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Bifurcation analysis of thermally coupled homogeneous–heterogeneous combustion

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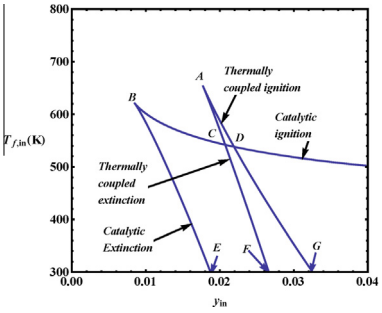
HIGHLIGHTS

- Phase diagrams corresponding to different bifurcations are presented.
- Dependence of ignitions and extinctions on system parameters is analyzed.
- Parameter regions where only catalytic/homogeneous ignition occurs are identified.
- For methane, predictions are compared to experimental data and CFD simulations.

GRAPHICAL ABSTRACT

Projection of the bifurcation set (ignition/extinction locus) for propane oxidation with a residence time of 3 ms and hydraulic radius of 1.32 mm in the inlet temperature–mole fraction plane.



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ABSTRACT

Using a two-mode lumped model, we present theory and comprehensive bifurcation analysis of thermally coupled homogeneous–heterogeneous combustion of propane and methane in short monolith, fibermat or gauze type reactors with a focus on the dependence of the ignition, extinction, hysteresis, double and boundary limit loci on the various design and operating parameters. We analyze the impact of inlet fuel mole fraction, inlet temperature, residence time and channel hydraulic radius on the relative position of the homogeneous and catalytic ignition and extinction points and identify the parameter regions in which either catalytic or homogeneous reaction dominates. We also identify the regions in which catalytic ignition leads either to an intermediate branch on which the homogeneous reaction rate is negligible or directly to a high conversion and temperature state thereby facilitating homogeneous ignition. For the case of methane oxidation, we examine both the lean and rich feeds with the operating pressure as the bifurcation variable and compare the predicted results with available experimental data and numerical simulations using detailed CFD models.

1. Introduction and literature review

Catalytic partial (complete) oxidation of hydrocarbons is of interest for the production of intermediate chemicals (power generation). In recent years, processes such as production of syngas from methane partial oxidation, oxidative dehydrogenation of ethane, and the conversion of methane to C_2^+ hydrocarbons have been perceived as attractive alternatives for basic chemical production (for example see [1–4]). Complete oxidation (combustion) of hydrocarbons with low emissions of NO_x and other pollutants is also of interest in power generation. However, the high operating

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temperatures, short residence times and highly exothermic nature of the oxidation processes pose a formidable engineering challenge, and without appropriate theoretical understanding, undesirable situations like runaways and side reactions might undermine the purpose of operation. Models describing these systems typically involve both catalytic and homogeneous reactions. These models must account for the effects of transport processes as well as the complex chemistry in an idealized manner in order to be amenable to theoretical and computational analysis while avoiding too much simplification. An article by Pfefferle [5] reviews the various models and parameter ranges in which they are valid for such systems. It is well-known that catalytic reaction systems exhibit complex behavior such as multiple steady states and hysteresis. It is therefore intuitively obvious that the coupling between catalytic and homogeneous chemistry should lead to even more complicated behavior. A comprehensive analysis of this system requires study of observables like solid/gas temperatures or conversion of reactants (or yield of intermediate products) with respect to changes in the system parameters such as inlet mole fraction of fuel, operating pressure, space/inlet velocity, diameter of the monolith channel and so forth.

Because of its obvious industrial relevance, there have been numerous experimental and computational studies on homoge neous–heterogeneous combustion in the past three decades. The work of Song et al. ([6–8]) analyzed a stagnation flow model using the methods of singularity theory. Later work of Vlachos et al. [9] used more detailed microkinetic models to understand homogeneous combustion near isothermal and adiabatic surfaces. There has also been a large amount of work using computational fluid dynamic (CFD) models to study catalytic combustion ([10,11]). Deutschmann et al. [12] investigated 1-D CFD models to understand transitions from catalytic to homogeneous combustion of propane on Pt foils using detailed homogeneous–heterogeneous chemistry. Later work of Deutschmann and coworkers ([13,14]) addressed catalytic combustion and partial oxidation of methane with 2-D and 3-D models. These papers also discuss the dependence of light-off behavior on system parameters. Karagiannidis et al. [15,16] use 2-D CFD simulations in a plane channel reactor and obtain combustion stability diagrams for propane and methane microreactors with more detailed chemistry. Pizza et al [17,18] studied flame dynamics in fuel-lean hydrogen/air flames and studied the effet of heterogeneous reactions on the suppression of the combustion instabilities. Stefanidis and Vlachos [19] solve 2-D CFD models for propane oxidation taking heat losses into account with global chemistry. They analyze the interplay between catalytic and homogeneous chemistry by describing how a catalyst-induced gas phase stabilization results at high inlet velocities due to synergistic thermal effects between the phases. The work of Chattopadhyay and Veser [20] studied heterogeneous-homogeneous interactions in Pt-coated microchannels with detailed surface and gas chemistries using a 2-D boundary layer model and investigated ignition behavior. These approaches, however, do not provide an exhaustive picture of the different possible bifurcation behaviors in the multi-dimensional parameter space. CFD models are not convenient for bifurcation analysis and detailed exploration of the parameter space but are useful to study specific types of solutions or reactor systems in more detail. Microkinetic modeling of a combustion system can involve hundreds of reactions making computation of bifurcations or high order singularities very challenging. This subverts their practicability in providing a detailed understanding of the system in the multi-dimensional parameter space. The work of Song et al. [6–8] studies bifurcations with global reaction kinetics, but the stagnation flow system used in their work is not realistic for industrial settings. In the present work, we circumvent this by basing our studies on a lumped two-mode model that describes short monolith, fibermat or gauze type reactors where flow is parallel to the catalyst surface.

There is considerable interest in understanding bifurcation phenomena because it answers important questions like how many solutions (or steady-states) exist in different operating regions, and how the system behaves with changes in various parameters. A recent review article [21] presents a good survey of the state of the art in this field. The alternatives to the bifurcation approach to modeling and simulation are large-scale numerical computation for the entire system and asymptotic analysis. In contrast to full numerical study and asymptotics, a bifurcation study helps provide insights about the physics by classifying the parameter space into different regions and aids further numerical explorations; however a purely numerical approach without theoretical guidance usually fails to provide much insight for complex systems. The singularity theory approach that we employ in this paper derives its power from being able to give global information about the system from a local analysis because of the use of a very powerful theory of unfolding of singularities and construction of phase diagrams in the space of design or operating parameters.

In our view, the bifurcation behavior of models that combine the thermal coupling between the catalytic and homogeneous reactions is not yet well-studied, even though this has been a problem of great practical importance for quite some time. A clear picture of essential features of the process as the parameters are changed is still not available. Thus, one major goal of this work is to determine an approximate phase diagram of the thermally coupled combustion process in the space of various design and operating parameters (e.g. inlet fuel mole fraction, inlet temperature, channel dimensions, operating pressure and space velocity). Even coarse phase diagrams that identify the parameter regions in which either the homogeneous or catalytic reaction dominates can provide not only physical insight but are also useful in designing laboratory scale experiments that may lead to a better understanding of the interactions between catalytic and homogeneous chemistry during the oxidation of hydrocarbons. There is an obvious trade-off in how detailed a model one wants to analyze and how fully one can analyze it with existing mathematical and computational prowess. If an understanding of essential features is desired, then we believe that a deep understanding of relatively simple systems, like the one studied in the present work, can go a long way.

The present article is structured as follows. We first give details of the development of the simplest nontrivial model that incorporates all the essential physics and chemistry and that is well-suited for bifurcation analysis. Next, we consider propane oxidation with stoichiometric feed and investigate the possible bifurcation phenomena for three limiting cases in which either the homogeneous reaction only occurs or catalytic reaction only occurs or both reactions are present but no interphase gradients exist. The insight obtained from these limiting cases is used to present a complete bifurcation analysis of propane oxidation in short monolith or gauze type reactors and the impact of inlet fuel mole fraction, residence time and channel hydraulic diameter on the various ignitions and extinctions. The important practical case of methane oxidation is also examined for the case of both lean and rich feeds with the operating pressure as the bifurcation variable and the predicted results are compared with available experimental results and calculations based on CFD models in the literature. In the last section, we summarize the results and conclude by pointing out some possible extensions to this work.

2. Model development

Since the bifurcation analysis of a full three-dimensional model of homogeneous-catalytic reaction system with convection and