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Bifurcation Analysis of Catalytic Partial Oxidations in Laboratory-Scale Reactors with Heat Loss

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Highlights

- Modeling of laboratory-scale reactors with active (catalyst) and inert sections.
- Identifying characteristic time scales that define ignition and extinction.
- Impact of packing geometry and tube diameter on hysteresis behavior.
- Impact of heat and mass dispersion on yield of intermediate product in CPO.

1. Introduction

Catalytic partial oxidation (CPO) is an attractive technology for the production of intermediate chemicals (e.g. ethylene and synthesis gas from methane, ethylene oxide from ethylene and so forth). Numerous experimental and computational studies can be found on these systems, aiming to achieve high selectivity towards desired intermediate products using very short contact times either in adiabatic or cooled reactors. In laboratory studies, packed bed reactors with catalyst particles sandwiched between inert packings (e.g. quartz particles) in small diameter tubes are often used to test catalyst activity and selectivity. In most laboratory reactors, the heat loss (gain) to (from) furnace is significant and the reactor is neither isothermal nor adiabatic. Further, axial as well as radial temperature gradients may exist within the catalyst, especially when highly exothermic partial oxidation reactions occur within the catalyst bed. It is well known that depending on the catalyst activity, adiabatic temperature rise and various other characteristic times, multiple steady-states with different product distribution can exist for the same operating conditions. An understanding of the ignition and extinction behavior as well as the impact of heat loss on these features is important in the interpretation of laboratory results, catalyst performance evaluation and kinetic parameter estimation. The main goal of this work is to provide a framework for such an understanding by applying the singularity and the bifurcation theory techniques to partial oxidation reactions carried out in laboratory scale reactors.

2. Methods

Since catalysts used in most laboratory studies are fine powders (less than 100μm in diameter), we neglect inter and intra-particle gradients and use a pseudo-homogeneous model to study the ignition-extinction behavior of laboratory scale packed bed reactors with sectionalized packing (inert-catalyst-inert as shown in figure 1). The steady-state and transient behavior of the reactor is governed by various characteristic times: catalyst contact time, reactor contact time, heat/mass dispersion time, heat loss time, and various kinetic time scales. The heat/mass dispersion coefficients are estimated considering both diffusive and convective contributions. The effective solid conductivity is estimated using conductive, convective and radiative contributions. The characteristic heat loss time is estimated using heat transfer coefficient on the tube inside, heat conductivity of wall material, free convection and radiation outside the wall, as discussed in [1]. The results are presented for a global kinetic model and a reaction scheme that is representative of oxidative coupling of methane (OCM) and also partial oxidation of ethylene to ethylene oxide. For the OCM case, the reaction scheme involves dimerization/deep oxidation of reactants and deep oxidation of intermediate (C_2) products. The calculation of ignition/extinction, hysteresis and isola loci is done by the methods described in [2,3] and by the continuation method.

3. Results and discussion

Figure 2a shows the computed bifurcation diagrams of oxygen conversion versus furnace temperature for the same volume of catalyst but packed in tubes of different diameters (A and B in

figure 1) and different inert length but at the same space time. Figure 2b shows the temperature profiles in the reactor at the extinction point for corresponding cases. It is observed that even in the adiabatic case, thin packing in a larger diameter tube leads to a large region of multiple steady-states. However, with heat loss this is no longer true for this specific case. The length of inert section also influences the region of multiplicity for packing arrangement B but not for A. From these computations for the case of a single reaction, it is clear that for the same operating conditions and catalyst properties, the hysteresis behavior of the system depends on the heat loss as well as the manner of packing.

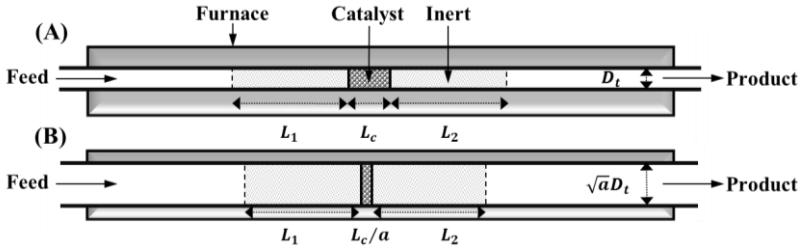

Figure 1. Schematic diagrams of lab scale packed-bed reactors with same volume of catalyst in tubes of different diameters.

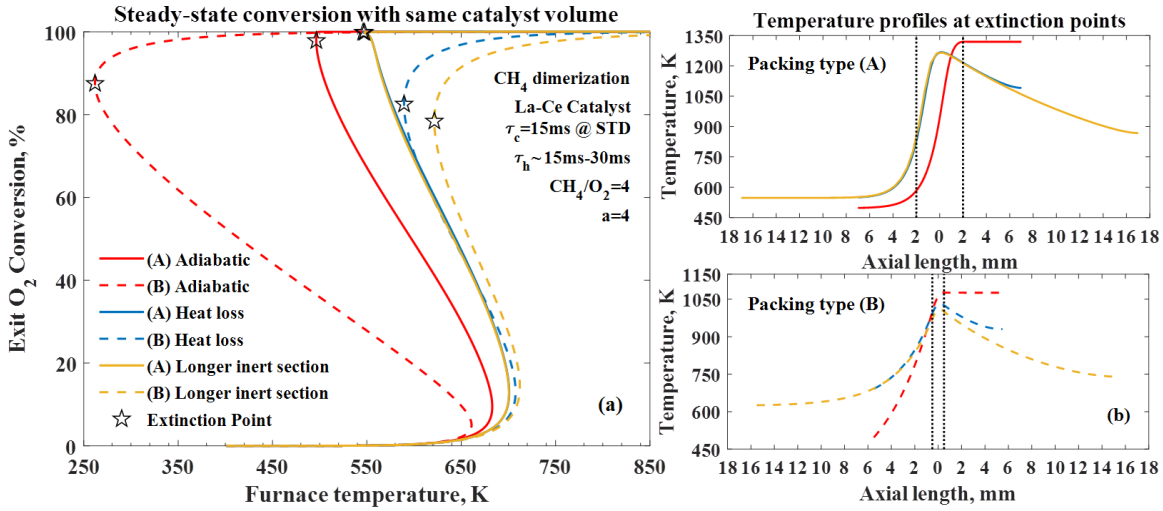

Figure 2. Impact of packing on ignition-extinction, oxygen conversion (a) and temperature distribution in packed bed (b)

4. Conclusions

We present a complete bifurcation analysis for the case of a single reaction. We also examine a three reaction global kinetic model of OCM and compute bifurcation diagrams of oxygen and methane conversion as well as C_2 product selectivity with furnace temperature and compare with the experiments presented in [1]. We also present results on the impact of heat loss on observed isolated branches when the space time is taken as the bifurcation variable. The main conclusion is that the ignition and extinction behavior as well as the observed C_2 product selectivity in laboratory OCM (and CPO) experiments are strongly influenced by the tube diameter, catalyst packing and heat loss (addition) to (from) the furnace. The results are used to provide guidelines for the interpretation of laboratory data, as well as for scale-up of such processes.

References

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Keywords
Ignition, extinction; autothermal operation, oxidative coupling.