ s}^{-1}$ (corresponding to La-Ce catalyst used in OCM studies, see (Sarsani et al., 2017)). A laboratory scale reactor may be considered to be isothermal if the actual heat exchange time



Figure 4.1: Comparison of the estimated heat loss time (solid line) of a typical laboratory scale reactor with axial hot spot criterion (dashed-dotted line). Also shown are 10% (dashed line) and 98.4% conversion lines (dotted line) of limiting reactant.($d_t = 4 \text{ mm}, \Delta T_{ad} = 900 \text{ K}$).

is about an order of magnitude smaller than that required by the hot spot criterion, and it may be considered as an adiabatic reactor when the actual heat loss time is order of magnitude greater than the heat loss time required by the hot spot criterion. The shaded areas in Fig.4.1 identify these regions. In the same figure, we have also shown the space time-furnace temperature curves corresponding to Damköhler number $Da = k(T_{fnc})\tau = 0.1$ (which corresponds to about 10% conversion of the limiting reactant) and Damköhler number Da = 4 (corresponding to conversion greater than 98.4% in the plug flow limit). The former of these curves defines the boundary for differential operation of the reactor while the latter defines the space time above which nearly complete conversion of the limiting reactant is attained. Examination of Fig.4.1 shows that isothermal operation with significant reactant conversion is possible only when the furnace temperature is very low and the space time is extremely high (and requiring unrealistically low flow rates and possible violation of other criteria such as the external transport limitations). The calculations in the figure also show that the operation of the reactor in this specific example is more likely to be in the mixed regime (neither isothermal nor adiabatic) over a substantial range of furnace temperatures and space times of practical interest. An important observation is that at higher temperatures, the reactor operation is closer to the adiabatic limit even for a small diameter tube. This example is used mainly to illustrate the practical difficulties in the design and testing of catalysts under near isothermal conditions for the case of highly exothermic reactions. It also provides the main motivation/justification for the analysis, understanding and interpretation of the ignition-extinction features of such laboratory scale reactors. [Remark: The example in *Fig.*4.1 also indicates that micro-reactors having tube diameters well below 1 mm may be needed to obtain close to isothermal operation in such cases.]



Figure 4.2: Schematic diagrams of laboratory scale reactors with the same volume of catalytic and inert sections packed in tubes of different diameters.

4.3 Description of Lab-Scale Catalytic Reactors

A schematic reactor setup of a laboratory-scale packed-bed reactor used in many partial oxidation reactions is shown in *Fig.*4.2. A quartz tube with small diameter is mounted in the furnace either vertically or horizontally with the furnace set at proper (set-point) temperature. Inert materials such as quartz chips are added in the fore and after sections to support the catalyst and to facilitate the heating of the inlet gas before it enters the catalyst bed. For illustration purpose, we have shown in *Fig.*4.2 two different ways of packing of the catalyst (A) and (B) having the same volume but in tubes of different diameters. We note that for a fixed volume of catalyst, the length of the catalyst bed is reduced by a factor *f*, when the interior diameter of the tube is increased by a factor \sqrt{f} . Even though both arrangements have the same volume of catalyst, for a fixed inlet volumetric flow rate (or space time), the various parameters (such as characteristic heat exchange time, heat and mass Peclet numbers) that determine the ignition and extinction behavior are different for the two arrangements.

As stated above, the focus of this work is on the impact of axial gradient and heat exchange between the reactor tube and furnace. Hence, the radial variations are ignored. This assumption may not be justified in the regions where the axial gradient is very strong, but it does not change the qualitative behavior. In most of the experiments, especially those designed for kinetic studies, fine powder catalysts with particle size of the order of $100 \,\mu m$ are used to minimize the impact of external and internal transport limitations. Thus, we assume that the average diameter of catalyst particle is small enough so that the inter and intra-particle temperature and concentration gradients can be neglected. We further assume that in a laboratory reactor with small length scale in all directions, the variation in physical properties and dispersion coefficients are small thus the average values can be used in the calculations. With these assumptions, a one-dimensional pseudo-homogeneous model, which is sufficient to capture the qualitative ignition-extinction behavior of lab-scale reactors is used in this work.

The steady-state species balance for pseudo-homogeneous model (with N reactions among S species), expressed in terms of mole fraction (or dimensionless concentration) of species j (y_j), is given by

$$\frac{\tau}{\tau_{M,j}}\frac{d^2y_j}{dz^2} - \frac{dy_j}{dz} + a(z)\tau \sum_{i=1}^N v_{ij}\widehat{r}_i(\overline{y},T) = 0; \quad j = 1, 2, .., S$$
(4.3)

while the energy balance may be expressed as

$$\frac{\tau}{\tau_H}\frac{d^2T}{dz^2} - \frac{dT}{dz} + a\left(z\right)\tau\sum_{i=1}^N \Delta T_{ad,i}\widehat{r}_i(\overline{y},T) - \frac{\tau}{\tau_h}(T - T_{fnc}) = 0; \qquad (4.4)$$

where a(z) is the activity profile

$$a(z) = \begin{cases} 0, & 0 \le z \le L_1/L \\ 1, & L_1/L \le z \le (L_1 + L_C)/L \\ 0, & (L_1 + L_C)/L \le z \le 1 \end{cases}.$$
(4.5)

Here, *L* is the total length of the packed reactor tube ($L = L_1 + L_C + L_2$) and τ is the space time based on total packed-bed volume ($\tau = L/\langle u \rangle$, where $\langle u \rangle$ is the average superficial velocity); T_f is the furnace set point temperature; v_{ij} and $\hat{r}_i(\bar{y}, T)$ represent the stoichiometric coefficient of species *j* in reaction *i* and the rate of reaction *i* (with units of reciprocal time). [Remark: \hat{r}_i is simply the reaction rate divided by the total concentration]. For a single step oxidation reaction with oxygen as the limiting reactant, the adiabatic temperature rise ΔT_{ad} may be expressed as:

$$\Delta T_{ad} = \frac{(-\Delta H_R)y^{in}}{\langle C_p \rangle \left(-\upsilon_i\right)},\tag{4.6}$$

where ΔH_R is the heat of reaction per mole of extent, y and y^{in} are the dimensionless concentration of limiting reactant (oxygen) in the feed, $\langle C_p \rangle$ is the average molar specific heat of the gas mixture and $(-v_i)$ is the stoichiometric coefficient of oxygen in the reaction. For multiple oxidation reactions, $\Delta T_{ad,i}$ for each reaction can be calculated by standard methods (Sarsani et al., 2017; Sun et al., 2018), and it is more convenient to write the heat generation term as $\sum_{i=1}^{N} \frac{(-\Delta H_{R,i})\hat{r}_i(\bar{y},T)}{\langle C_p \rangle}$ in Eq.4.4, where y_j and y_j^{in} are mole fractions. In the above formulation, $\tau_{M,j}$ and τ_H are the mass dispersion time of species j and the heat dispersion time, respectively. They can be calculated by the relations

$$\tau_{M,j}(\tau_H) = \frac{L^2}{D_{eff,j}(\alpha_{eff})},$$
(4.7)

where D_{eff} and α_{eff} are the effective mass and heat dispersion coefficients in the

bed, respectively. For a cylindrical reactor tube, the characteristic heat loss time τ_h is estimated by Eq.4.2 using the procedure outlined in (Sarsani et al., 2017; Sun et al., 2018). The model is completed by the boundary conditions

$$\frac{\tau}{\tau_{M,j}} \frac{dy_j}{dz} = y_j - y_j^{in} \ at \ z = 0,$$
(4.8)

$$\frac{dy_j}{dz} = 0 \ at \ z = 1,$$
 (4.9)

$$\frac{\tau}{\tau_H}\frac{dT}{dz} = T - T^{in} \quad at \ z = 0, \text{ and}$$
(4.10)

$$\frac{dT}{dz} = 0 \ at \ z = 1.$$
 (4.11)

We note that while it is convenient to use the total bed length in the formulation of the model, the reactor behavior depends mainly on the space time and dispersion times based on the length of the catalytic section. Thus, we define the space and dispersion times based on catalyst bed length

$$\begin{aligned} \tau_c &= \frac{L_c}{\langle u \rangle} = \tau(z_2 - z_1); \quad z_1 = \frac{L_1}{L}; \quad z_2 = \frac{L_1 + L_c}{L} \\ \tau_{M,cj} &= \frac{L_c^2}{D_{eff,j}}; \quad \tau_{Hc} = \frac{L_c^2}{\alpha_{eff}}, \end{aligned}$$

and the effective Peclet numbers

$$Pe_{eff,m,j} = \frac{\langle u \rangle L_c}{D_{eff,j}};$$
 $Pe_{eff,h} = \frac{\langle u \rangle L_c}{\alpha_{eff}},$

and use them while presenting and interpreting the results.

As noted in (Sarsani et al., 2017; Sun et al., 2018), in general, the characteristic heat loss time (τ_h) depends on tube diameter as well as the catalyst, furnace temperatures and other experimental conditions. Thus, the determination of the catalyst temperature and actual heat loss time is a trial and error procedure when experimental data are analyzed. For simplicity of analysis, here we use an average heat loss time that is independent of furnace and catalyst temperatures and directly proportional to the reactor tube diameter. Further, to reduce the number of parameters in the model, we restrict the analysis to cases in which the feed temperature is equal to the furnace temperature ($T^{in} = T_{fnc}$). This condition is usually satisfied in most laboratory scale reactors where there is either an inert packed or empty tube of sufficient length that heats up the incoming feed to the furnace temperature. [Remark: As discussed in the literature in the context of a CSTR (Balakotaiah & Luss, 1983), the case where $T^{in} \neq T_{fnc}$ may lead to more complex bifurcation phenomena than those discussed here for the common case of $T^{in} = T_{fnc}$].

4.3.1 Limiting Models

Before presenting any numerical calculations, it is helpful to look at some limiting cases of the above model. First, we note that when the characteristic heat loss time τ_h is much larger than the space time ($\tau_h \gg \tau$), we can drop the heat loss (exchange) term in the energy balance equation to obtain the model corresponding to the adiabatic limit. For this limiting case, the model can be simplified further by integrating the species and energy balance equations over the inert sections and applying the boundary (state variable and flux continuity) conditions. It can be shown that the existence of inert sections has no effect on the (steady-state) behavior of the system, in this adiabatic limit (as can be expected intuitively). The corresponding mathematical model may be obtained by replacing the dispersion and space times based on the length of the catalytic section (or simply ignoring the inert sections or setting their length to zero in the above formulation). We also note that in the adiabatic limit, the feed temperature plays the role of the furnace temperature.

The second limiting case of interest is obtained when $\tau_h \ll \tau$. In this limit (which is difficult to obtain in practice as discussed in the previous section), the reactor

is nearly isothermal ($T \approx T_{fnc}$) and the energy balance equation can be dropped. The species balances may also be simplified by ignoring the inert sections to obtain the isothermal axial dispersion model.

The third limiting case of interest is that corresponding to a very thin layer of catalyst sandwiched between inert sections. In this limiting case, the heat and species dispersion times within the catalyst bed can be much smaller than the space time (or the heat and mass Peclet numbers are much smaller than unity) and the reactor behavior can approach that of an ideal CSTR. We show in the next section that this limit can indeed be approached in laboratory scale reactors. [Remark: By proper choice of bed aspect ratio and range of space times, it is also possible to approach the adiabatic CSTR limit].

The fourth limiting case of interest is that in which the heat dispersion time is much smaller compared to the space time (due to a high conductivity bed, catalyst support and/or due to radiation effect at high temperatures) but the mass dispersion time is larger than the space time. This leads to the so called lumped thermal reactor (LTR) model (Sun et al., 2018). Again, we show in the next section that this limit can be approached in laboratory reactors in some range of space times for thin catalyst beds.

The final limiting case of interest is that of the plug flow model corresponding to the limit in which the heat and species dispersion times are much larger than the space time. As discussed by Balakotaiah (1996), this limit is practically very difficult to achieve in laboratory scale reactors in which heat effects are significant as the length of the catalyst bed needed to reach this limit is an exponentially increasing function of the adiabatic temperature rise. As shown in the next section, this limit may be approached by using very long catalyst beds, and/or high space velocities, and/or sufficient catalyst/feed dilution.

4.4 Adiabatic Analysis

As stated in the introduction, the main goal of this work is to examine the impact of reactor tube diameter, length of inert sections, catalyst bed aspect ratio, heat exchange time with the furnace, and the adiabatic temperature rise on the ignitionextinction behavior of laboratory scale reactors. In this section, we present the results of our computations for the case of a single reaction. For this purpose, we consider the methane dimerization reaction (in the oxidative coupling of methane)

$$2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O, \qquad \Delta H_r^0 = -177 \text{ kJ/mol}$$

as a representative (and highly exothermic) oxidation reaction. Further, we assume that the reaction is zeroth order in methane mole fraction (or methane is in excess) and first order in oxygen with rate constant $k(T) = 4 \times 10^7 \exp(-10500/T) \text{ s}^{-1}$. As outlined in a previous work (Sarsani et al., 2017), this simplified kinetic model is representative of the heat generation rate for La-Ce catalyst. We also note that this simplified one step reaction and kinetic model is sufficient to explain only the impact of various design and operating variables on the ignition-extinction behavior and cannot be used to predict product distribution (which will be illustrated in section 4.6).

4.4.1 Ideal Models and Operating Parameters

Before analyzing the impact of the various catalyst bed and reactor design parameters using the finite dispersion model, we firstly review and discuss the impact of the operating parameters on the ignition-extinction behavior of the limiting models (i.e. the CSTR model, the LTR model and the PFR model mentioned in section 4.3). This can be done by comparing the ignition and extinction loci of the limiting models in different operating parameter planes. The comparison of limiting models also provides physical insight on the impact of bed scale heat and mass dispersion on the ignition-extinction behavior, and thus leads to better understanding of the following discussions.

We show in *Fig.*4.3, a bifurcation diagram of reactor exit temperature versus inlet temperature for the above three ideal reactor models for a fixed ΔT_{ad} and τ .[Remark: The corresponding conversion χ is obtained by using the adiabatic invariant $T - T^{in} = \Delta T_{ad} \chi$.] As can be expected intuitively, the lumped thermal reactor model predicts the largest region of multiplicity while the PFR model displays no multiplicity [However, it shows parametric sensitivity where the temperature or conversion increases rapidly at some critical space time or inlet temperature and this point can be taken to be the point where both ignition and extinction coincide]. The impact of bed-scale heat and mass dispersion can be assessed by comparing the bifurcation diagrams of the three limiting reactor models. Comparing the curve of PFR model to that of LTR model shows that thermal dispersion moves both ignition and extinction points to lower feed temperature. Comparing the curves of CSTR and LTR models shows that the mass dispersion has negligible impact on ignition but can significantly influence extinction. [Remark: The bifurcation diagrams shown in *Fig.*4.3 remain qualitatively unchanged even if physical property variations are taken in account, and even the quantitative differences will be small].

The impact of reactor scale heat and mass dispersion and operating condition can be examined in different parameter spaces. In practice, the important operating variables are the feed temperature, space time and adiabatic temperature rise (which can be changed by adjusting the feed concentrations). Thus, we show the ignition-extinction loci of the limiting models (CSTR and LTR) in two of three operating parameters separately in *Fig.*4.4. The ignition loci of LTR are almost overlapped by those of CSTR for all three cases, while the LTR model always has a larger region of multiple steady-states (and hence autothermal operation) compared to that of CSTR. [The reason for the LTR model having a larger region of



Figure 4.3: Steady-state bifurcation diagrams of reactor exit temperature versus inlet temperature for the three ideal homogeneous reactor models. ($\tau = 10 \text{ ms}, \Delta T_{ad} = 900 \text{ K}$)

multiplicity compared to the CSTR is that mass dispersion lowers the average reactant concentration. For monotone kinetics, lower average concentration in the CSTR compared to LTR leads to lower reaction rate and hence smaller range of multiplicity.] *Fig.*4.4(*a*) shows the ignition-extinction locus in feed temperature – space time plane. For practical range of space times ($\tau \ge 0.1 \text{ ms}$) and with an adiabatic temperature rise of 900 K, multiple steady-states always exist for some range of feed temperatures. We also note that when feed temperature is below 400 K, the space time at ignition is unrealistically high, implying that initial heat input is needed to attain the ignited state. With a fixed adiabatic temperature rise, the region of multiplicity increases as feed temperature decreases or space time increases. The ignition and extinction loci move to lower space time as feed temperature increases. An important point to note is that for the values of catalyst activity and adiabatic temperature rise selected (which are typical for high temperature oxidations), an ignited steady-state exists and autothermal operation is feasible for space times of the order of milliseconds and feed temperatures around ambient values.

When the space time is fixed, the ignition-extinction behavior of the CSTR and LTR models is determined by the adiabatic temperature rise and feed temperature (*Fig.*4.4(*b*)). The region of multiplicity (or the range of the feed temperatures between ignition and extinction points) expands as the adiabatic temperature rise increases, as shown in *Fig.*4.4(*b*). For the space time selected (10 ms), both limiting reactor models predict that ignition-extinction behavior exists up to (the hysteresis point) at low values of adiabatic temperature rise ($\Delta T_{ad} = 246$ K for CSTR and $\Delta T_{ad} = 169$ K for LTR). The ignition locus is nearly independent of the adiabatic temperature rise, in contrast to the extinction locus. An interesting observation that follows from *Fig.*4.4(*b*) is that the operating temperature (which can be approximated by the sum of the feed temperature and adiabatic temperature rise) is nearly constant along the extinction locus for both CSTR and LTR models. (This observation is also true for autothermal operation as shown by Lovo and Balakota-iah (1992)). It is expected based on the assumption of nearly complete conversion of the limiting reactant at the extinction point.

A problem of considerable practical interest is the feasibility of autothermal operation with ambient feed (A detailed review and analysis of autothermal operation is provided in later discussions). Thus, it is of interest to examine the ignition and extinction locus in the plane of space time and adiabatic temperature rise with ambient feed temperature ($T_{in} = 300$ K). This is shown in *Fig.*4.4(*c*). An important



Figure 4.4: Comparison of steady-state adiabatic ignition-extinction loci of LTR and CSTR in different parameters spaces: (a) feed temperature versus space time ($\Delta T_{ad} = 900 \text{ K}$); (b) adiabatic temperature rise versus feed temperature ($\tau = 10 \text{ ms}$); (c) adiabatic temperature rise versus space time ($T^{in} = 300 \text{ K}$). 92

point to note here is that it is nearly impossible (for realistic space times) to observe ignition of an initially cold bed by increasing either the space time or inlet concentration of reactant (within practical limits). However, an ignited state can be established for space times lower than about 10 milliseconds for ΔT_{ad} greater than about 600 K, provided the bed is heated initially to the appropriate temperature and feed conditions are slowly adjusted (as in the case of all autothermal reactor start-up). Finally, we note that even with feed at ambient temperature, space times for autothermal operation could be lower than 1 ms provided ΔT_{ad} exceeds about 900 K. We note that this is the case with the two classical autothermal processes, namely, Andrussow and Ostwald. However, the catalysts used in these processes have even higher activity than that used to construct *Fig.*4.4.

4.4.2 Bed Aspect Ratio

As discussed earlier, in the adiabatic limit, the inert sections have no impact on the ignition-extinction behavior. However, the same volume of catalyst packed in tubes of different diameter leads to different reactor lengths (but at the same space time). The different catalyst bed aspect ratios result in different axial heat and mass Péclet numbers, which have a strong influence on the ignition-extinction behavior. We note that while both the heat and mass Péclet numbers vary with catalyst bed aspect ratio and space time, their ratio is nearly independent of space time and may be assumed to be constant. This ratio ($Pe_{eff,m}/Pe_{eff,h} = \alpha_{eff}/D_{eff,m}$) may be estimated to have a value of about 10 for most laboratory reactors but can approach 100 for highly conductive beds. Unless stated otherwise, in the calculations presented here, it is assumed that $D_{eff,m} = 10^{-4} \text{ m}^2/\text{ s}$, and $\alpha_{eff} = 10^{-3} \text{ m}^2/\text{ s}$, and these values are constant, independent of bed properties, flow conditions and temperature.

In the simulations, we fixed the catalyst volume at 50.265 mm^3 (= $\frac{\pi}{4}d_t^2 L_c$), and aspect ratios (bed length to diameter) of 64 ($L_c = 64 \text{ mm}$, $d_t = 1 \text{ mm}$), 8 ($L_c = 16 \text{ mm}$,



Figure 4.5: Adiabatic steady state ignition-extinction locus for catalyst beds with different packing aspect ratios but fixed catalyst volume (50.265 mm^3) and fixed catalyst contact time. ($\tau_c = 10 \text{ ms}$, $L_1 = L_2 = 0 \text{ mm}$).

 $d_t = 2 \text{ mm}$), $1(L_c = 4 \text{ mm}, d_t = 4 \text{ mm})$ and 1/8 ($L_c = 1 \text{ mm}, d_t = 8 \text{ mm}$) are used for comparison. *Fig.*4.5 shows the computed ignition and extinction locus for these aspect ratios and with a fixed and typical space time of $\tau_c = 10 \text{ ms}$ in the adiabatic temperature rise and furnace temperature plane. [Note: If the space time is fixed, then all adiabatic reactors of same bed length have the same ignition-extinction locus, irrespective of the diameter. However, if the flow rate and catalyst volume are fixed, then the reactor diameter increases as the bed length decreases. In giving

both bed length and aspect ratio, we have assumed the latter case applies]. We note that for the smallest aspect ratio of 1/8, the mass Peclet number may be calculated to be unity while the heat Peclet number is 0.1, and in this case, it may be shown that the computed ignition-extinction locus is very close to that of an ideal CSTR model. Further, for this case, multiple steady-states exist for any adiabatic temperature rise greater than $225 \,\mathrm{K}$ (which corresponds to CH_4/O_2 ratio greater than 23). Also, with an adiabatic temperature rise of $700 \text{ K} (CH_4/O_2 \approx 8)$, it is possible to obtain an ignited solution with furnace (or feed) at ambient temperature. The Peclet numbers increase (by a factor 16) as the tube diameter is reduced by a factor two, and though it is not clear from the figure, the extinction locus (and hysteresis point) moves in a non-monotonic way between aspect ratios 1/8 and 1, and to higher values of ΔT_{ad} as the aspect ratio increases beyond unity. The region of multiple solutions shrinks and moves to higher values of ΔT_{ad} at the highest aspect ratio of 64 (corresponding to heat Peclet number of 409.6 and mass Peclet number of 4096). The behavior shown in Fig.4.5 persists for other values of the space time, the main difference being, the region of multiplicity expands and moves to lower values of ΔT_{ad} and T^{in} as τ_c is increased and vice versa for decreasing τ_c .

Thus, even in the ideal adiabatic limit, the bed aspect ratio has a profound influence on the ignition-extinction locus. Further, it was shown that the behavior of very thin beds (aspect ratios smaller than 1/8) approaches that of a CSTR in some range of space times (where the effective Peclet numbers are below unity), while the largest region of multiple solutions is obtained for intermediate aspect ratios (and/or flow rates) corresponding to lumped thermal reactor model (where $Pe_{eff,h} < 1$ while $Pe_{eff,m} > 10$). In Fig.4.5, the lumped thermal limit is approached for bed aspect ratio between 1/8 and 1. The adiabatic plug flow reactor limit is much more difficult to attain and may be reached only for unrealistically long beds. For the parameter values used in Fig.4.5, this limit may be approached if $L_c > 64$ mm



Figure 4.6: Hysteresis loci of adiabatic packed-bed reactors with different contact times but same catalyst volume (50.265 mm^3) in the adiabatic temperature rise-bed aspect ratio plane. ($L_1 = L_2 = 0 \text{ mm}$).

and $\Delta T_{ad} < 900 \,\mathrm{K}$.

The boundary between unique and multiple solutions is defined by the hysteresis point where the ignition and extinction loci meet (see Fig.4.5). This boundary is shown in Fig.4.6 in the $L_c/d_t - \Delta T_{ad}$ plane for three values of the space time. For values of L_c/d_t and ΔT_{ad} below these curves, the reactor does not exhibit any hysteresis (ignition-extinction) behavior as the adiabatic temperature rise is too small or the bed aspect ratio is high so that there is insufficient thermal back-mixing. The following further observations can be made from these computations: (*i*) for small bed aspect ratios (very thin beds) the hysteresis locus approaches that of the ideal CSTR model, (*ii*) the hysteresis locus is not a monotonic function of the bed aspect ratio and exhibits a minimum at intermediate values of the aspect ratio, the minimum moving to lower aspect ratios and higher ΔT_{ad} as the space time is decreased, (*iii*) as stated earlier, for large aspect ratios, the bed length at which hysteresis disappears is an exponentially increasing function of ΔT_{ad} .

4.4.3 Bed Conductivity

Two interesting questions that arise in the context of thin bed (laboratory or full scale) adiabatic reactors are: (*i*) when does the behavior of the reactor approach that of an ideal reactor model? (*ii*) what is the impact of bed conductivity on the approach to the ideal limit(s)? We address these questions in this section by examining the extinction locus of adiabatic beds of finite aspect ratios and different effective bed conductivities.

*Fig.*4.7 shows the extinction locus (and the region of autothermal operation with ambient feed, which is the region above this locus) for the same volume of catalyst but with two different aspect ratios, 1/8 and 1, and also two different bed conductivities corresponding to α_{eff}/D_{eff} values of 10 and 100, respectively. The latter value corresponding to a bed effective thermal diffusivity $\alpha_{eff} = 10^{-2} \text{ m}^2/\text{ s}$ could be attained for highly conductive beds and/or due to radiative contribution to heat transfer at high temperatures or for monoliths with metallic substrates). The same figure also shows the extinction locus computed using the two ideal reactor models, namely that of CSTR (corresponding to $Pe_{eff,m} \ll 1$ and $Pe_{eff,h} \ll 1$) and the LTR model (corresponding to $Pe_{eff,m} \gg 1$ and $Pe_{eff,h} \ll 1$). The finite aspect ratio curves also mark (by the triangle symbols) the space times at which the effective heat or mass Peclet numbers take values of unity.

For bed aspect ratio of 1 (Fig.4.7.a), the extinction locus can be understood



Figure 4.7: Comparison of the adiabatic extinction loci of fixed aspect ratio catalyst beds (but different conductivities) with that of ideal models in the adiabatic temperature rise-catalyst contact time plane with ambient feed temperature. (a): $L_c = 4 \text{ mm}$, (b): $L_c = 1 \text{ mm}$. ($L_1 = L_2 = 0 \text{ mm}$, $T_{fnc} = T^{in} = 300 \text{ K}$).

by dividing it into three sections. In the first section corresponding to low and very low space times, the heat Peclet number $Pe_{eff,h} > 1$ and the mass Peclet number $Pe_{eff,m} \gg 1$. That is, both the heat (τ_H) and mass dispersion times (τ_M) are greater than the space time, and the extinction locus of finite dispersion model in this region is far from any ideal reactor model and is sensitive to the bed conductivity. In the second section, the heat Peclet number $Pe_{eff,h} < 1$ while the mass Peclet number $Pe_{eff,m} > 1$. The heat dispersion time is smaller than the space time while the mass dispersion time is still greater. In this case, the high conductivity bed approaches the LTR asymptote, which gives the largest region of autothermal operation. The lower conductivity bed also approaches the LTR asymptote but the extinction point is always above that of the high conductivity bed. In the third section, both effective heat and mass Peclet numbers are smaller than unity and the extinction locus of both beds approaches that of the CSTR asymptote.

For bed aspect ratio of 1/8 (*Fig.*4.7.*b*), the extinction locus of the finite dispersion model is generally bounded between the extinction loci of the two ideal models (CSTR and LTR) within the range of space times shown. In this case of thinner bed, the region of autothermal operation is larger. Also, the CSTR asymptote is at higher space times and the bed conductivity has very little influence on this asymptote within the range of space times of interest. The LTR model still bounds the extinction locus and may be reached at very small space times, outside the range of the computations.

4.5 Analysis of Non-Adiabatic Operation

4.5.1 Heat Exchange Time

As stated earlier, the heat exchange time between the furnace and the catalyst is a very important parameter that determines the ignition-extinction behavior. In packed-bed reactors with heat exchange, the temperature varies in both axial and radial direction. However, for small diameter lab-scale reactors, the length scale in radial direction is small and the catalyst or inert packing typically has much higher thermal conductivity than the gas, leading to higher effective radial conductivity (compared to an empty tube). We assume that the temperature drop is mainly at the reactor wall and the temperature within the catalyst bed is radially uniform. Thus, the external heat transfer term in the energy balance (Eq.4.4) is sufficient to qualitatively capture the impact of heat exchange with the furnace. The heat exchange time estimated by Eq.4.2 depends on various parameters and is typically in the range of a few milliseconds to 100 ms for lab scale reactors used in high temperature oxidations (Sarsani et al., 2017). Here, we make the approximation that the heat loss time τ_h varies only with the tube diameter, and then select several values within this typical range for qualitative analysis. [Remark: The heat exchange rate between reactor and the furnace is still position dependent due to the position dependent catalyst temperature].

Fig.4.8 shows the computed ignition-extinction locus in the furnace temperature and space time plane with a fixed adiabatic temperature rise of 800 K and with aspect ratios of 8, 1 and 1/8. We note that due to heat exchange with the furnace, the furnace temperature at extinction does not decrease monotonically with space time (as in the adiabatic case) but has a minimum and forms a closed loop in this plane. The reason for this is that when the heat exchange time is fixed (fixed reactor tube diameter and similar furnace conditions), larger space time results in more heat loss to the furnace, and quenching of the reactor. Equivalently, when the reactor temperature or exit conversion is plotted versus space time, an isolated branch (isola) with two extinction points exists, in addition to the low temperature, low conversion branch. The minimum in the extinction locus occurs at intermediate values of space time compared to the heat exchange time τ_h . For $\tau_c \ll \tau_h$, heat exchange is negligible and the ignition-extinction locus is close to that of the adiabatic limit (as expected intuitively), while for $\tau_c \gg \tau_h$, the reactor is close to



Figure 4.8: Steady-state ignition-extinction loci in furnace temperature-catalyst contact time plane for packed bed reactors with different aspect ratios. $(L_1 = L_2 = 0 \text{ mm}, \Delta T_{ad} = 800 \text{ K}).$



Figure 4.9: Steady-state bifurcation diagram of reactor exit conversion versus furnace tempeature. ($L_c = 16 \text{ mm}$, $L_1 = L_2 = 0 \text{ mm}$, $d_t = 2 \text{ mm}$, $\tau_h = 10 \text{ ms}$, $\tau_c = 30 \text{ ms}$, $\Delta T_{ad} = 800 \text{ K}$).

isothermal. The heat exchange causes the appearance of another ignition and extinction when the space time is comparable to the heat exchange time.

Fig.4.8 also shows that catalyst bed with higher aspect ratio has smaller region of multiplicity due to the larger heat exchange area. Another interesting observation from Fig.4.8 is the formation of a second loop in the extinction locus for beds with high aspect ratio. In this case, five steady-state solutions and 4 limit points may exist when the furnace temperature is varied. For example, in Fig.4.9 we plot a bifurcation diagram for the 16 mm long bed with a space time of 30 ms, all other parameters being kept at the same values. As the furnace temperature increases, the system ignites from the quenched branch (stable) to the ignited branch (stable) at the first ignition point IG1. There exists another stable branch in the middle with exit conversion over 90%. When four limit points exist, the second extinction point EX2 can be either to the left or to the right of the first extinction point EX1; for parameter values shown in Fig.4.9, it is to the left. When EX2 is on the right of EX1, the system quenches first to the middle branch and then to the quenched branch as furnace temperature decreases.

The formation of the extra stable branch is due to complex interaction between heat generation, heat exchange with the furnace and conduction along the bed. Fig.4.10 shows the temperature and conversion profiles corresponding to the two extinction points (EX1 and EX2 of Fig.4.9) as well as at points on the two ignited high conversion stable branches corresponding to a furnace temperature $T_{fnc} =$ 550 K. We note that at the first extinction point, the hot spot is at the reactor exit and it moves inside the bed as the furnace temperature is increased. At the second extinction point, the hot spot is near the front of the bed but with a lower peak temperature. In this case, the temperature along the bed also drops rapidly due to heat loss, and any further decrease in furnace temperature leads to a completely quenched state. This calculation slows that for longer catalyst beds the reaction zone may be confined to a small region near the inlet and temperature drop along the bed can be very large so that measuring the exit gas temperature does not give any useful information.

The ignition-extinction locus shown in *Fig.*4.8 may be used to explain the recently observed ignition-extinction behavior in laboratory scale testing of catalysts for oxidative coupling of methane (Zohour et al., 2013; Sarsani et al., 2017; Aseem,



Figure 4.10: Comparison of the axial temperature (a) and conversion (b) profiles along catalyst bed at extinction points (solid lines) and on the ignited branch with furnace temperature of 550 K (dashed lines). ($L_c = 16 \text{ mm}$, $L_1 = L_2 = 0 \text{ mm}$, $d_t = 2 \text{ mm}$, $\tau_h = 10 \text{ ms}$, $\tau_c = 30 \text{ ms}$, $\Delta T_{ad} = 800 \text{ K}$).



Figure 4.11: Steady-state bifurcation diagrams of exit conversion (a) and maximum catalyst temperature (b) versus average velocity for different furnace temperatures. ($L_c = 4 \text{ mm}$, $L_1 = L_2 = 0 \text{ mm}$, $d_t = 4 \text{ mm}$, $\tau_h = 20 \text{ ms}$, $\Delta T_{ad} = 800 \text{ K}$).

Jeba, Conato, Rimer, & Harold, 2018). In all these experiments, hysteresis behavior was observed as the furnace temperature was increased and then decreased after going past the point of ignition. We note that this observation (or lack of observation) of hysteresis depends not only on the catalyst activity (reaction kinetics) but also on other experimental variables such as tube diameter (bed aspect ratio), heat loss time, contact time and inlet concentrations. It will be extremely difficult to interpret the experimental observations (and determine the kinetic parameters) without a detailed understanding of the results shown here.

As noted in the literature (Balakotaiah & Luss. 1983), the bifurcation behavior becomes more complex when the furnace temperature is fixed and the flow rate or space time is varied in the experiments. Fig.4.11 shows plots of exit conversion and maximum catalyst temperature as a function of velocity (or flow rate) at three different furnace temperatures for a laboratory reactor with $\Delta T_{ad} = 800 \,\mathrm{K}$, $\tau_h = 20 \,\mathrm{ms}$, and catalyst bed depth of $4 \,\mathrm{mm}$. Here, the low velocity (or high space time) branches correspond to near isothermal conditions, where the conversion decreases as the gas velocity increases. However, as the gas velocity increases (or the space time becomes smaller than the heat exchange time), the conversion (and the catalyst bed temperature) increases with increasing flow rate until the blowout (extinction) point is reached. This unexpected behavior is mainly due to heat exchange and has been observed not only in catalytic partial oxidations (Sarsani et al., 2017) but also in monolith reactors used to carry out the methanation reaction (which is also a highly exothermic reaction), see Fukuhara et al. (Ratchahat, Sudoh, Suzuki, Watanabe, & Fukuhara, 2018). We note that if the flow rate is decreased after blowout, the same path is not retraced but ignition occurs at a different flow rate. Further, when the furnace temperature is lowered further, the high conversion and high temperature branch can become isolated as shown in *Fig.*4.12. In this figure, the exit conversion and maximum catalyst tem-



Figure 4.12: Steady-state bifurcation diagrams of exit conversion (a) and maximum catalyst temperature (b) versus average velocity for different packing aspact ratios ($T_{fnc} = 550 \text{ K}, \Delta T_{ad} = 800 \text{ K}$).

perature are plotted as a function of velocity for a low value of furnace temperature $T_{fnc} = 550$ K, and for three different bed aspect ratios. Here, the short bed with an aspect ratio 1/8 has an isola with two extinction points similar to that observed in a cooled CSTR (Balakotaiah & Luss, 1983). However, for the long bed with aspect ratio of 8, the isolated branch has six limit points (with two ignition and four extinction points). Further, though not shown in *Fig.*4.12, but can be seen from the cross-section of the bifurcation set shown in *Fig.*4.8, for other values of the furnace temperature, the long bed can have two isolas. Again, this unexpected behavior is due to the complex (nonlinear) interaction between convection, heat generation, dispersion (conduction) in the bed and heat exchange with the furnace. The occurrence of double isolas in fluidized bed reactors has been reported recently (Bizon, 2016).

4.5.2 Inert Sections

As discussed earlier, it is a common practice to add inert particles before and after catalyst bed in most lab-scale reactors. The presence of the inert section enhances the axial heat and mass dispersion and thus also strongly impacts the ignition-extinction behavior of the system. Since the inert materials such as quartz chips have similar thermal conductivity as catalytic materials, we make the assumptions that the inert sections and the active (catalytic) section have the same thermal conductivity for simplicity. We also assume that the fore and the after inert sections have the same length.

In *Fig.*4.13 we compare the bifurcation diagrams of exit conversion versus furnace temperature for packed-bed reactors with different inert section lengths when heat loss time and catalyst contact times are comparable. As the length of the inert section increases, the region of multiplicity decreases and the both ignition and extinction loci move to higher furnace temperatures. The impact of inert section also becomes weaker as its length increases. For this specific case, the hystere-



Figure 4.13: Steady-state bifurcation diagrams of exit conversion versus furnace temperature with various inert section lengths. ($L_1 = L_2$, $L_c = 5 \text{ mm}$, $\tau_h = 20 \text{ ms}$, $\tau_c = 20 \text{ ms}$, $\Delta T_{ad} = 800 \text{ K}$).



Figure 4.14: Axial tempeature difference between furnace and reactor bed (a) and reactant conversion profiles (b) under the same furnace temperature but with different length of inert sections. ($L_2 = L_1$, $L_c = 5 \text{ mm}$, $\tau_h = 20 \text{ ms}$, $\tau_c = 20 \text{ ms}$, $\Delta T_{ad} = 800 \text{ K}$, $T_{fnc} = 570 \text{ K}$).

sis behavior of the system changes only slightly as the length of the inert section increases from 5 mm to 10 mm. These results can be expected intuitively, as the presence of inert section enhances the axial heat dispersion in the tube, leading to higher heat losses in the fore and after sections of the bed. Because of the higher heat loss, the inert sections can reduce the hot spot temperature. This can be seen in *Fig.*4.14, in which the axial temperature difference ($\Delta T = T_{reactor} - T_{furnace}$) and conversion profiles under the same condition (at furnace temperature of 570 K in *Fig.*4.13) are compared for different length of inert sections. Reactor beds with shorter inert sections have sharper temperature profiles as well as greater differences between catalyst and furnace temperature. In this specific case, by adding inert sections of 5 mm, the hot spot temperature is reduced by around 200 K while the conversion at the exit only decreases slightly. For inert section lengths greater than 5 mm, the temperature difference ΔT at the entrance of reactor bed is close to zero. Increasing the inert section length beyond L_c only reduces the exit temperature while the temperature profile within the catalyst bed remains the same.

When heat loss time is much smaller than the catalyst contact time, the reactor approaches isothermal operation and the presence of inert section can lead to the disappearance of the region of multiplicity, as shown in Fig.4.15(a). [As stated earlier, when $\tau_h \ll \tau$ and τ_g , the operation is very close to isothermal]. In contrast, when the heat loss time is much greater than the catalyst contact time, the reactor is closer to adiabatic operation and the presence of inert section has little effect on the ignition-extinction locus, as shown in Fig.4.15(b).

4.5.3 Catalyst Dilution

When the catalyst particles are diluted by the inert particles in packed-bed reactors, the contact time increases while the amount of active sites of catalyst per unit reactor volume decreases. Thus, the ignition-extinction behavior of packed-bed reactors is also impacted by catalyst dilution. One such case is shown in Fig.4.16,



Figure 4.15: Steady-state bifurcation diagrams of exit conversion versus furnace temperature with various inert section lengths. (a): $\tau_h = 5 \text{ ms}$, $\tau_c = 20 \text{ ms}$, (b): $\tau_h = 20 \text{ ms}$, $\tau_c = 5 \text{ ms}$. ($L_2 = L_1$, $L_c = 5 \text{ mm}$, $\Delta T_{ad} = 800 \text{ K}$).

where bifurcation diagrams of maximum catalyst temperature versus furnace temperature are compared under the same volumetric flow rate. In case (a), inert and catalyst particles are packed separately with same length. In case (b), the catalyst is mixed with half the amount of total inert particles, while in case (c), all catalyst and inert particles are mixed uniformly. As expected, the dilution of catalyst particle results in high furnace temperature at ignition and extinction points, and it also reduces the region of multiplicity. For furnace temperatures below 700 K, the diluted catalyst beds also have lower maximum temperature. These observations are consistent with the fact that diluted catalyst bed has lower activity compared to the undiluted case.

However, as furnace temperature is increased beyond $700 \,\mathrm{K}$, the three maximum temperature curves intersect with each other and the diluted catalyst beds start to have higher maximum temperature compared to the undiluted one. This can be explained by the fact that when the furnace temperature is high, the reaction rate at the entrance is high enough to consume most of the reactant within a short length of the (diluted) bed. As shown in Fig. 4.17, after the limiting reactant enters the catalyst section, the conversion can approach 100% within $2 \,\mathrm{mm}$ to $3 \,\mathrm{mm}$ for all three cases. The heat released by the fast reaction and the presence of the heat loss together creates a peak of catalyst temperature close to the catalyst entrance. Further, for case (c), the thin reaction zone near the entrance reduces the heat loss to the furnace, resulting in a higher peak temperature. In contrast, in the undiluted or partial diluted cases where there is an inert section on either side of the reaction zone, there is more heat loss, resulting in a lower peak temperature. We note again that such behavior does not occur when furnace temperature is not high enough (for example, $T_{fnc} < 700 \,\mathrm{K}$ in this cases) or same length of inert section is always present before and after the catalyst section.



Figure 4.16: Steady-state bifurcation diagrams of maximum catalyst temperature versus furnace temperature with different catalyst dilutions but with constant $Da = k_0 \tau_c$. (a): $\tau_c = 20 \text{ ms}$, (b): $\tau_c = 40 \text{ ms}$, (c): $\tau_c = 60 \text{ ms}$. $(L = 5 \text{ mm}, \tau_h = 20 \text{ ms}, \Delta T_{ad} = 500 \text{ K})$.


Figure 4.17: Axial temperature and conversion profiles under the same furnace temperature but different catalyst dilutions and with constant $Da = k_0 \tau_c$. (a): $\tau_c = 20 \text{ ms}$, (b): $\tau_c = 40 \text{ ms}$, (c): $\tau_c = 60 \text{ ms}$. ($T_{fnc} = 750 \text{ K}$, L = 5 mm, $\tau_h = 20 \text{ ms}$, $\Delta T_{ad} = 500 \text{ K}$).

4.6 Selectivity Considerations in Multiple Reactions Case

So far, the analysis and calculations presented above are based on a single reaction with linear kinetics, which approximates the temperature sensitivity of the heat generation rate for most oxidation and other exothermic reactions. While the single reaction case is sufficient to understand the influence of various parameters on the ignition-extinction behavior, there are many practical cases in which the presence of hot spots can lead to undesired side reactions and hence loss of selectivity. Further, the additional heat released by the undesired reactions can also influence the ignition-extinction behavior as well as change in selectivity of the desired product. In this section, we illustrate this behavior using a three reaction global reaction network and kinetics that is representative of catalytic partial oxidations.

We consider a simplified model of catalytic OCM consisting of two parallel or competitive oxidation reaction pathways to form different oxidation products and one consecutive reaction pathway for deep oxidation of the primary C_2 product. Thus, we use the following three global reactions, which are generally accepted as the important reactions in catalytic OCM:

$$2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O, \qquad \Delta H_r^0 = -177 \text{ kJ/mol}, \quad (r.4.1)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \qquad \Delta H_r^0 = -802 \text{ kJ/mol and}$$
 (r.4.2)

$$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O, \quad \Delta H_r^0 = -1428 \text{ kJ/mol.}$$
 (r.4.3)

For this calculation, we assume that the reaction rates are first order in both methane and oxygen mole fractions and the kinetic parameters used in the simulation are listed in *Table* 4.1. [Remark: In the case of OCM, the desired methane dimerization reaction has higher activation energy than the deep oxidations. However, in many other catalytic partial oxidations, the undesired deep oxidation reactions

Reaction #	Frequency factor $k_0(s^{-1})$	Activation energy $E_i/R(\mathbf{K})$
r.4.1	$8 imes 10^6$	10500
r.4.2	3×10^4	4500
r.4.3	1×10^7	9000

Table 4.1: Kinetic parameters used in the 3 reaction global kinetic model

have higher activation energy than the desired reaction. This case can be treated similarly but interpretation of results will be different and it is not pursued here]. Also, for simplicity of calculation it is assumed that $D_{eff,m,j} = 10^{-4} \,\mathrm{m^2/s}$ for all species.

We illustrate first the effect of tube diameter (or characteristic heat exchange time τ_h) on the conversion of the reactants and selectivity of the products by considering the case of short contact time and lower adiabatic temperature rise (or higher methane to oxygen ratio) so that the region of hysteresis (if it exists) is very small. *Fig.*4.18 shows the computed methane and oxygen conversions as a function of the furnace temperature for varying values of the heat exchange time τ_h , ranging from zero (isothermal case) to infinity (adiabatic case). In the same figure, we also plot the dependence of the selectivity to the desired product (C_2H_6) and the undesired product (CO_2) as a function of the furnace temperature. We note that for each fixed heat loss time, the oxygen conversion approaches nearly 100%at higher furnace temperatures either immediately after ignition (near adiabatic or high values of τ_h) or more gradually (low values of τ_h). The methane conversion is a monotonic function of the furnace temperature at all values of τ_h , and it could be about two times larger in the adiabatic limit compared to the isothermal limit. The reason for this may be explained by the fact that at a fixed furnace temperature and higher value of τ_h (or larger tube diameters), the catalyst temperature is higher, which promotes the reaction of higher activation energy, which in this case is the dimerization, and which consumes more methane per mole of oxygen reacted than the deep oxidation reaction. Similarly, higher selectivity to C_2H_6 (or

lower selectivity to CO_2) is obtained with higher heat loss time. Again, the reason being higher activation energy for the desired dimerization reaction compared to the deep oxidation reactions. In this specific calculation, the selectivity to C_2H_6 under the adiabatic limit is around 30% higher compared to that under the isothermal limit. The simulations here indicate that packed-bed reactors with larger diameter (having larger τ_h) are preferred for catalytic OCM system for two reasons: (*i*) they have larger hysteresis region and are thus easier to reach the ignited branch with lower furnace temperature and provide higher per pass conversion of methane (*ii*) they provide higher reactant conversions and higher selectivity toward desired (C_2H_6) product on the ignited branch. The first of these observations is independent of kinetics while the second is due to kinetics (higher activation energy of the desired reaction).

Detailed temperature (or temperature difference between catalyst and furnace), reactant conversion and product mole fraction profiles at a furnace temperature of $T_{fnc} = 700$ K are shown in Fig.4.19 for various heat loss times. As the heat loss time increases from 2.3 ms to 100 ms, the maximum temperature difference between catalyst and the furnace increases from about 200 K to about 550 K with its position moving from the middle of the catalyst bed to the front part. In this case, it may be observed that even the smallest tube diameter $d_t = 2.3$ mm having $\tau_h = 2.3$ ms does not satisfy the hot spot criterion and hence the operation is neither isothermal nor adiabatic. We also note that as the heat loss time increases, the catalyst temperature at the bed entrance also increases, thus promoting reaction(s) of higher activation energy. This can lead to compositional changes at the entrance to the bed. In this specific case, with feed CH_4/O_2 ratio of 7.4, the ratio at the entrance to the catalyst bed increases from 7.7 to 9.1 (as the oxygen mole fraction decreases more rapidly than the methane mole fraction) as heat loss time increases. This locally high temperature and methane-rich conditions result in higher selectivity to



Figure 4.18: Steady-state bifurcation diagrams of methane (a), oxygen (b) exit conversion and ethane (c), carbon-dioxide (d) exit selectivity versus furnace tempeature with various heat loss times. ($L_c = 5 \text{ mm}$, $L_1 = L_2 = 5 \text{ mm}$, $\tau_c = 6 \text{ ms}$, $CH_4/O_2 = 7.4$).



Figure 4.19: Axial temperature (a), conversion (b), ethane mole fraction (c) and carbon-dioxide mole fraction (d) profiles with the same furnace temperature and various heat loss times. ($T_{fnc} = 700 \text{ K}$, $L_c = 5 \text{ mm}$, $L_1 = L_2 = 5 \text{ mm}$, $\tau_c = 6 \text{ ms}$, $CH_4/O_2 = 7.4$).

 C_2H_6 at catalyst entrance as shown in Fig.4.19(c). Also, the mole fraction or selectivity of C_2H_6 keeps increasing as the oxygen conversion or catalyst temperature increases and reaches a plateau slightly after where catalyst temperature reaches its maximum value. The mole fraction of CO_2 also increases along catalyst bed, however as shown in Fig.4.19(d), the exit CO_2 selectivity is not a monotonic function of the heat loss time due to the deep oxidation of C_2H_6 . [Note: Experiments show that the C_2 product selectivity exhibits a maximum when plotted as a function of catalyst or furnace temperature. The maximum is due to the occurrence of C_2 reforming reactions. The simplified kinetic model used here does not include these and other catalytic as well as homogeneous reactions that also play an important role in the oxidative coupling of methane. A more detailed analysis that includes multiple catalytic and homogeneous reactions is a topic of current investigation].

Fig.4.20 illustrates the impact of heat loss on multiple oxidations by comparing the ignition-extinction points and selectivity of C_2H_6 for two catalysts beds having same bed length and space time but different diameters (or heat exchange times), one being large (and closer to the adiabatic limit) while the second being small and where the heat loss time is comparable to the space time of 8 ms. We note that the ignited branch extends to much lower furnace temperatures for the larger diameter tube ($\tau_h = 70 \text{ ms}$) compared to the smaller ($\tau_h = 15 \text{ ms}$). Further, the C_2 product selectivity is always higher on the entire ignited branch in the former case compared to the latter.

Fig.4.21 illustrates the impact of bed aspect ratio on the extinction locus and product selectivity in adiabatic reactors in which multiple oxidation reactions occur. Here, we note that for the thinner bed, an ignited steady-state exists with methane conversion of 22%, oxygen conversion of near 100% and C_2H_6 selectivity of about 55% with ambient feed temperature (300 K). However, when the bed thickness is increased by a factor two at the same space time, only a quenched steady-state



Figure 4.20: Steady-state bifurcation diagrams of methane, oxygen exit conversion (a) and ethane, carbon-dioxide exit selectivity (b) versus furnace tempeature and with different heat loss times. ($L_c = 5 \text{ mm}$, $L_1 = L_2 = 5 \text{ mm}$, $\tau_c = 8 \text{ ms}$, $CH_4/O_2 = 4$).

(with practically zero conversion of the reactants and 100% CO_2 selectivity) exists for ambient feed temperature. The reactant conversions and C_2H_6 selectivity of the two beds approach each other when the feed temperature is higher than that corresponding to the extinction temperature ($T_{extinction}^{in} = 308.5 \text{ K}$) of the deeper bed. The conversion, bed temperature and product profiles are compared in *Fig.*4.22 for the two beds at $T_{extinction}^{in} = 308.6 \text{ K}$ for which an ignited state exists for both beds. We note that the temperature profile is more uniform for the shorter bed, while it is steep near the inlet region for the longer bed. Further, as the feed temperature is reduced (e.g. by 1 K), the reaction zone of the longer bed moves to the right and out of the reactor (blowout). We also note that for the shorter bed, the oxygen mole fraction at the bed entrance is about 12%, which indicates the upstream mixing or dispersion effect. In contrast, the oxygen mole fraction is 20% at the entrance to the longer bed. These comparisons clearly demonstrates the advantages of having shorter beds in creating and sustaining an ignited state in catalytic partial oxidations.

4.7 Region of Autothermal Operation

4.7.1 Heat Loss

The results presented above clearly indicate that the ignition-extinction behavior of laboratory scale packed-bed reactors is profoundly influenced by the tube diameter used (through heat exchange time and variation of the Peclet numbers), length of inert sections and catalyst bed aspect ratio. Further, as discussed above, in the context of catalytic partial oxidations, depending on the adiabatic temperature rise, inlet and coolant (furnace) temperatures, and reaction kinetics, there exists a range of space times over which multiple steady-states could exist. In practice, it is the location of the extinction point that is of interest as it determines the boundary of the region of autothermal operation. In this section, we determine



Figure 4.21: Adiabacit steady-state bifurcation diagrams of methane, oxygen exit conversion (a) and ethane, carbon-dioxide exit selectivity (b) versus furnace tempeature and with different aspect ratios. ($\tau_c = 12 \text{ ms}$, $CH_4/O_2 = 4$).



Figure 4.22: Axial temperature (a) and mole fraction (b) profiles with the same feed temperature but different catalyst bed lengths. ($T_f = 308.6 \text{ K}, \tau_c = 12 \text{ ms}, CH_4/O_2 = 4$).

this boundary for the special case in which the feed (and furnace) temperature is at ambient value, i.e., $T_{fnc} = T^{in} = 300 \text{ K}$. We also examine the impact of tube diameter and inert section length on this boundary and compare the model predictions with experimental results.

Recently, Sarsani et al. (2017) presented experimental data on the ignitionextinction behavior of laboratory scale reactors in which the highly exothermic oxidative coupling of methane was carried out. In these experiments, the tube diameters varied from $2.3 \,\mathrm{mm}$ to $34 \,\mathrm{mm}$, and the ignition-extinction behavior was observed by varying the furnace temperature as well as the space time. For the case of small tube diameters ($2.3 \,\mathrm{mm}$ and $4 \,\mathrm{mm}$), even with the more active La-Ce catalyst, these authors observed ignited (and isolated) branches only at furnace temperatures well above the ambient value. Only when larger tube diameters ($10.5 \,\mathrm{mm}$ and $34 \,\mathrm{mm}$) were used, they were able to demonstrate autothermal operation with ambient feed with a methane to oxygen ratio of about 4 (corresponding to an adiabatic temperature rise of $1150 \,\mathrm{K}$). We use the finite dispersion pseudo-homogeneous model presented in this work to compute the boundary of the region of autothermal operation and compare the same with the above cited experimental observations.

Fig.4.23 shows the results of the computation of the autothermal boundary in the plane of adiabatic temperature rise and space time, for a catalyst bed of depth 5 mm, tube diameter $d_t = 34 \text{ mm}$, and with fore and after sections of length 25 mm(as in the experiments reported in (Sarsani et al., 2017)), and with the assumption of a fixed $\tau_h = 75 \text{ ms}$. [In these calculations, the heat generation rate is again approximated by a single step oxidation reaction as in section 4 above]. For comparison, in the same figure we have also shown the same boundary for the adiabatic limit ($\tau_h = \infty$) and also for the case without inert sections. Also shown in this figure are photos of the reactor in the experiments at three different values of the space time (8, 16 and 24 ms). Of note here is the fact that the reactor quenched when



Figure 4.23: Left: Impact of heat loss and inert sections on the boundary of the region of autothermal operatrion (extinction locus) with ambient feed (furnace) temperature in the plane of adiabatic temperature rise-catalyst contact time. Right: Photograph of laboratory scale OCM reactors with ambient feed and catalyst contact time of 8 ms(a), 16 ms(b) and 24 ms(c). ($T_{fnc} = T^{in} = 300 \text{ K}$, $L_c = 5 \text{ mm}$, $L_1 = L_2 = 25 \text{ mm}$ when inert sections exist, $d_t = 34 \text{ mm}$, $\tau_h = 75 \text{ ms}$)

the space time was increased beyond 32 ms. The following observations may be drawn from the computations and the experimental results shown in *Fig.*4.23: (*i*) As expected, the heat loss has profound influence on the region of autothermal operation, shrinking it considerably (and completely eliminating it for lower values of ΔT_{ad}) (*ii*) The presence of inert sections also shrinks the region of autothermal operation. This result is also expected as the inert sections facilitate conduction in the axial direction and effectively increase the heat loss area (*iii*) The space times used in the experiments are marked in the diagram (points marked as (a), (b) and (c)), and show that the model predictions are in good agreement qualitatively (and also reasonable quantitative accuracy) with data (*iv*) As expected, the adiabatic part of the autothermal boundary (blowout or left extinction point) corresponding to space times less than an order of magnitude compared to the heat loss time is not significantly impacted by the heat losses.

When the calculations shown in Fig.4.23 are extended to smaller diameter tubes, we note that the feasible region of autothermal operation disappears or moves outside the range of interest (to very high values of ΔT_{ad} and/or very low values of space times, below 1 ms), which also explains the experimental observations.

The sensitivity of the extinction locus to heat loss from reactor is also an important consideration in the scale-up of autothermal reactors. Here, we extend the calculations in Fig.4.23 to reactors with large diameters. In this case, it is reasonable to assume that the heat loss time τ_h is proportional to the tube diameter (and independent of the temperature). Even with constant τ_h , the heat exchange rate between reactor and surroundings is position dependent as the catalyst temperature varies along the flow direction. Here, we choose some typical values of heat loss times that range from lab scale reactors (tube diameter about 34 mm) to larger reactors (with tube diameter of about 1 m) with 5 mm bed depth, and compute the extinction locus using the finite dispersion model. Fig.4.24(a) shows the bound-

ary of autothermal operation with ambient feed and surrounding temperature and with heat loss time τ_h from 75 ms to 2.25 s. The region of autothermal operation corresponds to the parameter values above the curve(s) in this figure. Due to the heat loss effect, the extinction locus goes through a minimum as the space time increases. The minimum point does not exist for the case of adiabatic operation. The location of the minimum point goes to higher space time and lower adiabatic rise as the heat loss time increases (as the system approaches the adiabatic limit). As explained in more detail elsewhere (Sarsani et al., 2017), the extinction at higher space times (to the right of the minimum) is due to heat loss through the reactor walls, while the extinction (blow-out) point to the left of the minimum is due to convective heat removal. Thus, when the space time (or flow rate) is varied, the ignited state is isolated with two extinction points for the same adiabatic temperature rise. This isola formation is a well known phenomenon in cooled reactors (Sarsani et al., 2017; Balakotaiah & Luss, 1983). We choose an adiabatic temperature rise of 900 K and plot the bifurcation diagram with space time as the parameter that is varied. As shown in Fig.4.24(b) and Fig.4.24(c), the isolated branches exist under different heat loss times. The steady-states on the upper part of an isolated branch are stable while those steady-states on the lower part are unstable. On the stable-isolated branch, the catalyst temperature is high and the reactant (oxygen) conversion is practically 100%. In all cases with isola, an un-ignited/quenched branch also co-exists under the same conditions. The quenched branch has practically 0% reactant (oxygen) conversion and the catalyst temperature is close to that of feed (coolant).

4.7.2 Catalyst Activity and Kinetics

We discuss and review briefly the impact of catalyst activity and reaction kinetics (specifically reaction order) on the extinction locus. It should be pointed out that these have already been addressed in the literature but in terms of dimensionless



Figure 4.24: (a) Comparison of the region of autothermal operation of the finite dispersion model for various heat loss times ($T_{fnc} = T^{in} = 300 \text{ K}, L = 5 \text{ mm}$); (b),(c) Plot of maximum bed temperature and exit conversion versus space time ($T_{fnc} = T^{in} = 300 \text{ K}, \Delta T_{ad} = 900 \text{ K}$).

parameters and in the context of hysteresis and multiplicity behavior, whereas the focus here is on the region of autothermal operation.

Fig.4.25(a) shows the boundary of the region of autothermal operation for catalysts of three different activities:

$$k_v(T) = 4 \times 10^7 \exp(-10500/T) \,\mathrm{s}^{-1},$$
 (4.12)

$$k_v(T) = 3.0 \times 10^{10} \exp(-23000/T) \,\mathrm{s}^{-1}, \text{ and}$$
 (4.13)

$$k_v(T) = 1.0 \times 10^{12} \exp(-12000/T) \,\mathrm{s}^{-1}.$$
 (4.14)

The first order rate constant for the first of these corresponds to a catalyst of intermediate activity (such as La - Ce catalyst used in OCM studies, see (Sarsani et al., 2017)). The second corresponds to a catalyst of lower activity (such as the $Mn - Na_2WO_4/SiO_2$ catalyst used in OCM studies) while the third corresponds to a hypothetical precious metal based catalyst (representative of the activity of the Pt - Rh gauzes used in classical autothermal processes or supported precious group metals (PGM) based catalyst used in catalytic after-treatment). Though the comparison in Fig.4.25(a) is qualitative, it shows that catalyst activity has a profound influence on the feasible region of autothermal operation and reactor productivity. For example, for ambient feed, the low activity catalyst requires space time of about a second while the highest activity catalyst requires only space times of microseconds. However, we note that while the observation is qualitatively true, the assumption of no inter and intra-phase gradients for the high activity catalyst is either not valid or requires extremely small particle size or washcoat thickness and inclusion of the inter and intra-phase gradients reduces the separation between the curves. Further, as shown below the autothermal boundary also moves to higher values of space time for beds with lower heat dispersion.

We note that autothermal operation on the ignited branch implies that the lim-

iting reactant (oxygen) concentration is very small (compared to that in the feed) and hence the dependence of the rate on the limiting reactant concentration is an important factor in the determination of the boundary of the region of autothermal operation. Depending on the reaction mechanism and/or the dominating reaction on the ignited branch, the apparent reaction order w.r.t oxygen can vary from less than unity to unity or more. Fiq.4.25(b) illustrates the impact of reaction order w.r.t oxygen on the boundary of the region of autothermal operation. This calculation leads to two important observations relevant to catalytic partial oxidations: (i) if the reaction order w.r.t oxygen at lower oxygen concentrations is below unity, the region of autothermal operation expands. For example, for ambient feed, the space time required could be an order of magnitude lower for a reaction of order 0.5 compared to a second order reaction [Equivalently, for a typical space time of $10 \,\mathrm{ms}$, the feed temperature required could be about 300 K lower] (*ii*) It is very important to have accurate kinetics at low to very low oxygen concentrations to assess the feasibility of autothermal operation and as shown in the next section, the selectivity of the desired intermediate products.

4.7.3 Bed Aspect Ratio

Since the extinction locus is a strong function of the bed scale thermal dispersion and a weaker function of the bed scale mass dispersion, both of which depend on the bed aspect ratio, the region of autothermal operation is also strongly impacted by the bed aspect ratio. We examine here the dependence of the autothermal region on the bed aspect ratio for fixed values of adiabatic temperature rise and space time. First, we note that for beds of small particles or monoliths with substrates of intermediate conductivity, the ratio of bed scale species to mass dispersion time τ_{Mj}/τ_H is about 10 (and could be as large as 100 for monoliths with high conductivity substrates). Thus, we fix this ratio at a typical value of 10, and show in *Fig.*4.26 the computed feed temperature at extinction as a function of bed



Figure 4.25: Comparison of extinction locus in the feed temperature and space time plane (a) for catalysts of different activity; (b) for different reaction orders with respect to limiting reactant (oxygen).

aspect ratio for three different space times using the finite dispersion model (with $\Delta T_{ad} = 900 \,\mathrm{K}$). As expected, the locus approaches that of the CSTR model for very small aspect ratios (thin beds) while it is non-monotonic and reaches a minimum for intermediate aspect ratios (shallow beds) corresponding to the LTR model. For very high bed aspect ratios, the extinction point moves to high feed temperatures and eventually disappears as the behavior approaches that of a PFR model [Remark: The calculations shown in *Fig.*4.26 assume that catalyst/reactor volume as well as space time (or volumetric flow rate) are fixed. Thus, reducing the bed depth (and increasing the bed diameter) not only expands the region of autothermal operation but also profoundly reduces the pressure drop. For example, the laminar contribution of the pressure drop term in the Ergun equation (or monolith channels with laminar flow) decreases as d_t^{-4} while the inertial contribution decreases even more strongly as d_t^{-6} . The main disadvantages of the large diameter shallow beds are related to flow distribution and transverse non-uniformities or instabilities].

4.8 Conclusions and Discussion

In this chapter, we have presented a comprehensive analysis of the impact of tube diameter (which relates to heat exchange time), catalyst bed aspect ratio and length of inert sections on the ignition-extinction behavior of laboratory scale reactors when the flow rate (space/contact time) or furnace temperature are varied experimentally. In addition to these experimental design and control variables, the observed ignition-extinction behavior also depends on the catalyst activity, reaction order (or reaction kinetics) as well as the adiabatic temperature rise (or concentration of reactants). The results presented here indicate that it is extremely difficult to obtain isothermal or near isothermal operation of laboratory scale reactors even in small diameter tubes (2 mm to 10 mm) for high temperature catalytic partial oxidation and similar highly exothermic reactions. In contrast, it is possible to select tube diameter, catalyst bed aspect ratio and operating conditions so that the reac-



Figure 4.26: Computed extinction loci showing the impact of catalyst bed aspect ratio on the region of autothermal operation.

tor operation is closer to adiabatic conditions, and in some cases closer to one of the ideal reactor models, namely CSTR or LTR models, in some range of space times. Thus, one main conclusion of this part is that it is a better practice to design laboratory scale reactors to emulate the more realistic (and scaled-up) case of adiabatic reactors, and relating the observed ignition-extinction features to the reaction mechanisms and kinetic parameters. [We also note that this approach is not practiced currently but hope that it will be in the future]. A second conclusion of this part of work is that even in adiabatic reactors, the catalyst bed aspect ratio has a profound influence on the region of autothermal operation as well as on the selectivity of intermediate products. In this respect, thin beds that lead to near uniform temperature over the entire bed are favored over longer beds that lead to strong axial temperature gradients. A third conclusion of this part of work is that the inert sections often used to hold the catalyst bed in place also influence strongly the region of autothermal operation, and only in the limit of very large tube diameters (or heat loss time much larger than the space time), where the operation is closer to the adiabatic limit, the influence of inert sections can be neglected. It is hoped that these observations provide practical guidelines for the design and operation of both laboratory and pilot-scale packed-bed catalytic reactors.

We now discuss some limitations and possible extensions of this work. As our main goal was to use the simplest model to explain all the observed qualitative features of laboratory scale packed-bed reactors, we have neglected the inter and intra-particle gradients as well as the radial temperature gradients. When these gradients become important (larger particles and/or more active catalysts and/or higher operating temperatures), the model has to be extended to include them and becomes a two-phase model. The bifurcation analysis of the two phase model along with the impacts of inter and intra phase gradients is presented in the next chapter.

Chapter 5 Scale-up and Autothermal Operation of Catalytic Packed-Bed Reactors for OCM

5.1 Preamble

It is a well known fact that open flow chemical reactors in which one or more exothermic (or autocatalytic) reactions occur may exhibit multiple steady-states (MSS), and the steady-state attained in a specific case (or experiment) depends on the start-up (or initial) conditions. The terms "autothermal reactor" or "autothermal operation" (AO) are used to describe the intentional operation of a reactor in the region of multiple steady-states. In AO, there is no heat addition to the reactor (except during start-up) and there is no intentional heat removal by cooling through reactor walls except for some minor heat loss to surroundings, and heat is removed mainly by convective flow using cold feed. The existence of MSS, and in particular, an ignited high conversion and high temperature steady-state (that may coexist with one or more partially ignited or guenched steady-states), is essential for AO. In practice, MSS (with an ignited state) may be generated by either forced (convective) heat exchange between reactants and products with internal heat exchange (which we shall refer to as autothermal operation of type I.a), external heat exchanger (type *I.b*), periodic flow reversal that traps the hot zone within the catalyst bed (type II) or sufficient heat conduction (or thermal back-mixing) within the reactor bed (type III). Schematic diagrams illustrating the three types of auto the rmal reactors are shown in Fiq.5.1. In AO, the ignited steady-state is attained by a proper start-up procedure in which the catalyst bed is initially heated to the appropriate temperature and the feed conditions are carefully varied so that no overheating of the catalyst or quenching of the reactor occurs. Classical examples of catalytic reactors with autothermal operation are the ammonia reactor (type

I.b), reverse flow reactor for destruction of volatile organic compounds (type *II*) and gauze reactors used in HCN synthesis (Andrussow process) and the Ostwald process for nitric acid manufacture by ammonia oxidation (type *III*). In general, the first two types are suitable for low to moderate adiabatic temperature rise (typically ΔT_{ad} in the range 10 to 200 K) while the third type for high adiabatic temperature rise (typically in the 200 to 1200 K range). Some well-known advantages of AO are: compact reactor (or minimal catalyst requirement), and/or operation with low (and possibly ambient) feed temperature, and/or high per pass conversion of limiting reactant, and/or high productivity, especially for highly active catalysts. It could be stated that AO is the best example of process intensification where the catalyst/reactor volume or productivity can be changed by one to three orders of magnitude (compared to near isothermal operation such as that in a cooled multitubular reactor). This chapter deals with the design and analysis of reactors for AO of type *III* in the context of oxidative coupling of methane. We give a brief historical review of multiple steady-states and autothermal operation before returning to the main topic.

The earliest observation of MSS dates back to Liljenroth (1918) in the context of ammonia oxidation on platinum gauzes while the earliest commercial processes using AO are the Ostwald and Andrussow processes (Hunt, 1958; Pirie, 1958). Thus, while autothermal reactor concepts are nearly a century old, the engineering science of AO was not developed until much later. In two classic papers Van Heerden (1953, 1958) examined the properties of adiabatic autothermic processes of type *I* and type *III* for the idealized case of a first-order exothermic reaction using idealized reactor and heat exchange (or conduction) models (e.g. ideal continuousflow stirred tank reactor, CSTR or plug flow reactor, PFR and tubular flow reactor with equal axial heat and mass dispersion coefficients). At present, the engineering science of AO of type *I* is well understood and is described in research and



Figure 5.1: Schematic diagrams illustrating the three main types of autothermal operation/reactors.

review articles (Lovo & Balakotaiah, 1992; Eigenberger & Ruppel, 2000) and textbooks (Froment, Bischoff, & De Wilde, 2010). Though the first patent on AO of type *II* was issued in 1938 (Cottrell, 1938), the engineering science and scaleup principles were developed much later through the work of Boreskov and Matros (Boreskov, Matros, & Kiselev, 1979; Boreskov & Matros, 1983) as well as many other researchers(Eigenberger & Nieken, 1988; Bhatia, 1991; Khinast & Luss, 1997; Kolios, Frauhammer, & Eigenberger, 2000).



Figure 5.2: Plot of reactor operating temperature versus space time for some industrial catalytic processes. (Adapted from Schmidt, 2004)

The main goal of this chapter is on reactor design and scale-up for autothermal operation of type *III* with specific focus on oxidative coupling of methane. We note that AO of type *III* is fundamentally different from the other two types in the sense that the former is not feasible for longer beds with negligible bed scale heat backflow or conduction (in the homogeneous limit). Further, the contact (space) time for AO of type *III* is usually in the range of 10^{-4} to 10^{-1} second (with typical value being about a few milliseconds) while for types *I* and *II*, it is usually greater than a second. This is illustrated in *Fig.*5.2 (which is adapted from Schmidt (2004)). This figure shows the space times and operating temperatures for some commer-

cial catalytic processes. As can be expected (based on the temperature dependence of the reaction rates), this figure shows that for high temperature processes (T > 400 °C), the space time decreases (exponentially), and is below a second. We also note that when the operating temperatures and space times are in the range (600 - 1200 °C) and ($10^{-4} - 10^{-1} \text{ s}$), respectively, it is not possible to remove heat through reactor walls by cooling due to limitations either on the reactor materials, and/or heat transfer fluids and/or heat exchange times. High temperature catalytic oxidative coupling of methane that falls into this category is the focus of this chapter.

In this chapter, we illustrate autothermal reactor design for the specific example of Oxidative Coupling of Methane (OCM) for which the adiabatic temperature rise is very high (600 to 1200 K) and it is impractical to design a multi-tube reactor with heat removal. We show that AO is possible with shallow-bed or "pancakereactor" for practical range of methane to oxygen ratios. We show that for a fixed adiabatic temperature rise and space time, the largest region of AO (measured by the difference between feed temperature at ignition and extinction) is obtained in the homogeneous limit (no inter and intra-particle gradients) and when the heat Peclet number approaches zero, mass Peclet number approaches infinity, and no heat loss (adiabatic case). From a practical point of view, this leads to a reactor design which is a thin and high conductivity bed with small particles (or if we use a monolith, a thin disk made-up of high conductivity substrate and properly chosen channel and washcoat dimensions). We also present some novel results on AO with longer beds (and any bed scale heat Peclet number) by using larger particles leading to multiple solutions at the particle level. However, when the particle size exceeds some critical value, intraparticle concentration gradients can reduce the effective activation energy and can eliminate the particle level multiplicity. In practice, intraparticle gradients can be avoided by using eggshell type catalyst, or for

the case of monoliths, using appropriate washcoat thickness. We discuss the impact of particle size, catalyst layer thickness and other bed properties on the region of AO. We also examine selectivity to C_2 products on the ignited branches in both cases of reactor level ignition and particle level ignition. With reactor level ignition, the formation of C_2 products is favored when both heat and mass Peclet number approaches zero (or very thin bed). With particle level ignition and in the external heat and mass transfer controlled region, the locally high CH_4/O_2 ratio at particle surface could lead to high C_2 products selectivity.

Since the optimum point of operation of all autothermal reactors falls on the ignited branch close to the extinction point, the determination of the location of the extinction point, which defines the boundary of the region of autothermal operation and greatly impacts the product distribution (as will be shown in the later discussion), is an important step. In the next section, we introduce and analyze the global kinetic model (Stansch, Mleczko, & Baerns, 1997) we used in the calculations in this chapter. In section 5.3 we present the ignition-extinction analysis of catalytic OCM in homogeneous limit with respect to various design and operating variables and discuss their impacts on the C_2 products selectivity. In section 5.4 we analyze autothermal operation of OCM reaction with inter-phase heat and mass transfer resistances and intra-phase concentration gradients. In the last section, we propose some feasible reactor designs for scale-up of the OCM process and then summarize the results of our analysis along with a discussion of some practical aspects of reactor scale-up for various systems.

5.2 Reaction Scheme and Kinetics

For discussion in this chapter, we refer to the recent literature on the calculation of ignition and extinction loci using ideal reactor (PFR, CSTR and LTR) models using global kinetics for OCM without catalyst as well as detailed micro-kinetic models that couple the homogeneous and catalytic chemistries (Sun et al., 2018;

Lengyel & West, 2018; Vandewalle, Lengyel, West, Van Geem, & Marin, 2019; Vandewalle, Van de Vijver, Van Geem, & Marin, 2019). Our main objective here is to demonstrate the feasibility of autothermal operation for beds of finite aspect ratio, examine the impact of inter and intra-phase gradients and examine the selectivity of the intermediate products. For this purpose, we use a ten reaction global kinetic scheme developed and validated by Stansch et al. (1997) for the La_2O_3/CaO catalyst. This scheme consists of three groups of reactions as follows:

(*i*) Primary oxidation reactions

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \ \bigtriangleup H^0_R = -802.3 \,\text{kJ/mol}$$
 (r.5.1)

$$2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O, \ \triangle H_R^0 = -175.7 \,\text{kJ/mol}$$
 (r.5.2)

$$CH_4 + O_2 \rightarrow CO + H_2 + H_2O, \ \triangle H_R^0 = -277.4 \,\text{kJ/mol}$$
 (r.5.3)

(ii) Secondary oxidation/oxidative dehydrogenation reactions

$$CO + 0.5O_2 \rightarrow CO_2, \ \triangle H^0_R = -283.0 \,\text{kJ/mol}$$
 (r.5.4)

$$C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O, \ \triangle H_R^0 = -105.7 \,\text{kJ/mol}$$
 (r.5.5)

$$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O, \ \triangle H_R^0 = -757.2 \,\mathrm{kJ/mol}$$
 (r.5.6)

(*iii*) Dehydrogenation/Reforming reactions

$$C_2H_6 \rightarrow C_2H_4 + H_2, \ \Delta H_R^0 = 136.2 \,\mathrm{kJ/mol}$$
 (r.5.7)

$$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2, \ \triangle H_R^0 = 210.1 \, \text{kJ/mol}$$
 (r.5.8)

$$CO + H_2O \rightarrow H_2 + CO_2, \ \triangle H_R^0 = -41.2 \,\text{kJ/mol}$$
 (r.5.9)

$$H_2 + CO_2 \rightarrow CO + H_2O, \ \triangle H_R^0 = 41.2 \,\text{kJ/mol}$$
 (r.5.10)

[We note that reactions r.5.9 and r.5.10 may be written as a single reversible water-

gas shift reaction, but we listed them as in the work of Stansch et al. (1997). Similarly, the endothermic reactions r.5.7 and r.5.8 become reversible at high enough temperatures but this is not considered in this kinetic model]. The adiabatic temperature rise for the various oxidation reactions as well as the equilibrium temperature rise under different feed conditions (inlet temperature and methane to oxygen ratio) was calculated and tabulated in Sun et al. (2018). For example, with an ambient feed ($T^{in} = 300$ K and P = 1 bar), the adiabatic temperature rise for the primary coupling (dimerization) reaction r.5.2 varies from 1152 K (892 K, 729 K) to 621 K as the methane to oxygen ratio in the feed increases from 4.0 (6.0, 8.0) to 10.0. We note that r.5.7 is a homogeneous reaction while other reactions are coupled homogeneous and catalytic reactions. [Remarks: In the above kinetic model, the rates of all reactions are based on unit catalyst bed volume or mass. Separation of the homogeneous and heterogeneous contributions is not possible in the above global kinetic model. It is best to interpret it as a coarse-grained model over length scales that includes the combined effect].

The kinetic scheme of Stansch et al. (1997) is shown in *Table* 5.1 and *Table* 5.2. The values of kinetic parameters such as the frequency factors, activation energies and reaction orders of each species are also listed. In their experiments, kinetic parameters are validated for temperature range from 973 K to 1228 K, contact time range from 0.35 ms to 115.7 ms, oxygen partial pressure range from 1 kPa to 20 kPa and methane partial pressure range from 10 kPa to 95 kPa. Since this kinetic model is explained and discussed in the literature, we only bring out several key points relevant for autothermal reactor design. First, the inhibition effect of O_2 is only detected in methane dimerization reaction forming ethane (r.5.2) and high partial pressure of O_2 . Second, the methane dimerization reaction (r.5.2) has the lowest apparent reaction order with respect to oxygen partial pressure but the highest reaction order with respect to methane partial pressure (Table 5.2). A third

and very important observation is that the dimerization reaction has higher apparent activation energy than the deep oxidation and partial oxidation reactions (r.5.1and r.5.3). *Fig.*5.3 shows the comparison of reaction rate and apparent activation energy for the primary oxidation reactions (r.5.1, r.5.2, r.5.3) with partial pressure of $P_{CH_4}: P_{O_2}: P_{CO_2} = 95: 1: 4$ (as oxygen is the limiting reactant and its conversion on the ignited branch is high). The apparent activation energy is calculated using following equation as

$$\frac{E_a}{R} = \left[\frac{d\widehat{r}}{dT} - \frac{m+n+1}{T}\widehat{r}\right]\frac{T^2}{\widehat{r}},$$
(5.1)

where *R* is the gas constant, *m* and *n* are the reaction orders with respect to methane and oxygen and *r* is the reaction rate (with unit of s^{-1}). As the temperature goes up, the apparent activation energy of all three primary oxidation reactions decrease while the apparent energy of methane dimerization remains the highest one. As a result, the reaction rate of methane dimerization only becomes faster than that of deep oxidation and and partial oxidation of methane to *CO* as temperature increases. So the formation of the *C*₂ product is favored at high temperatures until the secondary oxidations and/or endothermic chemistry becomes important. Equivalently, there is an optimum temperature for obtaining the highest *C*₂ selectivity on the ignited branches.

To analyze the temperature dependence of this global kinetic model, we simulate the reaction system using isothermal PFR model with CH_4 to O_2 ratio of 8 in feed and space time of 10 ms (Fig.5.4). Due to the high activation energy of OCM, a temperature above 950 K is necessary to get over 90% conversion of the limiting reactant oxygen and over 10% conversion of methane. Also with temperature below 950 K, the dominant products are CO and CO_2 , the selectivity towards C_2 product is low (< 30%). In this temperature range (T < 950 K), selectivity towards CO starts with low values but reaches a local maximum of 59% at temperature



oxidation reactions in OCM. ($P_{CH_4}: P_{O_2}: P_{CO_2} = 95:1:4$)

around 830 K. As the temperature increases further, the formation of C_2 products becomes dominating. The maximum C_2 product selectivity is about 64.4% at 1088 K in isothermal PFR under the conditions used here. With even higher temperatures, the C_2 product decreases as the non-oxidative endothermic reactions (reforming, pyrolysis and water-gas shift) starts to dominate in the system. All the observations here are consistent with our previous calculations of the apparent activation energy. Although the exact product distribution may change with the feed condition and the reactor design, the optimum operation window for the OCM reaction is around 1050 - 1100 K temperature range for the La_2O_3/CaO catalyst used here. An ignited branch with high temperature is essential to activate the methane dimerization reaction, while the temperature should be carefully controlled to avoid the endothermic chemistries at even higher temperatures.

As a comparison, Fig.5.5 shows the simulation result of an isothermal CSTR model using the identical conditions as in Fig.5.4. The results of isothermal CSTR model and isothermal PFR model share some common features such as the temperature dependence of the product distribution: the deep and partial oxidation reactions dominate in low to moderate temperature range, the dimerization reaction becomes dominant at high temperatures while the endothermic chemistries becomes significant at even higher temperatures. The main differences between isothermal CSTR and isothermal PFR are the performance of C_2 product selectivity and the CH_4 conversion. The calculation result of the CSTR model shows much higher C_2 product selectivity comparing to that of PFR model, and the main component of C_2 product is ethylene instead of ethane. Under isothermal condition and with the same operating conditions, the only difference between these simulations is the extent of mixing. So the extra C_2 and ethylene selectivity is due to the combined impact of kinetics and bed level backmixing. As discussed previously (and also as shown in Table.5.2), the methane dimerization reaction (r.5.2) and the



Figure 5.4: Simulation results of exit methane and oxygen conversion (a), CO and CO_2 selectivity (b), C_2H_4 and C_2H_6 selectivity (c) and COx and C_2 product selectivity (d) in isothermal PFR reactor ($CH_4/O_2 = 8$, $\tau = 10$ ms).

ethane oxidative dehydrogenation reaction (r.5.5) have the lowest reaction order with respect to oxygen and are more favored than the other oxidation reactions in CSTR, due to the assumption of full species mixing in CSTR model results in much lower overall oxygen concentration in the reactor (we show more detailed discussions with finite dispersion model in the following section). The higher selectivity towards C_2 product then leads to higher CH_4 conversion by the stoichiometry of the reactions. In the OCM chemistry, the CH_4 conversion and C_2 selectivity are related by the stoichiometry. For example, the stoichiometry of the dimerization reaction (r.5.2) implies that 4 mol of CH_4 are consumed for each mole of oxygen



Figure 5.5: Simulation results of exit methane and oxygen conversion (a), CO and CO_2 selectivity (b), C_2H_4 and C_2H_6 selectivity (c) and COx and C_2 product selectivity (d) in isothermal CSTR reactor ($CH_4/O_2 = 8$, $\tau = 10$ ms).

reacted, while the deep oxidation reaction (r.5.1) shows that only 0.5 mole of CH_4 is consumed per mole of oxygen. Thus, if only these two reactions are assumed to occur and oxygen is completely consumed, the relationship between methane conversion (χ) and C_2 selectivity (S) is given by

$$\chi = \frac{4}{R_{mo}(8-7S)}; 0 \le S \le 1, R \ge 4$$
(5.2)

where R_{mo} is the methane to oxygen ratio in the feed. Thus, for any fixed R_{mo} , high C_2 selectivity also leads to high methane conversion [We note that $\frac{\partial \chi}{\partial S} > 0$ for all S and $\frac{\partial \chi}{\partial S}(S = 0.8) = \frac{4.86}{R_{mo}}$, which implies that around a base point of $R_{mo} = 4.86$ and

Table 5.1: Reaction rate expressions (Stansch et al., 1997)

$$\begin{bmatrix} r_{j} = \frac{k_{0,j}e^{-E_{a,j}/RT}P_{C}^{m_{j}}P_{O_{2}}^{n_{j}}}{(1+K_{j,CO_{2}}e^{-\Delta H_{ad,CO_{2,j}}/RT}P_{CO_{2}})^{2}}, j = 1, 3 - 6 \\ r_{2} = \frac{k_{0,2}e^{-E_{a,2}/RT}(K_{O_{2}}e^{-\Delta H_{ad,O_{2,j}}/RT}P_{O_{2}})^{n_{2}}P_{CH_{4}}}{[1+(K_{O_{2}}e^{-\Delta H_{ad,O_{2}}/RT}P_{O_{2}})^{n_{2}}+K_{j,CO_{2}}e^{-\Delta H_{ad,CO_{2,j}}/RT}P_{CO_{2}}]^{2}} \\ r_{7} = k_{0,7}e^{-E_{a,7}/RT}p_{C_{2}H_{6}} \\ r_{8} = k_{0,8}e^{-E_{a,8}/RT}p_{C_{2}H_{4}}^{m_{8}}p_{H_{2}O} \\ r_{9} = k_{0,9}e^{-E_{a,9}/RT}p_{CO_{2}}^{m_{9}}p_{H_{2}O} \\ r_{10} = k_{0,10}e^{-E_{a,10}/RT}p_{CO_{2}}^{m_{10}}p_{H_{2}}^{n_{10}} \end{bmatrix}$$

S = 0.8, every one point increase in selectivity also leads to one point increase in methane conversion].

These features of the kinetics used here (reaction orders with respect to oxygen concentration and activation energy various reactions) add up together to make the methane dimerization the most favored primary oxidation reaction on the ignited branch where the temperature is high. Finally, since methane dimerization reaction is the only primary oxidation reaction forming C_2 product directly from CH_4 in this kinetic scheme, the features outlined here are crucial when we are trying to design an autothermal reactor for OCM to obtain high C_2 product selectivity and high CH_4 conversion per pass. We first present calculations and discuss the case of packed bed reactors with small catalyst particles in the pseudo-homogeneous limit, and then discuss the C_2 product selectivity on an ignited single catalyst particle with external gradients (mass transfer controlled regime).

5.3 Analysis of Catalytic Oxidative Coupling of Methane in the Homogeneous Limit

In the previous chapter, we presented a preliminary analysis of the autothermal reactor design for OCM process, and discussed the impact of reactor aspect ratio (with the same reactor volume and space time and a fixed CH_4/O_2 ratio) and catalyst activity on the region of autothermal operation. The variation of the region of multiple steady-states due to the unequal heat and mass dispersion time
				```	,	,		
step	$k_{0,j}$	$E_{a,j}$	$K_{j,CO_2}$	$\Delta H_{ad,CO_2}$	$K_{O_2}$	$\Delta H_{ad,O_2}$	$m_{j}$	$n_j$
	$\frac{\text{mol}}{\pi \circ \mathbf{Po}^{(m+m)}}$	<u>kJ</u> mol	$\frac{1}{P_{a}}$	kJ mol	$\frac{1}{P_{a}}$	<u>kJ</u> mol		
1	$\frac{g \cdot s \cdot Fa}{0.00 \cdot 10^{-5}}$	40	$\frac{1a}{0.05 \cdot 10^{-12}}$	175	1 a	mor	0.94	0.76
T	$0.20 * 10^{-5}$	48	$0.23 * 10^{}$	-173			0.24	0.70
2	23.2	182	$0.82 * 10^{-13}$	-186	$0.23 * 10^{-11}$	-124	1.0	0.4
3	$0.52 * 10^{-6}$	68	$0.36 * 10^{-13}$	-187			0.57	0.85
4	$0.11 * 10^{-3}$	104	$0.40 * 10^{-12}$	-168			1.0	0.55
5	0.17	157	$0.45 * 10^{-12}$	-166			0.95	0.37
6	0.06	166	$0.16 * 10^{-12}$	-211			1.0	0.96
7	$1.2 * 10^{7}$	226						
8	$9.3 * 10^{3}$	300					0.97	0
9	$0.19 * 10^{-3}$	173					1.0	1.0
10	$0.26 * 10^{-1}$	220					1.0	1.0

Table 5.2: Kinetic parameters (Stansch et al., 1997)

was also examined. The largest region of multiple steady-states, or equivalently, the lowest feed temperature at the extinction point was obtained when the reactor approaches lumped thermal reactor asymptote. We also showed that higher selectivity towards  $C_2$  product was obtained when the reactors approaches very thin bed limit (CSTR). In this section, calculations are presented for a shallow bed using the finite dispersion model. The steady-state species and energy balances, together with the boundary conditions can be found in chapter 4. The partial pressures of the species are converted to concentrations by the ideal gas law ( $C_j = P_j/(RT)$ ) and the total pressure of feed gas is fixed at 1 atm. Here we use different effective mass diffusion coefficients of different species in the bed  $(D_{f,eff,j})$  depends both on the molecular diffusivity  $(D_{M,j})$  as well as convective contribution (depends on  $\langle u \rangle d_p$ ) to dispersion and these coefficients can be calculated by the expressions shown in the Appendix. The  $D_{M,j}$  is the binary gas phase diffusivity coefficient of species j in methane (methane is excess in the fluid mixture) and is calculated by Fuller equation (Fuller & Schettler, 1966). Similarly, the effective heat coefficient ( $\alpha_{s,eff,j}$ ) also depends on the solid phase thermal diffusivity  $\alpha_s$  and the convective contribution to the dispersion. In general, the molecular diffusion term  $(D_{M,j})$  and the interstitial dispersion term ( $\langle u \rangle d_p$ ) are of the same order of magnitude ( $10^{-4}m^2/s$ ), but with  $d_p \rightarrow 0$  or at low velocities the latter may be neglected. In this section, we keep  $d_p = 0.1 \text{ mm}$  for all calculations in pseudo-homogeneous limitation.

## 5.3.1 Limiting Models

For catalyst particles smaller than 40 mesh or about 0.42 mm, the characteristic inter-phase heat and mass transfer times are of the order of 100 microseconds, as shown in Table.5.3. These values are smaller than the typical operating space time of OCM reaction by about two orders of magnitude. Thus, the pseudo-homogeneous model limit can be reached when using catalyst particles below this size. In this pseudo-homogeneous limit, the ignition-extinction behavior is generated at reactor level due to bed scale heat and mass dispersion. The pseudo-homogeneous model has 5 key parameters, which are the space time  $(\tau)$ , the characteristic heat and mass dispersion times  $(\tau_H, \tau_{M,j})$ , the temperature of feed mixture  $(T^{in})$  and the composition of the feed mixture (or adiabatic temperature rise  $\Delta T_{ad}$ ). The number of parameters can be further reduced under limiting conditions. As discussed in the previous chapter, in the thin bed limit, the heat and mass dispersion times are much smaller then the space time, thus the pseudohomogeneous model can be simplified to the ideal CSTR model with algebraic equations. In the long bed limit, the heat and mass dispersion times are much larger than the space time and pseudo-homogeneous model can be reduced to the ideal PFR model. If the heat dispersion time is much smaller compared to the space time while the mass dispersion time is much greater than the space time, the pseudo-homogeneous model approaches the Lumped Thermal Reactor (LTR) model. It corresponds to perfect heat/thermal backmixing and zero species backmixing. The high bed effective conductivity may due to high conductivity catalyst support and/or combined conduction and radiation effect at high temperatures. In these ideal models, the extent of heat and mass backmixing is assumed to be zero or infinity, the ignition-extinction behavior of each model is only determined by the

operating conditions ( $\tau$ ,  $T^{in}$  and feed composition).

The steady-state behaviors of these three limiting models are compared in Fig.5.6 with  $CH_4/O_2$  ratio of 8 and and a space time of 10 ms. The exit temperature of PFR changes monotonically and continuously as feed temperature increases, while the CSTR and LTR show regions with multiple steady-states with respect to feed temperature. In this region of multiplicity, an ignited branch coexists with a quenched branch (and also an unstable solution branch in the middle) under the same feed temperatures. On the ignited branch, high reactor temperature and reactant conversion are maintained with lower feed temperatures (compared to the PFR limit) due to the backmixing effect in the catalyst bed, as shown in Fiq.5.6(a) and (b). Comparison of the PFR and LTR models shows that the backmixing of heat has strong impact on the region of multiplicity. Comparison of the CSTR and LTR results show that the backmixing of species also impacts on the region of multiplicity and the product distribution. The stronger mass dispersion lowers the average reactant concentration and hence lowers the reaction rate, which leads to smaller region of multiplicity in CSTR compared to LTR. However, as discussed in the kinetic analysis section, the lower oxygen concentration also favors the methane dimerization reaction and hence leads to higher  $C_2$  selectivity in CSTR limit compared to that of LTR limit and PFR limit (as shown in Fig.5.6(c)).

Comparisons between the limiting/ideal models shows the importance of the heat and mass backmixing for the ignition-extinction behavior and the product distribution. When ignition-extinction behavior exists, with proper start-up the system can be operated on the ignited branch with no heat supply at steady-state but still maintains high conversion and selectivity. The catalyst temperature is controlled by high velocity low temperature feed flow. For a given type of catalyst, like the  $La_2O_3/CaO$  catalyst used here, and with the assumption of thin bed limit, the region of multiplicity can be expanded in three ways by varying the operating condi-



Figure 5.6: Computed bifurcation diagrams of catalyst temperature, methane conversion and  $C_2$  product selectivity versus feed temperature for ideal homogeneous thin bed (CSTR model) limit, long bed (PFR model) limit and the Lumped Thermal Reactor (LTR) model. ( $CH_4/O_2 = 8, \tau = 10 \text{ ms}$ )



Figure 5.7: Computed ignition-extinction locus of the thin bed (CSTR) limit in the feed temperature-space time plane for different  $CH_4/O_2$  feed ratios.

tions. Fig.5.7 shows the ignition-extinction loci in the feed temperature-space time plane with reducing  $CH_4/O_2$  ratios. For a fixed methane to oxygen ratio in the feed, the region of multiplicity increases with increasing space time or with decreasing feed temperature. Although the ignition locus is not very sensitive to the  $CH_4/O_2$ ratio, the region of multiplicity can still increases as  $CH_4/O_2$  ratio decreases due to the thermal sensitivity of the extinction locus. Under adiabatic condition and for  $La_2O_3/CaO$  catalyst, an ignited branch can exist with ambient feed and with space time about 0.1 ms in the thin bed limit.

#### 5.3.2 Analysis with Finite Dispersion

## **Bed Aspect Ratio**

As shown in chapter 4, adiabatic reactors approaching the LTR limit have the largest region of multiplicity when exothermic reactions are dominating in the reactor. Fiq.5.8(a) shows one such example which compares the computed bifurcation diagrams of oxygen conversion as a function of feed temperature with different catalyst bed aspect ratios ( $\tau = 10 \,\mathrm{ms}$ , and  $CH_4/O_2 = 8$ ) using the finite dispersion pseudo-homogeneous model. Although the oxygen conversion on the ignited branches is practically 100% for all three catalyst bed lengths, the feed temperature at extinction point can be very different. As shown in section 2, under adiabatic condition, the region of multiplicity increases as the bed length decreases. The  $5\,\mathrm{mm}$  bed has an extinction feed temperature of  $571\,\mathrm{K}$  and thus has the smallest region of multiplicity compared to the other three cases. However, the change of extinction point with bed depth is non-monotonic, as can be seen for the case when the length of the catalyst bed is 2 mm. The extinction feed temperature of the 2 mmbed is slightly lower than that of  $1 \,\mathrm{mm}$  bed with the choice of parameter values. The reason is, for a  $2 \,\mathrm{mm}$  bed, the heat dispersion inside catalyst bed is small enough so that the temperature profile is close to uniform. However, the mass dispersion time is still large enough to create a sharp concentration profile in the catalyst bed. The  $2 \,\mathrm{mm}$  bed here is thus closer to the LTR asymptote while the  $1 \,\mathrm{mm}$  bed is closer to the CSTR asymptote. The exit temperatures of four bed depths are compared in Fig.5.8(b). On the quenched branch, the exit temperature increases linearly with feed temperature with a slope around 1. On the ignited branch, longer beds have higher exit temperature for the same feed temperature. With the same oxygen conversion (as shown in Fig.5.8(a)), the higher temperature of longer bed on the ignited branch is due to the different methane conversion, or the different product distribution resulting from the different methane conversion. This can be

explained more clearly by examining Fig.5.9, which shows the methane conversion and  $C_2$  product selectivity versus feed temperature, respectively, for the same set of parameters values used in Fig.5.8. Although the longer bed has higher temperature on the ignited branch, the corresponding methane conversion is lower and the  $C_2$  selectivity is also lower. These observations are self-consistent as reactions forming  $C_2$  products generally consume more methane but release less heat with the same oxygen conversion, while oxygen is the limiting reactant and is fully converted for all cases. The higher selectivity towards  $C_2$  product in shorter beds on the ignited branch may be explained by the mass dispersion inside the catalyst beds. The stronger mass dispersion results in lower overall oxygen concentration in shorter beds. As we mentioned before in the discussion of the kinetic scheme, the methane dimerization reaction, which is strongly favored with low oxygen concentration is thus more pronounced in the shorter beds. We also note that both methane conversion and  $C_2$  selectivity (on the ignited branch past the extinction point) continue to increase, reach a maximum and then decrease.

## Space Time

In practice, the space time is tuned by varying flow velocity ( $\langle u \rangle$ ) or by varying bed depth (*L*) and should be considered separately. Using lower flow rate with fixed bed depth or using longer catalyst bed with fixed flow rate leads to longer space time. However, they could have opposite impact on the extent of backmixing. A lower flow rate reduces the effective Peclet numbers ( $Pe_{m,eff} = \langle u \rangle L/D_{eff}$ ,  $Pe_{h,eff} = \langle u \rangle L/\alpha_{eff}$ ) and leads to stronger backmixing, whereas using a longer catalyst bed increases the effective Peclet number and results in weaker mixing effect.

**Flow Velocity** Fig.5.10(a) shows the adiabatic steady-state temperature at the reactor exit versus feed temperature, for a short bed of 2 mm depth and with in-



Figure 5.8: Calculated steady-state exit oxygen conversion (a) and exit temperature (b) versus feed temperature for catalytic OCM reaction on  $La_2O_3/CaO$  catalyst using adiabatic finite dispersion model for different bed depths. ( $CH_4/O_2 = 8$ ,  $\tau = 10$  ms)



Figure 5.9: Calculated steady-state exit methane conversion (a) and  $C_2$  product selectivity (b) versus feed temperature for catalytic OCM reaction on  $La_2O_3/CaO$  catalyst using adiabatic finite dispersion model for different bed depths. ( $CH_4/O_2 = 8$ ,  $\tau = 10$  ms)

creasing space time (decreasing flow velocity). Both ignition and extinction points move to lower feed temperatures as space time increases (or flow velocity decreases). However, the region of multiplicity increases as flow velocity decreases since the extinction points are more sensitive compared to the ignition points. The exit temperature on the ignited branch is also lower with lower flow velocity for the same feed temperature. Since the conversion of the limiting reactant, oxygen is practically 100% on the ignited branch for all flow velocities (and thus not shown) in this figure), the lower exit temperature on the ignited branch may be explained by the relative reaction rate of the deep and the partial oxidation reactions. With the same amount of oxygen converted, the partial oxidation reactions release less heat but consume more methane compared to the deep oxidation reactions. As a result, we can also observe higher methane conversion and higher  $C_2$  product selectivity with lower flow velocity under the same feed temperature, as shown in Fiq.5.10(b) and (c). A larger space time with lower flow rate enhances the bed level backmixing, and thus generates larger region of autothermal operation and favors the formation of  $C_2$  products.

**Bed Depth** When the flow velocity is fixed, the steady-state bifurcation diagrams with different bed depths are compared in Fig.5.11. Since both space time and heat (mass) Peclet number increase linearly with bed depth when the flow velocity is fixed, increasing the bed depth could have two fold impact on the ignition-extinction behavior of the reactor. When a region of multiplicity exist, a higher space time may lead to larger region of multiplicity when the exothermic reactions are dominating in the reactor (as shown in Fig.5.7). However, larger Peclet numbers could reduce region of multiplicity due to lower extent of backmixing (as shown in Fig.5.6). The actual region of multiplicity should depend on the relative impact of these two phenomena. As a result, the bed depth has relatively



Figure 5.10: Computed bifurcation diagrams of the homogeneous finite dispersion model with varying space time by flow velocity and with fixed bed length ( $CH_4/O_2 = 8$ , L = 2 mm)

weaker impact on the ignition-extinction behavior compared to that of flow velocity. Since the heat (mass) dispersion time have stronger dependence on the bed depth  $(\tau_M(\tau_H) = L^2/D_{eff}(L^2/\alpha_{eff}))$  compared to the space time ( $\tau = L/ < u >$ ). The reactor can still approaches PFR asymptote with fixed flow rate when the catalyst bed is long enough.

There are two important observations regarding the  $C_2$  selectivity from Fig.5.9(c)Fig.5.10(c) and Fig.5.11(c). The first observation is the location of the maximum  $C_2$  selectivity and the operation window (range of feed temperature) to get high  $C_2$ selectivity. The C2 selectivity is typically maximized slightly away from the extinction point on the ignited branch, and then decreases as feed temperature keeps increasing. As the flow velocity increases, this maximum point moves closer to the extinction point. If the velocity is too high, the  $C_2$  selectivity can reach maximum value at the extinction point, then keep decreasing monotonically on the whole ignited branch, the operating window to get high  $C_2$  selectivity is also very small with high flow rates. This could be explained by the catalyst temperature on the ignited branch. Under adiabatic condition, the heat generated by the reaction is removed convectively by the cold feed. Thus for higher flow rates, higher feed temperature is required at extinction point to maintain an ignited state and leads to higher catalyst temperature. If the feed/catalyst temperature is further increased on the ignited branch, the system quickly exceeds the optimum temperature for dimerization reaction and the deep oxidation reactions and non-oxidative reactions start to dominate. The second observation is that the maximum  $C_2$  selectivity is strongly impacted by the backmixing of mass in the catalyst bed. Comparison of the maximum  $C_2$  selectivity in Fig.5.9(c) Fig.5.10(c) and Fig.5.11(c) shows that the maximum C₂ selectivity generally decreases monotonically with increasing effective mass Peclet number ( $Pe_{m,eff} = \tau_M/\tau$ ). The stronger mass backmixing inside the catalyst bed leads to lower overall oxygen concentration, and the dimerization



Figure 5.11: Computed bifurcation diagrams of the homogeneous finite dispersion model with varying space time by bed length and with fixed flow velocity ( $CH_4/O_2 = 8$ ,  $\langle u \rangle = 0.5 \text{ m/s}$ ).

reaction is thus strongly favored compared to the deep oxidation reactions.

## Methane to Oxygen Ratio

As shown in Fig.5.7, the  $CH_4/O_2$  ratio in feed is an important operating parameter for the ignition-extinction analysis, since it determines the adiabatic temperature rise of the OCM system. Lower  $CH_4/O_2$  ratio in the feed leads to higher adiabatic temperature rise and thus larger region of multiplicity. Here we further discuss the impact of  $CH_4/O_2$  ratio on the  $C_2$  product selectivity and  $CH_4$  conversion for a bed with finite dispersion. Fig.5.12 shows the computed steady-state bifurcation diagrams with  $CH_4/O_2$  ratio from 4 to 12, with bed depth L = 2 mm and space time  $\tau = 10 \text{ ms}$ . Similar to the thin bed limit, the  $CH_4/O_2$  ratio or the thermal effect has minor impact on the ignition points but greatly impacts the extinction points. Lower  $CH_4/O_2$  ratio (higher adiabatic temperature rise) not only leads to larger region of multiplicity, but also leads to higher catalyst temperature at the extinction points, although the feed temperature required at the extinction point is reduced.

The corresponding  $CH_4$  conversion and  $C_2$  product selectivity are shown in Fig.5.12(b) and (c). With higher  $CH_4/O_2$  ratio, the  $C_2$  product selectivity is higher (under the same catalyst temperature) but the  $CH_4$  conversion is lower (and thus lower yield), the feed temperatures required at the ignited states are also higher. From a practical point of view, one important consideration here is the operating window to obtain high  $C_2$  selectivity. The higher adiabatic temperature rise with lower  $CH_4/O_2$  ratio leads to faster increases of catalyst temperature on the ignited branch. As a result, the  $CH_4$  conversion and  $C_2$  product selectivity also decrease faster after the maximum point. The operating window for optimum  $C_2$  selectivity is thus smaller with lower  $CH_4/O_2$  ratio.



Figure 5.12: Computed bifurcation diagrams of the homogeneous finite dispersion model with varying  $CH_4/O_2$  ratio in feed ( $L = 2 \text{ mm}, \tau = 10 \text{ ms}$ ).

# 5.4 Analysis of Catalytic Oxidative Coupling of Methane with Inter and Intra-Phase Gradient (Scale-up)

Prior modeling and experimental work has shown that when the adiabatic temperature rise is sufficiently high and/or catalyst activity is high and/or particle (or channel size) is large enough, ignition and extinction phenomena could occur at the catalyst particle (or in case of monoliths at the channel diameter) scale (Froment et al., 2010). Further, if all the particles in a packed bed reactor are ignited, the reactor operation is either in the external mass transfer controlled regime or combined pore diffusion and external mass transfer controlled regime. The mechanism for the existence of multiple steady-states at the particle level is due to inter-phase (solid to fluid) and intra-phase (within the catalyst) temperature and concentration gradients and is different (and independent) of that at the reactor scale heat and mass dispersion discussed in the previous section. This can be seen more clearly in monolith reactors with straight channels, where reactor level multiplicity is due to heat and mass dispersion along the length of the channel while the local multiplicity is due to radial (or transverse) gradients in the channel. Particle level (local) multiplicity was illustrated using two-phase models of catalytic reactors by Wicke and Vortmeyer (1959), Liu and Amundson (1962), Eigenberger (1972) and many others. The impact of inter and intra-phase gradients on the ignition (light-off) behavior of monolith reactors was illustrated by Ramanathan, Balakotaiah and West (2003). However, an analysis of the impact of inter and intra-phase gradients on the boundary of the region of autothermal operation (extinction locus) and  $C_2$  product selectivity in the OCM reaction has not been elucidated in the literature and is the focus of this section.

A schematic diagram of a packed-bed reactor with large catalyst particles is shown in Fig.5.13. The particles used can be either pure catalyst particles or



Figure 5.13: Schematic diagram of a parcked bed reactor with large catalyst particles and an eggshell catalyst particle with particle diameter of  $d_p$  and catalyst layer thickness of  $\delta_c$ .

eggshell type particles with catalytic layer and inert core. Inter phase gradients and intra particle gradients can exist around and inside the catalyst particle. The particle level ignition could occur if the inter phase gradients are strong, as shown by the red color particle in the figure. In order to illustrate the impact of inter and intraphase gradients on the OCM reaction, we use a two-phase cell model (Lapidus & Amundson, 1977; Becker, 1993) that assumes constant physical properties in gas phase. We also use the common assumption of negligible intraparticle temperature gradient (or uniform particle or washcoat temperature) but include concentration gradient. With the same notation as that used in the previous section, the cell model for the adiabatic case may be expressed as

$$C_{f,j}^{in} - C_{f,j} + \frac{\tau}{\tau_{mi,j}} (1 - \varepsilon_b) (C_{s,j} - C_{f,j}) + \tau \varepsilon_b \sum_{i=1}^N v_{ij} r_{g,i} (\overline{C_f}, T_f) = 0 \text{ ar(6.3)}$$

$$T_f^{in} - T_f + \frac{\tau}{\tau_{hi}} (1 - \varepsilon_b) (T_s - T_f) + \tau \varepsilon_b \sum_{i=1}^N (-\Delta H_{R,i}) r_{g,i}(\overline{C}_f, T_f) / C p_v = 0, \quad \textbf{(5.4)}$$

where the inter-phase heat  $(\tau_{hi})$  and mass  $(\tau_{mi,j})$  transfer times can be expressed in terms of the solid to fluid heat and mass transfer coefficients and interfacial area per unit volume as

$$\tau_{mi,j} = \frac{1}{k_{c,j}a_v} ; \tau_{hi} = \frac{Cp_v}{ha_v}.$$
(5.5)

where  $a_v$  is the ratio of catalyst surface area over catalyst volume ( $a_v = 6/d_p$  for spherical catalyst particle). The heat (*h*) and mass ( $k_{c,j}$ ) transfer coefficients are calculated using following expressions (Wakao et al., 1978, 1979):

$$\frac{k_{c,j}d_p}{D_{M,j}} = 2 + 1.1 (\frac{d_p \langle u \rangle}{\nu_f})^{1/2} (\frac{\nu_f}{D_{M,j}})^{2/3}$$
 and (5.6)

$$\frac{hd_p}{k_f} = 2 + 1.1 (\frac{d_p \langle u \rangle}{\nu_f})^{1/2} (\frac{\nu_f}{\alpha_f})^{2/3},$$
(5.7)

where  $\nu_f$  is the kinematic viscosity,  $k_f$  is the thermal conductivity and  $\alpha_f$  is the thermal diffusivity of fluid phase.

The species and energy balances for a particle may be written as

$$\frac{D_{eff,j}}{R^2} \left( \frac{d^2 C_{s,j}}{d\xi^2} + \frac{2}{\xi} \frac{d C_{s,j}}{d\xi} \right) + \rho_p \sum_{i=1}^N v_{ij} r_{s,i}(\overline{C}_s, T_s) = 0 \text{ and}$$
(5.8)

$$\frac{(T_f - T_s)}{\tau_{hi}} + \sum_{i=1}^{N} (-\Delta H_{R,i}) \left\langle \rho_p r_{s,i}(\overline{C_s}, T_s) \right\rangle / Cp_v = 0,$$
(5.9)

where  $D_{eff,j}$  is the effective intra-particle diffusion coefficient. The value of  $D_{eff,j}$  depends on various properties such as molecular structure, mean pore size and pore size distribution of catalyst particles. It can be smaller than the gas phase diffusivity by one to two orders of magnitude. Here we choose  $D_{eff,j}$  to be a tenth of gas phase diffusivity as a base case in most of our calculations. A parametric sensitivity study also is provided to show the impact of intra-particle duffusion

limitation on the ignition-extinction behavior. The  $\langle \rho_p r_{s,i}(\overline{C_s}, T_s) \rangle$  is the volumetric averaged reaction rate calculated using following expression as

$$\left\langle \rho_p r_{s,i}(\overline{C_s}, T_s) \right\rangle = \frac{\int_{(d_p - 2\delta_c)/d_p}^1 \rho_p r_{s,i}(\overline{C_s}, T_s) \,\xi^2 d\xi}{\int_{(d_p - 2\delta_c)/d_p}^1 \xi^2 d\xi}.$$
(5.10)

For an eggshell type catalyst particle,  $\xi$  is in the range from  $(d_p - 2\delta_c)/d_p$  to 1, where  $\delta_c$  is the catalyst layer thickness. For a pure catalyst particle,  $\delta_c = d_p/2$  so that  $\xi$  is in the range from 0 to 1. The boundary conditions for a catalyst particle:

$$\frac{dC_{s,j}}{d\xi} = 0, \text{ at } \xi = (d_p - 2\delta_c)/d_p \text{ and}$$
(5.11)

$$\frac{dC_{s,j}}{d\xi} = \frac{Rk_{m,j}}{D_{eff,j}} (C_{f,j} - C_{s,j}), \text{ at } \xi = 1.$$
(5.12)

The differential equations of particle species balances are discretized by the central difference method, 40 - 80 mesh points are used for a 1 mm catalyst particle (or 20 - 40 mesh points for 0.1 mm catalyst layer thickness). The volumetric averaged reaction rate is calculated by the trapezoidal rule. The final algebraic equation system is solved simultaneously together with the arclength equation using the continuation method. To reduce the numerical error due to discretization, multiple calculations are done for each case until there is no change in the computed result with increasing number of mesh points.

In addition to the dimensionless space time ( $\tau$ ), this model has two additional characteristic times, namely  $\tau_{mi}$  (interphase mass transfer time) and  $\tau_{hi}$  (interphase heat transfer time) and  $\tau_{ip}$  (intraparticle diffusion time). In general, these characteristic times depend on the catalyst particle, local flow conditions, temperature and operating pressure. These can be estimated based on the well established correlations for packed-beds and monoliths (Froment et al., 2010). We note

Table 5.3: Typical values of the inter and intra-particle characteristic times of oxygen for fixed flow rate (average velocity of 0.1m/s, temperature at 500 K and (1000 K), pressure of 1 atm and catalyst layer of 0.1 mm for eggshell particles

$d_p(\text{mm})$	$ au_{mi}(ms)$	$\tau_{hi}(\mathrm{ms})$	$ au_{ip}(\mathrm{ms})$ , full	$ au_{ip}(ms)$ , eggshell
0.5	0.2(0.1)	0.4(0.2)	1.3(0.4)	1.8(0.5)
1	0.9(0.3)	1.5(0.6)	5.1(1.5)	1.8(0.5)
2	3.2(1.2)	4.9(2.1)	6.1(20.4)	1.8(0.5)
4	10.5(4.2)	15.8(7.0)	81.6(24.3)	1.8(0.5)
8	34.0(14.4)	49.3(22.8)	326.5(97.1)	1.8(0.5)

Table 5.4: Typical values of the inter-particle characteristic times of oxygen for fixed particle size (particle diameter of 2 mm, temperature at 500 K and (1000 K) and pressure of 1 atm

< u > (m/s)	$\tau_{mi}(ms)$	$\tau_{hi}(ms)$
0.05	3.7(1.4)	6.0(2.4)
0.1	3.2(1.2)	5.0(2.1)
0.2	2.6(1.1)	4.0(1.7)
0.4	2.1(0.9)	3.1(1.4)

that depending on the particle (channel) size and other bed properties, these values could be smaller or larger than the space time and hence could influence the ignition-extinction behavior. A comprehensive bifurcation analysis of the above model is not available in the literature. Here we present a detailed discussion to demonstrate the autothermal operation of the OCM reaction with inter and intraphase gradients.

## 5.4.1 Analysis of Single Catalyst Particle

## **External Heat and Mass Transfer**

The computed inter-phase heat and mass transfer times for the limiting reactant oxygen (in methane-oxygen mixture at 1000 K) are shown in *Table.5.3* and *Table.5.4*. Similarly, the estimated intra-particle mass transfer (diffusion) times for full and eggshell type catalyst particles of different size are also shown. We note that the inter-phase heat and mass transfer time for particle sizes of practical interest (e.g. 2 - 4 mm) is of the same order of magnitude as the space time. (As can be expected from the heat and mass transfer correlations, for small particles,

the interphase transfer time increases quadratically with the particle size, while for larger particles it is proportional to  $d_p^{1.5}$ ). The standard correlations (Eqs.5.6 and 5.7) indicate that the diffusive and convective contributions to the external transfer become comparable as the particle Reynolds number approaches unity (and are equal at  $Re_p \approx 3.0$ ). For  $Re_p \ll 3$ , the particle to fluid heat and mass transfer phenomena are dominated by the diffusive contribution and hence the inter-phase transfer time is nearly independent of velocity, while for  $Re_p \gg 3$ , it decreases with velocity. As is well known, with finite inter-phase transfer time that is of the same order of magnitude as the characteristic reaction time, ignition (and extinction) could occur at the particle level. With particle level ignition, the reactor can be operated on the ignited branch. When all the particles in the bed are ignited, the reactor is in the external heat and mass transfer (or combined external mass transfer and pore diffusion) controlled regime. The catalyst temperature, limiting reactant conversion and product distribution in a shallow bed of finite size particles are greatly impacted by the properties of the catalyst pellet, number of layers and gas velocity or space time. We discuss the impact of these variables below in some detail.

**Particle Size** The steady-state bifurcation diagrams of a bed consisting of a single layer of catalyst particles of different size and with fixed flow velocity, are shown in Fig.5.14. An important observation is that the region of multiplicity increases with increasing particle size (specifically, the extinction point moves to lower feed temperatures). The solid phase temperature with larger particle is higher on the ignited branch. However, the fluid phase conversion is lower due to the stronger inter-phase resistance, as shown in Fig.5.14(b). As the particle size increases, the location (feed temperature) of the maximum  $C_2$  product selectivity moves to lower to lower the maximum selectivity value increases slightly, as shown in Fig.5.14(c). The change of the location and the maximum  $C_2$  product selectivity

are impacted by the catalyst temperature as well as methane to oxygen ratio at the particle surface, which in turn depend on the particle size and local fluid velocity. Since there is excess methane in the feed and the external mass transfer rate of methane is higher than that of oxygen, the methane to oxygen ratio at the surface of the pellet can be higher than that in the bulk fluid phase when the particle is ignited and is in the external mass transfer (or combined external mass transfer and pore diffusion) controlled regime. As the desired methane dimerization reaction has lower reaction order with respect to oxygen compared to the undesired reactions, higher methane to oxygen ratio at the particle surface could lead to higher  $C_2$  product selectivity.

**Flow Velocity** *Table*.5.4 shows the estimated external heat and mass transfer times for a 2 mm particle with increasing flow velocity. The flow velocity has weaker impact on external heat and mass behavior comparing to that of particle size. When the flow velocity is doubled, the external heat and mass transfer time are only slightly reduced (or the external heat and mass transfer rate is only slightly enhanced).

The steady-state bifurcation diagrams for single catalyst particle of 2 mm and for increasing flow velocity is shown in *Fig.*5.15. The region of multiple steady-state reduces as flow velocity increases due to a combined impact of shorter space time and faster external heat and mass transfer rate (shorter external heat and mass transfer time). Although a lower flow velocity results in lower external heat transfer rate (less heat removal rate from particle), the particle temperature on the ignited branch could be lower. The reason is that the lower flow velocity also leads to much higher space time and hence more heat could be transferred (removed) from solid to fluid phase. Due to the same reason, reducing the flow velocity also leads to lower external mass transfer rate, however, the oxygen conversion on the ignited



Figure 5.14: Bifurcation diagram of particle temperature, oxygen conversion and  $C_2$  product selectivity versus feed temperature for a fixed flwo velocity and for particles of different sizes. ( $CH_4/O_2 = 8$ , < u >= 0.1 m/s)



Figure 5.15: Bifurcation diagram of particle temperature, oxygen conversion and  $C_2$  product selectivity versus feed temperature for a fixed particle size and for different flow velocity. ( $CH_4/O_2 = 8$ ,  $d_p = 2 \text{ mm}$ )



Figure 5.16: Profiles of oxygen and  $C_2$  mole fractions within the catalyst particle at extinction point and at maximum  $C_2$  selecivity. ( $CH_4/O_2 = 8$ , < u > = 0.1 m/s)

branch increases due to the increasing in the space time. Fig.5.15(c) also shows that lower flow velocity also favor the formation of  $C_2$  product. This can be explained by the oxygen concentration in the fluid phase. The low oxygen concentration in bulk fluid phase leads to low oxygen concentration around the particle surface, which favors the methane dimerization reaction in the catalyst particle. Finally, the operating window to get high  $C_2$  product selectivity is also narrower for the cases with higher flow rates, due to the faster increase of particle temperature.

Before further discussion, an important point to note here is the utilization of large particles or the impact of intra-particle concentration gradients. Fig.5.16 shows the concentration (mole fraction) profiles of the limiting reactant  $O_2$  and  $C_2$ 

products at the extinction points and at points with maximum  $C_2$  product selectivity, for the steady-state bifurcation diagrams shown in Fig.5.14. At the extinction points, oxygen is fully converted within about 0.35 mm as it diffuses inside the catalyst particle (The dimensionless depths from the surface of the particle are about 0.70, 0.35 and 0.17 for the 1 mm, 2 mm and 4 mm particle, respectively). If the system is operated further on the ignited branch at the point with maximum  $C_2$  product selectivity, the depth of the reaction zone for the 2 mm particle is only about 10% of the particle radius (or outer layer of thickness 0.1 mm and about 29% of the particle volume is utilized). Also, in the OCM reaction, the formation of the  $C_2$  products is only favored when dimerization reaction is dominant, so the  $C_2$  selectivity can only increase before the full conversion of  $O_2$ . After  $O_2$  is fully converted inside the catalyst particle, the mole fraction of  $C_2$  products may be constant or gradually decrease depending on the operating conditions and particle size. These observations suggest that for this specific catalyst and typical operating conditions selected  $(CH_4/O_2$  ratio of 8, feed temperatures in the 500 to 600 K and space times of 10 to  $40 \, \mathrm{ms}$  and effective diffusivity that is about a tenth of the gas phase value), pore diffusional limitations become important on the entire ignited branch for particle diameters greater than about 0.7 mm (or mesh size about 25). This critical particle size reduces further as we move on the ignited branch and is about 0.2 mm(or mesh size about 70) at the point of maximum  $C_2$  selectivity. Since pore diffusional effects always reduce the selectivity of  $C_2$  products (as shown in *Fig.*5.18), eggshell type catalyst particles with outer thin catalyst layer and inner inert and/or high conductivity core can be a better choice for the catalytic OCM reaction.

To illustrate the impact of catalyst particle size (and external heat and mass transfer) at a fixed space time on the region of autothermal operation, we have plotted the steady-state bifurcation diagrams for a bed with a single layer of eggshell particles with only the outer 0.1 mm active layer in Fig.5.17. Here, the  $CH_4/O_2$  ratio



Figure 5.17: Bifurcation diagram of particle temperature, oxygen conversion and  $C_2$  product selectivity versus feed temperature for fixed space time.  $(CH_4/O_2 = 8, \tau = 40 \text{ ms})$ 

is again fixed at 8 and the base case corresponds to a 4 mm particle with the same flow velocity as in *Fig.*5.14. As expected, the exit  $CH_4$  conversion and  $C_2$  product selectivity for a 4 mm particle with a catalyst layer of 0.1 mm are nearly identical to the case of catalyst particle of full activity. Thus, the differences seen between particles of different size is mainly due to external heat and mass transfer effect. In this respect, we note that increasing the particle size (and hence the interphase heat and mass transfer time) increases the range of autothermal operation, specifically, very little change in the ignition point but much lower feed temperature at the extinction point. However, the reduced mass transfer rate has also reduced the conversion of oxygen and methane on the ignited branch though the selectivity to  $C_2$  products is about the same. More important, we note that while the extinction point moved to lower feed temperatures, the operating window (distance between the feed temperatures at extinction point and the point of maximum  $C_2$  selectivity) decreases with increase in particle size.

To summarize, the particle size has greater impact on the external heat and mass transfer time compared to the flow velocity. Using larger catalyst particles with fixed flow velocity results in larger external heat and mass transfer time and space time. Comparing to the space time, the external heat and mass transfer time have stronger dependence on the particle size and hence have stronger impact on the ignition-extinction behavior. Using lower flow velocity with fixed particle size also results in larger external heat and mass transfer time. But the external heat and mass transfer time have weaker dependence on the flow velocity compared to the space time. For single catalyst particle in external heat and mass transfer control regime, the flow rate has stronger impact on the operating window to achieve high  $C_2$  product selectivity whereas the particle size has stronger impact on the location or the feed temperature with maximum  $C_2$  product selectivity. Using higher flow rate leads to smaller optimum operating window, while the maximum

 $C_2$  product selectivity could be obtained with lower feed temperature when larger catalyst particle is used.

## Internal diffusion limitation

Other than external heat and mass transfer, intra-particle or pore diffusion limitation is also an important issue for catalytic OCM reaction. Depending on the mean pore size and pore size distribution of the catalyst pellet, the effective diffusivities in the porous catalyst can be smaller than the gas phase diffusivity by one to two orders of magnitude. In order to illustrate the impact of pore diffusion, we simulate the ignition-extinction behavior of bed with a layer of single eggshell particles with different effective internal diffusivities under same operation conditions. To show a base case with minimal intra-particle diffusion limitation, we assume the internal diffusivity is same as that in the gas phase. As shown in Fig.5.18, the region of multiplicity always shrinks and the the maximum  $C_2$  product selectivity always reduces as the pore diffusivity decreases. The operating window also become smaller with decreased pore diffusivity. With strong internal diffusion limitation, the point at which  $C_2$  product selectivity is maximized moves toward the extinction point and beyond some value, the  $C_2$  selectivity decreases monotonically on the ignited branch. Thus, internal or pore diffusional limitation not only reduces the region of autothermal operation but also reduces the  $C_2$  product selectivity, the design of the catalyst pellet to avoid pore diffusional effects should be an important aspect of the scale-up of the OCM reactors

#### 5.4.2 Analysis of Multi-Layered Shallow Beds with Eggshell Particles

In the previous case, same particle size and flow rate are used to keep the external heat and mass transfer time (and the extinction point) the same. However, the space time increases linearly with the number of the particle layers and the productivity of the reactor is reduced. In practice, it is of interest to know the impact of catalyst bed length at a fixed space time on the ignited branch. There are two



Figure 5.18: Bifurcation diagrams illustrating the impact of pore diffusion on particle temperature and  $C_2$  selectivity. ( $CH_4/O_2 = 8$ , < u > = 0.1 m/s,  $d_p = 4 \text{ mm}$ ,  $L_c = 0.1 \text{ mm}$ )



Figure 5.19: Computed ignited branch for a shallow packed-bed showing  $O_2$  conversion,  $CH_4$  conversion and  $C_2$  selectivity with different layers of eggshell type particles and with fixed velocity. ( $CH_4/O_2 = 8$ , < u > = 0.1 m/s,  $d_p = 4 \text{ mm}$ ,  $L_c = 0.1 \text{ mm}$ )



Figure 5.20: Computed ignited branch for a shallow packed-bed showing  $O_2$  conversion,  $CH_4$  conversion and  $C_2$  selectivity with different layers of eggshell type particles and with fixed particle size and spact time. ( $CH_4/O_2 = 8$ ,  $\tau = 40$  ms,  $d_p = 2$  mm,  $L_c = 0.1$  mm)



Figure 5.21: Computed ignited branch for a shallow packed-bed showing  $O_2$  conversion,  $CH_4$  conversion and  $C_2$  selectivity with different layers of eggshell type particles and with fixed flow velocity and space time. ( $CH_4/O_2 = 8$ ,  $\tau = 80 \text{ ms}$ , < u >= 0.1 m/s,  $L_c = 0.1 \text{ mm}$ )

ways to fixed the space time in a shallow bed reactor. In the first way, more catalyst layers are added but the flow velocity is also increased proportionately. The reactor productivity can hence be increased. In the second way, the number of particle layer should be increased (decreased) with decreasing (increasing) particle size and with the fixed flow velocity. We compared the reactant conversion and  $C_2$  product selectivity in separately in *Fig.*5.20 and *Fig.*5.21.

For the cases with fixed particle size and space time (Fig.5.20), the extinction point moves slightly to higher feed temperatures (by 25 K) due to the smaller external heat and mass transfer time with higher flow velocity (the total space time remains the same). As the number of particle layer increase from 1 to 4, the oxygen conversion reaches 100% while the difference in maximum exit  $CH_4$  conversion is negligible. The reason is that the  $CH_4$  conversion increases with the number of particle layers but decreases with lower  $C_2$  selectivity. The  $C_2$  product selectivity decreases due to higher oxygen concentration in gas phase (although the exit oxygen concentration is lower with higher flow velocity and more particle layers, the overall oxygen concentration in the bed is higher). Finally, the operating window to get high  $CH_4$  conversion and high  $C_2$  selectivity decreases as flow velocity increases due to the faster increase of particle temperature (as shown in Fig.5.15).

For the cases of fixed flow rate and space time (Fig.5.21), we note that having smaller particles moves the extinction point to higher feed temperatures but increases the methane and oxygen conversions, while the maximum  $C_2$  selectivity remains nearly constant. The operating window is also slightly reduced. Finally, we note that the results for a bed of four layers of 2 mm particles approach the homogeneous model limit for the same space time. This observation leads us to conclude that the best OCM reactor with catalyst pellets is a shallow bed consisting of a few layers of particles whose size is determined by the kinetic parameters of the specific catalyst.

Before closing this section, it should be pointed out that the above analysis ignored the variation of physical properties in transverse direction of catalyst bed, assumed uniform activity in the catalyst bed and was limited to 1-D two-phase adiabatic models. More detailed 2 and 3-D models that include these effects show the existence of transverse non-uniformities, especially when the operation is close to the extinction point (Balakotaiah, Christoforatou, & West, 1999; Viswanathan & Luss, 2008). However, it is possible to eliminate these transverse non-uniformities by operating (at some distance) away from the extinction point, minimizing the non-uniformities in bed porosity and activity, increasing the bed conductivity in the radial direction and/or by proper start-up conditions. Though some literature studies dealt with this topic (Viswanathan & Luss, 2008), a detailed analysis of transverse non-uniformities using 2 and 3-D models in the context of autothermal reactor stability is a subject for further investigation.

## 5.5 Autothermal Reactor Design for OCM

The discussion in this chapter leads to several main conclusions: (*i*) autothermal operation is feasible in the homogeneous limit (small particles) for thin beds (1 to 5 mm) for space times of the order of 10 ms for feed temperatures exceeding about 500 K and methane to oxygen ratios in the desired range (6 to 8). 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 70 to 80% range (with the actual value attained depending on other parameters), while the methane conversion is around 20%. Also, for the kinetics studied, thinner beds lead to better selectivity while there is an optimum bed thickness for attaining the largest region of autothermal operation (lowest feed temperature at extinction). (*ii*) AO is also feasible using beds with larger particles whenever particle level ignition could occur. However, the catalyst bed volume (or space time) in this case could be one order of magnitude larger than that in the homogeneous limit. The reason for this being lower



Figure 5.22: Schematic diagrams of some possible autothermal reactor designs for catalytic OCM. (a) Thin bed with small particles or high cell density monolith or gauze/fibermat/nano-fibers. (b) Shallow packed bed with larger (eggshell) catalyst particles. (c) Low cell density monolith with high conductivity substrate (coated or filled with catalyst particles).

heat generation rate per unit bed volume either due to intra-particle diffusion or inter-phase heat and mass transfer resistance or having egg shell eggshell catalysts. In this case, the catalyst particle size is in the usual range of 2 to 5 mm with active catalyst layer thickness of 100 to 200  $\mu$ m. (*iii*) Operation of the reactor with all particles ignited and in the external mass transfer controlled regime can lead to better selectivity of  $C_2$  products, while the presence of intra-particle diffusional effect reduces the selectivity. (*iv*) Strong intra-particle diffusion can severely reduce or even eliminate the region of autothermal operation, and this effect can be avoided by using eggshell catalysts with appropriate catalyst layer thickness.
We note that the  $La_2O_3/CaO$  catalyst is one among many studied for the OCM reaction. The activity of this catalyst is lower than that of other catalysts such as La - Ce or La - Sr but is higher than that of the more widely studied Mn - Ce $Na_2WO_4/SiO_2$  catalyst. Based on the observations and discussion above, we propose some potential autothermal reactor designs for OCM with catalysts of different activity. Schematic diagrams of these reactors are shown in *Fig.*5.22. As discussed above, for highly active catalysts, the best designs are those approaching the pseudo-homogeneous and thin-bed (LTR or CSTR) limit, such as thin catalyst beds with very small catalyst particles or high cell density monoliths or gauzes/fibermats/nano-fibers, arranged as a thin bed. The actual bed dimensions depend on the feed conditions, catalyst operating temperature and kinetics (which determines the selectivity) and are selected so that the lowest possible feed temperature and/or the highest  $C_2$  product selectivity and/or highest possible per pass methane conversion is attained. For catalysts with intermediate or low activity, larger catalyst particles or a monolith with lower cell density may be used in the reactor as autothermal operation with low feed temperature and high  $C_2$  product selectivity is still possible due to external heat and mass transfer control. However, to obtain acceptable reactant conversions, a slightly deeper catalyst bed with several layers of catalyst particles or longer monolith channels might be needed to get complete conversion of the limiting reactant. Further, in order to keep the reactor design close to the LTR asymptote, materials with high conductivity such as silicon carbide can be used as substrate to enhance the thermal conductivity (or heat backflow).

# Chapter 6 Summary and Suggestions for Future Work

### 6.1 Summary

In the first main part of this work, we have presented ignition-extinction analysis of gas phase oxidative coupling of methane using a simplified reaction network with global kinetics and three ideal reactor models (i.e. CSTR, LTR and PFR). The global kinetics involves various oxidation, pyrolysis and reforming reactions and is validated using both literature data and new data obtained under nearly isothermal condition. The results show that the exothermic oxidation (exothermic) chemistry dominates on the ignited branch near the extinction point, while the dehydrogenation and reforming (endothermic) chemistries dominate as the space time or feed temperature is increased. Further, the best ethylene yields are obtained on the ignited branch close to the extinction point while best  $C_2$  yields may be obtained at higher space times or feed temperatures. Three ideal models (CSTR, LTR and PFR) are used to analyze the ignition-extinction features of gas phase OCM reaction in the adiabatic limit. The ideal modes can be derived from the more general case of 1-D axial dispersion model, as shown in chapter 4. We show that the type of reactor used has profound influence on the width of the region of multiplicity and hence the ability to operate the reactor autothermally on the ignited branch. There is no hysteresis (or the width of the hysteresis region is zero) in PFR due to zero backmixing or dispersion in the flow direction. Whereas the lumped thermal model (LTR) with zero mass/species dispersion and perfect heat/thermal dispersion is shown to have the largest region of multiplicity. When the  $CH_4/O_2$  ratio is high, the ignition and extinction points may only exist at either high feed temperature and/or space time. However, it is possible to operate the OCM reactor on an ignited branch with feed at near ambient condition for practical range of space times

(1 ms to 1 s) for low  $CH_4$  to  $O_2$  ratios (e.g. 1.7 to 2.5). The result here indicates the feasibility and benefits of autothermal operation of OCM reactor. The large amount of heat supply and high space time can be avoided by running the reactor in the region of multiplicity on the ignited branch, while the productivity of the valuable  $C_2$  products is maintained. Thus, determination of this region of multiplicity (or region of autothermal operation) for more practical cases is desired for reactor design of OCM process.

A second result of this work is the ignition-extinction analysis of laboratory scale reactors with heat exchange to surroundings using a finite dispersion model. We show the impact of tube diameter (which relates to heat exchange time), catalyst bed aspect ratio and length of inert sections and catalyst dilution on the ignitionextinction behavior of typical packed bed reactors used in research for catalyst testing. Through the analysis in this part, we first conclude feasibility of limiting models in lab-scale experiments. When highly exothermic reactions are carried in laboratory scale reactors, it is very hard to obtain isothermal or near isothermal condition even in small diameter tubes (2 mm to 10 mm). The hot spot in catalyst bed could lead to misinterpretation of the experimental data. In contrast, it is possible to select tube diameter, catalyst bed aspect ratio and operating conditions so that the reactor operation is closer to adiabatic conditions, and in some cases closer to one of the ideal reactor models, namely CSTR or LTR models, in some range of space times. As a second major result of this work, we present the impact of heat loss, catalyst activity, kinetic and bed level heat/mass dispersion on the region of autothermal operation. We show that the inert sections often used to hold the catalyst bed in place can strongly reduce the region of autothermal operation, and this influence can only be neglected in the limit of very large tube diameters (large heat loss time) where the operation is closer to the adiabatic limit. Further, in the adiabatic limit and with the same catalyst volume, the catalyst bed aspect ratio could still influence the region of autothermal operation due to the bed level dispersion. Under this condition, the thin bed with near uniform temperature over the entire bed leads to the largest region of autothermal operation (LTR asymptote) where as a very thin bed with both uniform concentration and temperature within the catalyst bed leads to the CSTR asymptote. We also show that the region of autothermal operation can be greatly extended when more activity catalyst is used or when the reaction order with respect to the limiting reactant (oxygen) is below unity.

In the first two parts, the feasibility of autothermal operation of OCM reaction and the impact of various parameters on the region of autothermal operation are studied thoroughly. In the last part of this work, we presented ignition-extinction analysis of catalytic OCM reaction over a specific type of catalyst  $(La_2O_3/CaO)$ using a global kinetic model. The emphasis here is to investigate the product distribution, especially  $C_2$  product selectivity and methane conversion under autothermal operation condition. We also examined the cases where the catalyst particles are large enough such that the inter-phase heat and mass transfer resistance and intra particle diffusion limitation can not be neglected. In the homogeneous limit (small catalyst particles), the optimal bed depth may be determined by the selectivity considerations. The kinetic information on the ignited branches is also important in determining the optimal bed aspect ratio. For example, if the desired oxidation steps have lower apparent order with respect to oxygen compared to the undesired steps, very thin beds can lead to better selectivity of the desired product but may have smaller range of AO compared to the optimum bed depth (LTR asymptote). With larger catalyst particles, the particle level ignition could occur due to the strong inter-phase heat and mass gradients. The main advantage of creating interphase gradients is when the bed scale heat Peclet number cannot be made sufficiently small, in which case the two mechanisms can be combined to expand

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the region of AO. Another advantage is that the  $C_2$  products selectivity could be enhanced as the formation of  $C_2$  is favored by the high  $CH_4$  to  $O_2$  ratio in the mass transfer controlled regime. However, creation of interphase temperature gradients by using larger particles leads to higher reactor/catalyst volumes and higher space time at which heat loss may become significant. As result, the region of autothermal operation shrinks and the capital costs of the reactor could be higher. Further, for all positive order reactions on the ignited branch (low oxygen concentrations), intra-particle diffusion can severely reduce or even eliminate the region of autothermal operation (as well as influence the selectivity of desired products), and this effect can be reduced by using egg-shell type catalysts. Based on the discussion in this part, a best catalyst bed design for the OCM reaction could be a low cell density and high wall conductivity monolith that is filled with catalyst particles of smaller size, essentially emulating many parallel adiabatic channels with effective heat Peclet number less than unity. Such a design also minimizes the radial temperature variations and tendency to form transverse patterns.

### 6.2 Suggestions for Future Work

We now discuss some possible extensions of the results presented here. (i) In this work, we considered the bed level ignition and particle level ignition separately and investigated the impact of catalyst bed design and catalyst particle design on the ignition-extinction behavior and selectivity of desired products. In more practical cases, the two mechanisms, i.e. reactor scale heat backflow and interphase gradients, can be combined to design a reactor having a larger region of multiplicity (or autothermal operation). The analysis presented in this work can be extended to two-phase models that account for particle scale ignition as well as bed scale heat conduction. (ii) The design of the autothermal reactors in this work is based on simplified models (one dimensional pseudo-homogeneous model or cell model), while it is well known that various types of flow instabilities and non-uniform tem-

perature patterns can occur in large scale packed bed reactors, especially those with large bed diameters. Thus, the extension of the results presented here to two or three dimensional models with physical property variations will be of interest in assessing the operational stability of shallow bed autothermal reactors. (*iii*) In this work, we examined only the steady-state behavior of autothermal reactors. However, as stated in the introduction, proper start-up is a very important aspect of autothermal reactor scale-up. An important aspect of the start-up procedure is how to choose the proper initial conditions and vary the inlet reactant composition and temperature so that the catalyst 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 with an appropriate model.

Another consideration in the scale-up of OCM process is the operating pressure. Most of the laboratory studies on OCM (both catalytic and gas phase) are carried out at low pressure, typically 1 atm. However, the operation at higher pressures is more economical. Hence, the impact of operating pressure on the bifurcation behavior and more importantly on the yield of  $C_2$  products need to be well understood before scaling-up of the process. While it is known that the rates of homogeneous reactions depend on pressure, generally increasing, the catalytic reaction rates may not be sensitive to the operating pressure. As the OCM is known for complex coupled homogeneous-heterogeneous reactions, the operating pressure could have profound influence on the kinetic and reaction scheme. Further, the transport properties such as species diffusivities are also strongly dependent on pressure. Hence, the operating pressure can be an important factor to determine the length of the bed (in the mass transfer controlled regime) and may have strong impact on the selectivity of the intermediate  $C_2$  products.

Finally, it is hoped that the presented ignition-extinction analysis of the OCM

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reaction in this work can lead to further investigations on the reactor design, catalyst development and scale-up principles and to the successful commercialization of the OCM process. It is also hoped that the ideas provided in this work can help the reactor designs for other high temperature, short contact time catalytic partial oxidation reactors.

### References

- 1. Fischer, F., & Tropsch, H. (1926). The synthesis of petroleum at atmospheric pressures from gasification products of coal. *Brennstoff-Chemie*, *7*, 97-104.
- Adris, A. M., Pruden, B. B., Lim, C. J., & Grace, J. R. (1996). On the reported attempts to radically improve the performance of the steam methane reforming reactor. *The Canadian Journal of Chemical Engineering*, 74(2), 177-186.
- Simpson, A. P., & Lutz, A. E. (2007). Exergy analysis of hydrogen production via steam methane reforming. *International Journal of Hydrogen Energy*, 32(18), 4811-4820.
- 4. Bharadwaj, S. S., & Schmidt, L. D. (1995). Catalytic partial oxidation of natural gas to syngas. *Fuel Processing Technology, 42*(2-3), 109-127.
- 5. Trimm, D. L. (1997). Coke formation and minimisation during steam reforming reactions. *Catalysis Today*, *37*(3), 233-238.
- Bradford, M. C. J., & Vannice, M. A. (1999). CO2 reforming of CH4. *Catalysis Reviews*, 41(1), 1-42.
- Usman, M., Daud, W. W., & Abbas, H. F. (2015). Dry reforming of methane: Influence of process parameters—A review. *Renewable and Sustainable Energy Reviews*, 45, 710-744.
- 8. Tang, P., Zhu, Q., Wu, Z., & Ma, D. (2014). Methane activation: the past and future. *Energy & Environmental Science*, 7(8), 2580-2591.

- Arora, S., & Prasad, R. (2016). An overview on dry reforming of methane: strategies to reduce carbonaceous deactivation of catalysts. *RSC Advances,* 6(110), 108668-108688.
- Jang, W. J., Shim, J. O., Kim, H. M., Yoo, S. Y., & Roh, H. S. (2019). A review on dry reforming of methane in aspect of catalytic properties. *Catalysis Today*, 328, 15-26.
- 11. Fisher, F., & Tropsch, H. (1928). Conversion of methane into hydrogen and carbon monoxide. *Brennst.-Chem.*, 9.
- Rostrupnielsen, J. R., & Hansen, J. B. (1993). CO2-reforming of methane over transition metals. *Journal of Catalysis*, 144(1), 38-49.
- Muraza, O., & Galadima, A. (2015). A review on coke management during dry reforming of methane. *International Journal of Energy Research*, 39(9), 1196-1216.
- Liander, H. (1929). The utilisation of natural gases for the ammonia process.
   Transactions of the Faraday Society, 25, 462-472.
- Prettre, M., Eichner, C., & Perrin, M. (1946). The catalytic oxidation of methane to carbon monoxide and hydrogen. *Transactions of the Faraday Society, 42*, 335b-339.
- Tsang, S. C., Claridge, J. B., & Green, M. L. H. (1995). Recent advances in the conversion of methane to synthesis gas. *Catalysis Today*, 23(1), 3-15.
- Balachandran, U., Dusek, J. T., Mieville, R. L., Poeppel, R. B., Kleefisch, M. S., Pei, S., Kobylinski, T. P., & Bose, A. C. (1995). Dense ceramic membranes for partial oxidation of methane to syngas. *Applied Catalysis A: General,* 133(1), 19-29.

- 18. York, A. P., Xiao, T., & Green, M. L. (2003). Brief overview of the partial oxidation of methane to synthesis gas. *Topics in Catalysis*, 22(3-4), 345-358.
- Gangadharan, P., Kanchi, K. C., & Lou, H. H. (2012). Evaluation of the economic and environmental impact of combining dry reforming with steam reforming of methane. *Chemical Engineering Research and Design, 90*(11), 1956-1968.
- Ayabe, S., Omoto, H., Utaka, T., Kikuchi, R., Sasaki, K., Teraoka, Y., & Eguchi, K. (2003). Catalytic autothermal reforming of methane and propane over supported metal catalysts. *Applied Catalysis A: General, 241*(1-2), 261-269.
- Song, C., & Pan, W. (2004). Tri-reforming of methane: a novel concept for catalytic production of industrially useful synthesis gas with desired H2/CO ratios. *Catalysis Today*, 98(4), 463-484.
- 22. Holmen, A. (2009). Direct conversion of methane to fuels and chemicals. *Catalysis Today, 14*2(1-2), 2-8.
- Ma, S., Guo, X., Zhao, L., Scott, S., & Bao, X. (2013). Recent progress in methane dehydroaromatization: From laboratory curiosities to promising technology. *Journal of Energy Chemistry*, 22(1), 1-20.
- 24. Hammond, C., Conrad, S., & Hermans, I. (2012). Oxidative methane upgrading. *ChemSusChem*, 5(9), 1668-1686.
- Horn, R., & Schlögl, R. (2015). Methane activation by heterogeneous catalysis. *Catalysis Letters*, 145(1), 23-39.
- 26. Karakaya, C., & Kee, R. J. (2016). Progress in the direct catalytic conversion of methane to fuels and chemicals. *Progress in Energy and Combustion*

Science, 55, 60-97.

- 27. Guéret, C., Daroux, M., & Billaud, F. (1997). Methane pyrolysis: thermodynamics. *Chemical Engineering Science*, *5*2(5), 815-827.
- Navarro, R. M., Pena, M. A., & Fierro, J. L. G. (2007). Hydrogen production reactions from carbon feedstocks: fossil fuels and biomass. *Chemical Reviews*, *107*(10), 3952-3991.
- Holmen, A., Rokstad, O. A., & Solbakken, A. (1976). High-temperature pyrolysis of hydrocarbons.
   Methane to acetylene. *Industrial & Engineering Chemistry Process Design and Development*, 15(3), 439-444.
- Olsvik, O., & Billaud, F. (1994). Thermal Coupling of Methane-A Comparison Between Kinetic-Model Data and Experimental-Data. *Thermochimica acta,* 232(1), 155-169.
- Holmen, A., Olsvik, O., & Rokstad, O. A. (1995). Pyrolysis of natural gas: chemistry and process concepts. *Fuel Processing Technology, 42*(2-3), 249-267.
- Koert, T., van Santen, R. A. (1991). A low temperature reaction sequence for methane conversion. Journal of the Chemical Society, *Chemical Communication*s, (18), 1281-1283.
- Koerts, T., Deelen, M. J., & Van Santen, R. A. (1992). Hydrocarbon formation from methane by a low-temperature two-step reaction sequence. *Journal of Catalysis, 138*(1), 101-114.
- Belgued, M., Pareja, P., Amariglio, A., & Amariglio, H. (1991). Conversion of methane into higher hydrocarbons on platinum. *Nature*, 352(6338), 789.

- Belgued, M., Amariglio, H., Pareja, P., Amariglio, A., & Saint-Just, J. (1992). Low temperature catalytic homologation of methane on platinum, ruthenium and cobalt. *Catalysis Today, 13*(2-3), 437-445.
- Spivey, J. J., & Hutchings, G. (2014). Catalytic aromatization of methane. Chemical Society Reviews, 43(3), 792-803.
- Mamonov, N. A., Fadeeva, E. V., Grigoriev, D. A., Mikhailov, M. N., Kustov,
   L. M., & Alkhimov, S. A. (2013). Metal/zeolite catalysts of methane dehydroaromatization. *Russian Chemical Reviews*, 82(6), 567.
- Wang, L., Tao, L., Xie, M., Xu, G., Huang, J., & Xu, Y. (1993). Dehydrogenation and aromatization of methane under non-oxidizing conditions. *Catalysis Letters*, 21(1-2), 35-41.
- Solymosi, F., Cserényi, J., Szöke, A., Bánsági, T., & Oszko, A. (1997). Aromatization of methane over supported and unsupported Mo-based catalysts. *Journal of Catalysis, 165*(2), 150-161.
- Wang, D., Lunsford, J. H., & Rosynek, M. P. (1997). Characterization of a Mo/ZSM-5 catalyst for the conversion of methane to benzene. *Journal of Catalysis*, 169(1), 347-358.
- Liu, S., Wang, L., Ohnishi, R., & Ichikawa, M. (1999). Bifunctional catalysis of Mo/HZSM-5 in the dehydroaromatization of methane to benzene and naphthalene XAFS/TG/DTA/MASS/FTIR characterization and supporting effects. *Journal of Catalysis, 181*(2), 175-188.
- 42. Xu, Y., Bao, X., & Lin, L. (2003). Direct conversion of methane under nonoxidative conditions. *Journal of Catalysis, 216*(1-2), 386-395.

- Ma, S., Guo, X., Zhao, L., Scott, S., & Bao, X. (2013). Recent progress in methane dehydroaromatization: From laboratory curiosities to promising technology. *Journal of Energy Chemistry*, 22(1), 1-20.
- Guo, X., Fang, G., Li, G., Ma, H., Fan, H., Yu, L., ... & Tan, D. (2014). Direct, nonoxidative conversion of methane to ethylene, aromatics, and hydrogen. *Science*, 344(6184), 616-619.
- 45. Otsuka, K., & Wang, Y. (2001). Direct conversion of methane into oxygenates. *Applied Catalysis A: General,* 222(1-2), 145-161.
- 46. Tabata, K., Teng, Y., Takemoto, T., Suzuki, E., Banares, M. A., Pena, M. A.,
  & Fierro, J. G. (2002). Activation of methane by oxygen and nitrogen oxides. *Catalysis Reviews, 44*(1), 1-58.
- 47. Walker, G. S., Lapszewicz, J. A., & Foulds, G. A. (1994). Partial oxidation of methane to methanol-comparison of heterogeneous catalyst and homogeneous gas phase reactions. *Catalysis Today*, 21(2-3), 519-526.
- 48. Spencer, N. D. (1988). Partial oxidation of methane to formaldehyde by means of molecular oxygen. *Journal of Catalysis, 109*(1), 187-197.
- 49. Hargreaves, J. S., Hutchings, G. J., & Joyner, R. W. (1990). Control of product selectivity in the partial oxidation of methane. *Nature, 348*(6300), 428.
- Berndt, H., Martin, A., Brückner, A., Schreier, E., Müller, D., Kosslick, H., ...
   & Lücke, B. (2000). Structure and catalytic properties of VOx/MCM materials for the partial oxidation of methane to formaldehyde. *Journal of Catalysis,* 191(2), 384-400.
- 51. Alvarez-Galvan, M. C., Mota, N., Ojeda, M., Rojas, S., Navarro, R. M., & Fierro, J. L. G. (2011). Direct methane conversion routes to chemicals and

fuels. Catalysis Today, 171(1), 15-23.

- Periana, R. A., Taube, D. J., Evitt, E. R., Löffler, D. G., Wentrcek, P. R., Voss, G., & Masuda, T. (1993). A mercury-catalyzed, high-yield system for the oxidation of methane to methanol. *Science*, *259*(5093), 340-343.
- Periana, R. A., Taube, D. J., Gamble, S., Taube, H., Satoh, T., & Fujii, H. (1998). Platinum catalysts for the high-yield oxidation of methane to a methanol derivative. *Science*, *280*(5363), 560-564.
- 54. Labinger, J. A. (2004). Selective alkane oxidation: hot and cold approaches to a hot problem. *Journal of Molecular Catalysis A: Chemical, 220*(1), 27-35.
- Keller, G. E., & Bhasin, M. M. (1982). Synthesis of ethylene via oxidative coupling of methane: I. Determination of active catalysts. *Journal of Catalysis*, 73(1), 9-19.
- 56. Lee, J. S., & Oyama, S. T. (1988). Oxidative coupling of methane to higher hydrocarbons. *Catalysis Reviews Science and Engineering*, *30*(2), 249-280.
- 57. Ito, T., & Lunsford, J. H. (1985). Synthesis of ethylene and ethane by partial oxidation of methane over lithium-doped magnesium oxide. *Nature, 314*(6013), 721.
- Aika, K. I., Moriyama, T., Takasaki, N., & Iwamatsu, E. (1986). Oxidative dimerization of methane over BaCO 3, SrCO 3 and these catalysts promoted with alkali. *Journal of the Chemical Society, Chemical Communications*, (15), 1210-1211.
- 59. Moriyama, T., Takasaki, N., Iwamatsu, E., & Aika, K. I. (1986). Oxidative dimerization of methane over promoted magnesium oxide catalysts. Important factors. *Chemistry Letters, 15*(7), 1165-1168.

- Ito, T., Tashiro, T., Watanabe, T., Toi, K., & Ikemoto, I. (1987). Activation of methane on the MgO surface at low temperatures. *Chemistry Letters*, 16(9), 1723-1726.
- Fang, T., & Yeh, C. T. (1981). Interactions of methane with ThO2SiO2 surface at 1073 K. Journal of Catalysis, 69(1), 227-229.
- 62. Otsuka, K., Jinno, K., & Morikawa, A. (1985). The catalysts active and selective in oxidative coupling of methane. *Chemistry Letters, 14*(4), 499-500.
- Lin, C. H., Campbell, K. D., Wang, J. X., & Lunsford, J. H. (1986). Oxidative dimerization of methane over lanthanum oxide. *The Journal of Physical Chemistry*, 90(4), 534-537.
- Otsuka, K., Liu, Q., Hatano, M., & Morikawa, A. (1986). Synthesis of ethylene by partial oxidation of methane over the oxides of transition elements with LiCl. *Chemistry Letters*, 15(6), 903-906.
- Otsuka, K., & Komatsu, T. (1987). Active catalysts in oxidative coupling of methane. *Journal of the Chemical Society, Chemical Communications*, (5), 388-389.
- Hutchings, G. J., Scurrell, M. S., & Woodhouse, J. R. (1989). Oxidative coupling of methane using oxide catalysts. *Chemical Society Reviews, 18*, 251-283.
- Amenomiya, Y., Birss, V. I., Goledzinowski, M., Galuszka, J., & Sanger, A. R. (1990). Conversion of methane by oxidative coupling. *Catalysis Reviews— Science and Engineering, 32*(3), 163-227.
- 68. Lunsford, J. H. (1995). The catalytic oxidative coupling of methane. *Angewandte Chemie International Edition in English, 34*(9), 970-980.

- Zavyalova, U., Holena, M., Schlögl, R., & Baerns, M. (2011). Statistical analysis of past catalytic data on oxidative methane coupling for new insights into the composition of high-performance catalysts. *ChemCatChem, 3*(12), 1935-1947.
- Mleczko, L., & Baerns, M. (1995). Catalytic oxidative coupling of methane reaction engineering aspects and process schemes. *Fuel Processing Technology, 42*(2-3), 217-248.
- Dautzenberg, F. M., Schlatter, J. C., Fox, J. M., Rostrup-Nielsen, J. R., & Christiansen, L. J. (1992). Catalyst and reactor requirements for the oxidative coupling of methane. *Catalysis Today*, *13*(4), 503-509.
- 72. Edwards, J. H., Tyler, R. J., & White, S. D. (1990). Oxidative coupling of methane over lithium-promoted magnesium oxide catalysts in fixed-bed and fluidized-bed reactors. *Energy & Fuels, 4*(1), 85-93.
- Mleczko, L., Pannek, U., Niemi, V. M., & Hiltunen, J. (1996). Oxidative coupling of methane in a fluidized-bed reactor over a highly active and selective catalyst. *Industrial & Engineering Chemistry Research*, 35(1), 54-61.
- Mleczko, L., & Marschall, K. J. (1997). Performance of an internally circulating fluidized-bed reactor for the catalytic oxidative coupling of methane. *The Canadian Journal of Chemical Engineering*, 75(3), 610-619.
- Liu, S., Tan, X., Li, K., & Hughes, R. (2001). Methane coupling using catalytic membrane reactors. *Catalysis Reviews*, 43(1-2), 147-198.
- Wang, W., & Lin, Y. S. (1995). Analysis of oxidative coupling of methane in dense oxide membrane reactors. *Journal of Membrane Science*, 103(3), 219-233.

- 77. Kao, Y. K., Lei, L., & Lin, Y. S. (1997). A comparative simulation study on oxidative coupling of methane in fixed-bed and membrane reactors. *Industrial & Engineering Chemistry Research*, *36*(9), 3583-3593.
- Karakaya, C., & Kee, R. J. (2016). Progress in the direct catalytic conversion of methane to fuels and chemicals. *Progress in Energy and Combustion Science*, 55, 60-97.
- 79. Wei, Y., Yang, W., Caro, J., & Wang, H. (2013). Dense ceramic oxygen permeable membranes and catalytic membrane reactors. *Chemical Engineering Journal, 220*, 185-203.
- Sarsani, S., West, D., Liang, W., & Balakotaiah, V. (2017). Autothermal oxidative coupling of methane with ambient feed temperature. *Chemical Engineering Journal, 328*, 484-496.
- McBride, B. J., & Gordon, S. (1996). Computer program for calculation of complex chemical equilibrium compositions and applications. NASA-Lewis Publication 1331.
- Sofranko, J. A., Leonard, J. J., & Jones, C. A. (1987). The oxidative conversion of methane to higher hydrocarbons. *Journal of catalysis*, 103(2), 302-310.
- Driscoll, D. J., Martir, W., Wang, J. X., & Lunsford, J. H. (1985). Formation of gas-phase methyl radicals over magnesium oxide. *Journal of the American Chemical Society, 107*(1), 58-63.
- Campbell, K. D., Morales, E., & Lunsford, J. H. (1987). Gas-phase coupling of methyl radicals during the catalytic partial oxidation of methane. *Journal of the American Chemical Society, 109*(25), 7900-7901.

- Nelson, P. F., Lukey, C. A., & Cant, N. W. (1988). Isotopic evidence for direct methyl coupling and ethane to ethylene conversion during partial oxidation of methane over lithium/magnesium oxide. *The Journal of Physical Chemistry*, 92(22), 6176-6179.
- Nelson, P. F., & Cant, N. W. (1990). Oxidation of C2 hydrocarbon products during the oxidative coupling of methane over a lithium/magnesia catalyst. *Journal of Physical Chemistry*, 94(9), 3756-3761.
- 87. Lane, G. S., & Wolf, E. E. (1988). Methane utilization by oxidative coupling:
  I. A study of reactions in the gas phase during the cofeeding of methane and oxygen. *Journal of Catalysis, 113*(1), 144-163.
- Asami, K., Omata, K., Fujimoto, K., & Tominaga, H. (1988). Vapor-phase oxidative coupling of methane under pressure. *Energy & fuels, 2*(4), 574-577.
- Zanthoff, H., & Baerns, M. (1990). Oxidative coupling of methane in the gas phase. Kinetic simulation and experimental verification. *Industrial & Engineering Chemistry Research*, 29(1), 2-10.
- 90. Chen, Q., Hoebink, J. H., & Marin, G. B. (1991). Kinetics of the oxidative coupling of methane at atmospheric pressure in the absence of catalyst. *Industrial & Engineering Chemistry Research*, 30(9), 2088-2097.
- Geerts, J. W. M. H., Chen, Q., Van Kasteren, J. M. N., & Van Der Wiele, K. (1990). Thermodynamics and kinetic modeling of the homogeneous gas phase reactions of the oxidative coupling of methane. *Catalysis Today*, 6(4), 519-526.
- 92. Mackie, J. C., Smith, J. G., Nelson, P. F., & Tyler, R. J. (1990). Inhibition of C2

oxidation by methane under oxidative coupling conditions. *Energy & Fuels, 4*(3), 277-285.

- Metcalfe, W. K., Burke, S. M., Ahmed, S. S., & Curran, H. J. (2013). A hierarchical and comparative kinetic modeling study of C1- C2 hydrocarbon and oxygenated fuels. *International Journal of Chemical Kinetics*, 45(10), 638-675.
- Westbrook, C. K., & Dryer, F. L. (1981). Simplified reaction mechanisms for the oxidation of hydrocarbon fuels in flames. *Combustion science and technology*, 27(1-2), 31-43.
- Westbrook, C. K., & Dryer, F. L. (1984). Chemical kinetic modeling of hydrocarbon combustion. *Progress in Energy and Combustion Science*, *10*(1), 1-57.
- Olsvik, O., Rokstad, O. A., & Holmen, A. (1995). Pyrolysis of methane in the presence of hydrogen. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology, 18*(5), 349-358.
- Sundaram, K. M., & Froment, G. F. (1977). Modeling of thermal cracking kinetics—I: Thermal cracking of ethane, propane and their mixtures. *Chemical Engineering Science*, 32(6), 601-608.
- Robertson, R. W., & Hanesian, D. (1975). An optimization study of the pyrolysis of ethane in a tubular reactor. *Industrial & Engineering Chemistry Process Design and Development, 14*(3), 216-221.
- Balakotaiah, V., & West, D. H. (2014). Thermal effects and bifurcations in gas phase catalytic partial oxidations. *Current Opinion in Chemical Engineering,* 5, 68-77.

- 100. Gundlapally, S. R., & Balakotaiah, V. (2011). Heat and mass transfer correlations and bifurcation analysis of catalytic monoliths with developing flows. *Chemical Engineering Science*, 66(9), 1879-1892.
- 101. Wakao, N., & Funazkri, T. (1978). Effect of fluid dispersion coefficients on particle-to-fluid mass transfer coefficients in packed beds: correlation of Sherwood numbers. *Chemical Engineering Science*, 33(10), 1375-1384.
- 102. Wakao, N., Kaguei, S., & Funazkri, T. (1979). Effect of fluid dispersion coefficients on particle-to-fluid heat transfer coefficients in packed beds: correlation of Nusselt numbers. *Chemical Engineering Science*, 34(3), 325-336.
- 103. Bird, R. B., Stewart, W. E., & Lightfoot, E. N. (2007). *Transport phenomena*. John Wiley & Sons.
- 104. Balakotaiah, V. (1989). Simple runaway criteria for cooled reactors. *AIChE Journal*, 35(6), 1039-1043.
- 105. Balakotaiah, V., & Luss, D. (1991). Explicit runaway criterion for catalytic reactors with transport limitations. *AIChE Journal*, *37*(12), 1780-1788.
- 106. Balakotaiah, V., Kodra, D., & Nguyen, D. (1995). Runaway limits for homogeneous and catalytic reactors. *Chemical Engineering Science*, 50(7), 1149-1171.
- 107. Mears, D. E. (1971a). Diagnostic criteria for heat transport limitations in fixed bed reactors. *Journal of Catalysis, 20*(2), 127-131.
- 108. Weisz, P. B., & Hicks, J. S. (1962). The behaviour of porous catalyst particles in view of internal mass and heat diffusion effects. *Chemical Engineering Science*, 17(4), 265-275.

- 109. Mears, D. E. (1971b). Tests for transport limitations in experimental catalytic reactors. Industrial & Engineering Chemistry Process Design and Development, 10(4), 541-547.
- 110. Doraiswamy, L. K., & Tajbl, D. G. (1974). Laboratory catalytic reactors. *Catalysis Reviews Science and Engineering*, 10(1), 177-219.
- 111. Kapteijn, F., & Moulijn, J. A. (2008). Laboratory catalytic reactors: Aspects of catalyst testing. *Handbook of Heterogeneous Catalysis: Online*, 1361-1398.
- 112. Hickman, D. A., Degenstein, J. C., & Ribeiro, F. H. (2016). Fundamental principles of laboratory fixed bed reactor design. *Current Opinion in Chemical Engineering*, 13, 1-9.
- 113. Pak, S., & Lunsford, J. H. (1998). Thermal effects during the oxidative coupling of methane over Mn/Na2WO4/SiO2 and Mn/Na2WO4/MgO catalysts. *Applied Catalysis A: General, 168*(1), 131-137.
- 114. Lee, J. Y., Jeon, W., Choi, J. W., Suh, Y. W., Ha, J. M., Suh, D. J., & Park, Y. K. (2013). Scaled-up production of C2 hydrocarbons by the oxidative coupling of methane over pelletized Na2WO4/Mn/SiO2 catalysts: observing hot spots for the selective process. *Fuel, 106*, 851-857.
- 115. Zohour, B., Noon, D., & Senkan, S. (2013). New insights into the oxidative coupling of methane from spatially resolved concentration and temperature profiles. *ChemCatChem*, 5(10), 2809-2812.
- 116. Kalthoff, O., & Vortmeyer, D. (1980). Ignition/extinction phenomena in a wall cooled fixed bed reactor: Experiments and model calculations including radial porosity and velocity distributions. *Chemical Engineering Science, 35*(7), 1637-1643.

- 117. Mariani, N. J., Keegan, S. D., Martínez, O. M., & Barreto, G. F. (2012). Thermal behavior of laboratory-scale catalytic packed beds. *Chemical Engineering Journal, 198*, 397-411.
- 118. Gu, T., & Balakotaiah, V. (2016). Impact of heat and mass dispersion and thermal effects on the scale-up of monolith reactors. *Chemical Engineering Journal, 284*, 513-535.
- 119. Dommeti, S. M., Balakotaiah, V., & West, D. H. (1999). Analytical criteria for validity of pseudohomogeneous models of packed-bed catalytic reactors. *Industrial & Engineering Chemistry Research*, 38(3), 767-777.
- 120. Chakraborty, S., & Balakotaiah, V. (2004). Multi-mode low-dimensional models for non-isothermal homogeneous and catalytic reactors. *Chemical Engineering Science*, 59(17), 3695-3724.
- 121. Sun, Z., Kota, A., Sarsani, S., West, D. H., & Balakotaiah, V. (2018). Bifurcation analysis of methane oxidative coupling without catalyst. *Chemical Engineering Journal, 343*, 770-788.
- 122. Balakotaiah, V., & Luss, D. (1983). Multiplicity features of reacting systems: dependence of the steady-states of a CSTR on the residence time. *Chemical Engineering Science*, 38(10), 1709-1721.
- 123. Balakotaiah, V. (1996). Structural stability of nonlinear convection-reaction models. *Chemical Engineering Education, 30*, 234-239.
- 124. Lovo, M., & Balakotaiah, V. (1992). Multiplicity features of adiabatic autothermal reactors. *AIChE Journal, 38*(1), 101-115.
- 125. Aseem, A., Jeba, G. G., Conato, M. T., Rimer, J. D., & Harold, M. P. (2018). Oxidative coupling of methane over mixed metal oxide catalysts: Steady state

multiplicity and catalyst durability. *Chemical Engineering Journal, 331*, 132-143.

- 126. Ratchahat, S., Sudoh, M., Suzuki, T., Watanabe, R., & Fukuhara, C. (2018). Advantage of structured catalyst system for CO2 methanation under extremely high fow rate. ISCRE25 abstract, Florence, Italy.
- 127. Bizon, K. (2016). Autothermicity, multiplicity, yield and selectivity of catalytic processes in a polytropic fluidized bed reactor. *Chemical Engineering Journal, 288*, 834-844.
- Liljenroth, F. G. (1918). Starting and stability phenomena of ammonia-oxidation and similar reactions. *Chemical and Metallurgical Engineering*, 19(6), 287-293.
- 129. Hunt, L. B. (1958). The ammonia oxidation process for nitric acid manufacture. *Platinum Metals Review*, 2(4), 129-134.
- 130. Pirie, J. M. (1958). The manufacture of hydrocyanic acid by the Andrussow process. *Platinum Metals Review*, 2(1), 7-11.
- 131. Van Heerden, C. (1953). Autothermic processes. *Industrial & Engineering Chemistry, 45*(6), 1242-1247.
- 132. Van Heerden, C. (1958). The character of the stationary state of exothermic processes. *Chemical Engineering Science*, *8*(1-2), 133-145.
- 133. Lovo, M., & Balakotaiah, V. (1992). Multiplicity features of adiabatic autothermal reactors. *AIChE Journal, 38*(1), 101-115.
- 134. Eigenberger, G., & Ruppel, W. (2000). Catalytic Fixed-Bed Reactors. *Ullmann's Encyclopedia of Industrial Chemistry*.

- 135. Froment, G. F., Bischoff, K. B., & De Wilde, J. (2010). *Chemical reactor analysis and design* (3rd ed.). New York: Wiley.
- 136. Cottrell, F. G. (1938). U.S. Patent No. 2,121,733. Washington, DC: U.S. Patent and Trademark Office.
- Boreskov, G. K., Matros, Y. S., & Kiselev, O. V. (1979). Catalytic processes carried out under nonstationary conditions. I. Thermal front in a fixed bed of catalyst. *Kinet. Catal.(USSR)(Engl. Transl.);(United States), 20*(3).
- Boreskov, G. K., & Matros, Y. S. (1983). Unsteady-state performance of heterogeneous catalytic reactions. *Catalysis Reviews Science and Engineering*, 25(4), 551-590.
- 139. Eigenberger, G., & Nieken, U. (1988). Catalytic combustion with periodic flow reversal. *Chemical Engineering Science*, *43*(8), 2109-2115.
- 140. Bhatia, S. K. (1991). Analysis of catalytic reactor operation with periodic flow reversal. *Chemical Engineering Science, 46*(1), 361-367.
- 141. Khinast, J., & Luss, D. (1997). Mapping regions with different bifurcation diagrams of a reverse-flow reactor. *AIChE Journal*, *43*(8), 2034-2047.
- 142. Kolios, G., Frauhammer, J., & Eigenberger, G. (2000). Autothermal fixed-bed reactor concepts. *Chemical Engineering Science*, *55*(24), 5945-5967.
- 143. Schmidt, L. D. (2004). The Engineering of Chemical Reactions (3rd ed.).Oxford University Press, USA.
- 144. Stansch, Z., Mleczko, L., & Baerns, M. (1997). Comprehensive kinetics of oxidative coupling of methane over the La2O3/CaO catalyst. *Industrial & Engineering Chemistry Research*, 36(7), 2568-2579.

- 145. Lengyel, I., & West, D. H. (2018). Numerical bifurcation analysis of largescale detailed kinetics mechanisms. *Current Opinion in Chemical Engineering*, 21, 41-47.
- 146. Vandewalle, L. A., Lengyel, I., West, D. H., Van Geem, K. M., & Marin, G. B. (2019). Catalyst ignition and extinction: A microkinetics-based bifurcation study of adiabatic reactors for oxidative coupling of methane. *Chemical Engineering Science*, 199, 635-651.
- 147. Vandewalle, L. A., Van de Vijver, R., Van Geem, K. M., & Marin, G. B. (2019). The role of mass and heat transfer in the design of novel reactors for oxidative coupling of methane. *Chemical Engineering Science*, *198*, 268-289.
- 148. Fuller, E. N., Schettler, P. D., & Giddings, J. C. (1966). New method for prediction of binary gas-phase diffusion coefficients. *Industrial & Engineering Chemistry, 58*(5), 18-27.
- 149. Wicke, E., & Vortmeyer, D. (1959). Zündzonen heterogener Reaktionen in gasdurchströmten Körnerschichten. Zeitschrift für Elektrochemie, *Berichte der Bunsengesellschaft für physikalische Chemie, 63*(1), 145-152.
- 150. Liu, S. L., & Amundson, N. R. (1962). Stability of adiabatic packed bed reactors. An elementary treatment. *Industrial & Engineering Chemistry Fundamentals*, 1(3), 200-208.
- 151. Eigenberger, G. (1972). On the dynamic behavior of the catalytic fixed-bed reactor in the region of multiple steady states—II. The influence of the boundary conditions in the catalyst phase. *Chemical Engineering Science*, 27(11), 1917-1924.
- 152. Ramanathan, K., Balakotaiah, V., & West, D. H. (2003). Light-off criterion

and transient analysis of catalytic monoliths. *Chemical Engineering Science, 58*(8), 1381-1405.

- 153. Lapidus, L., & Amundson, N. R. (Eds.). (1977). *Chemical Reactor Theory: A Review: Dedicated to the Memory of Richard H. Wilhelm.* Prentice-Hall.
- 154. Becker, R. (Ed.). (1993). *Computer-aided design of catalysts* (Vol. 51). CRC Press.
- 155. Balakotaiah, V., Christoforatou, E. L., & West, D. H. (1999). Transverse concentration and temperature nonuniformities in adiabatic packed-bed catalytic reactors. *Chemical Engineering Science*, *54*(11), 1725-1734.
- 156. Viswanathan, G. A., c, M., & Luss, D. (2008). Transversal hot zones formation in catalytic packed-bed reactors. *Industrial & Engineering Chemistry Research*, 47(20), 7509-7523.
- 157. Balakotaiah, V., & Dommeti, S. M. (1999). Effective models for packed-bed catalytic reactors. *Chemical Engineering Science*, *54*(11), 1621-1638.
- 158. Chen, J. C., & Churchill, S. W. (1963). Radiant heat transfer in packed beds. *AIChE Journal*, 9(1), 35-41.
- 159. Subramanian, S., & Balakotaiah, V. (1996). Classification of steady-state and dynamic behavior of distributed reactor models. *Chemical Engineering Science, 51*(3), 401-421.

Appendices

## Appendix A: Estimation of Effective Heat and Mass Peclet Numbers

The effective Peclet numbers to be used in pseudo-homogeneous models of laboratory-scale packed-bed reactors with small particles can be estimated using a procedure similar to that discussed by Balakotaiah and Dommeti (1991) and Gu and Balakotaiah (2016) for monolith reactors. Here, we summarize the results and skip the details.

The effective heat Peclet number may be expressed as

$$\frac{1}{Pe_{h,eff}} = \frac{\varepsilon_b k_{f,eff}}{L \langle u \rangle \rho_f C_{pf}} + \frac{(1 - \varepsilon_b) k_{s,eff}}{L \langle u \rangle \rho_f C_{pf}} + \frac{\langle u \rangle}{L} \frac{\rho_f C_{pf}}{ha_v (1 - \varepsilon_b)},$$
(A.1)

where *h* is the fluid-to particle (interphase) heat transfer coefficient,  $a_v$  is the surface area per unit catalyst volume ( $a_v = \frac{6}{d_p}$  for a bed of spherical particles), and other symbols have their usual meaning. Here, the first term represents the fluid contribution to heat dispersion, second terms is the solid contribution while the third term is due to interfacial resistance. We note that at high temperatures, the effective bed conductivity [ $k_{eff} = \varepsilon_b k_{f,eff} + (1 - \varepsilon_b) k_{s,eff}$ ] may be a strong function of temperature and radiative properties of the bed. It may be estimated by procedures similar to that discussed by Chen and Churchill (1963). Similarly, the effective mass Peclet number may be expressed as

$$\frac{1}{Pe_{m,eff}} = \frac{\varepsilon_b D_{f,eff}}{L \langle u \rangle} + \frac{(1 - \varepsilon_b) D_{s,eff}}{L \langle u \rangle} + \frac{\langle u \rangle}{L} \frac{1}{k_c a_v (1 - \varepsilon_b)},$$
(A.2)

where  $k_c$  is the fluid-to particle (interphase) mass transfer coefficient. The effective dispersion coefficient in the fluid phase,  $D_{f,eff}$  depends both on the molecular diffusivity as well as convective contribution to dispersion and may be expressed

$$D_{f,eff} = D_M + 0.5 \langle u \rangle d_p. \tag{A.3}$$

The above expressions may be combined with the standard packed-bed correlations for h and  $k_c$  (Wakao, Kaguei, & Funazkri, 1979):

$$Sh = \frac{k_c d_p}{D_M} = 2 + 1.1 \left(\frac{\langle u \rangle d_p}{\nu_f}\right)^{0.6} \left(\frac{\nu_f}{D_{mf}}\right)^{1/3} \text{ and}$$
(A.4)

$$Nu = \frac{hd_p}{k_f} = 2 + 1.1 \left(\frac{\langle u \rangle d_p}{\nu_f}\right)^{0.6} \left(\frac{\nu_f}{\alpha_f}\right)^{1/3}.$$
 (A.5)

[The j-factor correlations may also be used but these are not valid in the limit of very small particle Reynolds numbers, which can be reached in lab-scale reactors]. From the above expressions, we note that the effective Peclet numbers depend on particle size, fluid velocity as well as other bed properties. We note that for beds of small particles, the inter-phase contributions may be neglected. Further, noting that the main contribution to heat dispersion is the solid phase while the main contribution to mass dispersion is the fluid phase, the ratio of the Peclet numbers for beds of small particles may be expressed as

$$\frac{Pe_{m,eff}}{Pe_{h,eff}} = \frac{(1-\varepsilon_b)k_{s,eff}}{\rho_f C_{pf}[D_M + 0.5 \langle u \rangle d_p]}.$$
(A.6)

In general, the molecular diffusion term  $(D_M)$  and the interstitial dispersion term  $(\langle u \rangle d_p)$  are of the same order of magnitude  $(10^{-4}m^2/s)$ , but  $d_p \to 0$  or at low velocities the latter may be neglected and Eq.A.6 further simplifies to

$$\frac{Pe_{m,eff}}{Pe_{h,eff}} = \frac{(1-\varepsilon_b)k_{s,eff}}{\rho_f C_{pf} D_M} = \frac{\alpha_{s,eff}}{D_M}.$$
(A.7)

This ratio is has a typical value of about 10 for most laboratory scale packed-bed reactors but could take values of 100 for highly conductive beds. [Remark: In

contrast to laboratory scale reactors, for packed-beds of large particles, the ratio  $Pe_{m,eff}/Pe_{h,eff}$  approaches unity. However, in this case, inter and intra-particle gradients become significant and pseudo-homogeneous models are not applicable].

## Appendix B: Numerical Solution of Nonlinear Algebraic Equations by Pseudo-arclength Method

The differential equations of particle species balances are discretized by the central difference method. To reduce the numerical error due to discretization, multiple calculations are done for each case until there is no change in the computed result with increasing number of mesh points. The calculation of ignition/extinction, hysteresis and isola loci is done by the methods described by Balakotaiah and Luss (1983), Subramanian and Balakotaiah (1996) and by the continuation method. The pseudo-acrlength continuation method is used to avoid problems at singular points, where the Jacobian matrix can be singular if we use the standard continuation method. Here, we summarize the procedures used in this thesis.

**Pseudo-acrlength continuation:**The discretized algebraic equations may be expressed as

$$\mathbf{G}(\mathbf{u},\lambda) = 0, \tag{B.1}$$

where  $\mathbf{u}$  is the vector of unknowns (solution) and  $\lambda$  is a bifurcation parameter (or a physical parameter). It is required to find the solution for some  $\lambda$ -intervals, that is, a path of solutions ( $\mathbf{u}(s), \lambda(s)$ ), where *s* is the arc-length parameter. At a solution point  $s = s_0$ , we can compute the tangent by differentiation with respect to *s* ( $\dot{\mathbf{u}}(s_0), \dot{\lambda}(s_0)$ )

$$\mathbf{G}_u \dot{\mathbf{u}}_0 + \dot{\lambda}_0 \mathbf{G}_\lambda = 0, \tag{B.2}$$

and the arclength equation

$$\|\dot{\mathbf{u}}_0\|^2 + \|\dot{\lambda}_0\|^2 = 1.$$
 (B.3)

Eq.B.2 is generated by the differentiation of G with respect to s, while Eq.B.3 is the

arclength equation. The system defined by Eq.B.2 and Eq.B.3 may be integrated by treating it as an initial value problem in *s*:

$$\dot{\mathbf{u}} = -\mathbf{G}_u^{-1}\mathbf{G}_\lambda\dot{\lambda}$$
 and (B.4)

$$\dot{\lambda} = \pm (\|\mathbf{G}_u^{-1}\mathbf{G}_\lambda\|^2 + 1)^{-1/2},$$
 (B.5)

which gives the solution curve. Hence, the choice of the sign depends on the integration direction of this initial value problem. In the pseudo-arclength continuation, Eq.B.3 can be approximated by a linearization equation (or normalization equation):

$$N(\mathbf{u}(s),\lambda(s)) = \dot{\mathbf{u}}_0^T(\mathbf{u}(s) - \mathbf{u}(s_0)) + \dot{\lambda}_0(\lambda(s) - \lambda(s_0)) - (s - s_0) = 0.$$
 (B.6)

This equation forces the new solution point to lie on a hyperplane perpendicular to the tangent vector to the solution curve at  $s_0$  and at a distance  $(s - s_0)$  from it. In addition, we require the original equations

$$\mathbf{G}(\mathbf{u}(\mathbf{s}), \lambda(s)) = 0 \tag{B.7}$$

to be satisfied, so that  $\mathbf{u}(\mathbf{s})$  and  $\lambda(s)$  are on the true solution curve. In general, we solved this coupled equation system Eq.B.6 and Eq.B.7 for  $\mathbf{u}(\mathbf{s})$  and  $\lambda(s)$  with given step size  $ds = (s - s_0)$ . We implement the procedure described here for our simulation system and by MatLab code and use various integration methods. Here we show the Newton's method as an example for illustration. In the Newton's method, we solve the following linear system at each iteration to update the solutions:

$$\begin{bmatrix} \mathbf{G}_{u} & \mathbf{G}_{\lambda} \\ N_{u}^{T} & N_{\lambda} \end{bmatrix} \begin{bmatrix} \delta \mathbf{u} \\ \delta \lambda \end{bmatrix} = -\begin{bmatrix} \mathbf{G} \\ N \end{bmatrix}.$$
 (B.8)

When computing the solution curve of lumped thermal reactor model, we used the shooting method together with the pseudo-acrlength continuation method. The reactor temperature is taken as a fitting or guessing parameter (w). The species balance equations are integrated with an initial guess of reactor temperature ( $w_0$ ), the parameter w is then updated by the Newton's method at each iteration step (k) until it satisfies the energy balance (F(w) = 0):

$$w^{k+1} = w^k - \frac{F(w^k)}{F'(w^k)}.$$
(B.9)

The energy balance is then coupled with the arclength equation and solved simultaneously by the pseudo-acrlength continuation method described above.