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# Numerical bifurcation analysis of large-scale detailed kinetics mechanisms

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Despite the benefits of studying dynamical behavior of chemically reacting systems by bifurcation analysis, its utilization for large mechanisms is greatly limited by the lack of available software, and clear and published strategies for improving the technique. This paper reviews recent progress, and reports strategies we identified that greatly improve reliability and speed of computations. These are tested by combining two open-source software packages: AUTO-07p (bifurcation analysis) and Cantera (kinetics mechanism interpreter). Examples are shown for one-parameter and two-parameter bifurcation curves of methane partial oxidation. Cool and hot-flame regions and their dependence on secondary parameters can be identified and used to gain insight to previously unexplored operating regimes and potentially new reactor designs. Invariance in the bifurcation diagram provides evidence of successful mechanism reduction.

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## Introduction

In chemical engineering, bifurcation analysis has been proven to be a powerful tool to identify regions of reactor instabilities, multiple steady-states [1–3] and optimum operating conditions [4,5•] in one-dimensional or higher-dimensional parameter spaces. Most of historical bifurcation analysis studies were performed on models that contain only a few, at most tens of, chemistry variables [6–8]. Examples of industrially important phenomena that are studied by bifurcation analysis include thermal ignition-extinction, and periodic behavior (spatial or temporal) mostly with simplified reactor configurations [9,10]. Although numerical integration for kinetics is broadly used for analyzing detailed chemical mechanisms, their bifurcation analyses are rare because of lack of reliable and available software. The use of detailed kinetics mechanisms in reaction engineering, both for homogeneous and heterogeneous catalytic reactions, has greatly increased in the past 20 years. Their use allows identification of not only major species distributions, but also trace amounts of chemicals that may affect product quality, process reliability, health and the environment. Consequently, their development and analysis has become important not only in academic research (see [11•] for a review) but also in industrial process and product development [12–14]. Additionally, detailed kinetics mechanisms are more suitable for extrapolation than power-law type kinetics expressions of global reactions, as they are dominantly built from elementary reactions that are based on solid theory with wide-range of validity [15,16]. The combination of extensive computational and experimental validation studies has made it possible to create a number of high fidelity reaction mechanisms for combustion modeling (see [17,18•,19] as examples). It is obvious that for a given problem we want to use the simplest mechanism which is accurate in the range of interest. Often speed is an important consideration when integrating kinetics into more complex models (e.g. CFD, optimization, or flow sheet simulation). Consequently, there have been significant efforts to simplify detailed kinetics mechanisms [20•,21,22••,23] of which eliminating redundant species and their reactions is of particular interest for our purpose. These simplified mechanisms may differ in performance and dynamical behavior for the same set of reactants. Mapping ranges of oscillations, multistability and potentially more complex dynamical behavior in an easily available and reliable tool in one and higher dimensional parameter spaces would enable more complete classification of mechanisms. Despite the need, bifurcation analysis is rarely used for this purpose with large-scale kinetics mechanisms. The main reason, we believe, lies in numerical instabilities of the underlying computational methods which arise when the system of equations contains variables whose values span 15–20 orders of magnitude. Although progress has been made in the past few years, general availability of tools and methods is still lacking. Here we will review the current state of the field, and report strategies that can help to open paths for accelerated future progress.

## Current state

Historically there have been attempts to analyze detailed kinetics mechanisms by bifurcation analysis; however, the progress has been limited. The most notable results

are from Vlachos *et al.*, who studied hydrogen and methane combustion and flame behavior with mechanisms up to 32 species and 177 reactions [8,24]. Although the mechanisms were limited in size, the studies gave valuable information on the dynamical behavior both in one-parameter and two-parameter spaces [25]. Since the early 2010s measurable progress has been made, which was initiated by integrating detailed kinetics mechanism interpreters to bifurcation analysis codes in multiple research groups. Shan *et al.* [26,27] developed a bifurcation analysis code integrated with mechanism-specific subroutines that allowed automatic generation of the Jacobian for accurate and rapid detection of bifurcations. The mechanism targeting dimethylether flame chemistry contained 55 species and 290 reactions. Diarra *et al.* (http://flame-structure-2014.com/wp-content/uploads/David-Diarra.pdf) followed a similar approach to encode kinetics; however, they used the Matlab-based MATCONT continuation code developed by Kuznetsov and coworkers [28]. Acampora and Marra [29] integrated some of MATCONT's algorithms (modified and simplified for efficiency) as the bifurcation analysis part, but used Cantera as the kinetics interpreter [30•] (http://www.cantera.org) to be able to access a wider variety of chemical mechanisms. Their code was capable of computing one-parameter bifurcation curves and identifying limit and Hopf bifurcation points, but not the continuation of such points in two or higher dimension parameter spaces. Despite the limitations, the reported performance of the code is remarkable considering that it scales nearly linearly with the number of variables and is capable of computing one-parameter bifurcation curves of a 482-species reaction mechanism (with 19 072 reactions) in 42 min on a laptop computer. Kooshkbaghy and coworkers [22••] integrated AUTO-07p [31] (http://sourceforge.net/projects/auto-07p) as the bifurcation analysis code and Chemkin [32] (http://www.ansys.com/products/fluids/ansys-chemkin-pro) as the mechanism interpreter. The code was used to analyze n-heptane oxidation with about 150 chemistry variables, and could compute both one-parameter and two-parameter bifurcation curves. Overall, all of the above efforts are significant achievements; however, they are difficult to reproduce by other authors without significant software development as they combine in-house developed codes with either free (AUTO-07 and Cantera) or commercial (Matlab and Chemkin) software. While not reducing the merits of the results of their studies, their software selections put significant limitations on faster development and broader use of the techniques in the scientific community.

## Strategies for improvements

Among the many factors that have been limiting faster development, we believe the most critical is the lack of suitable software. A number of groups developed codes (reviewed above) that are capable of analyzing large-scale kinetics mechanisms for certain bifurcation behavior; however, none were made available to the scientific community either as public domain, open-source, or to commercial codes for further testing and development. Both AUTO-07p and Cantera are good examples of how open-source software helps progress by expanding applications involvement and integration to other scientific software.

In our efforts we used AUTO-07p for bifurcation analysis and Cantera as the mechanism interpreter to test their combined performance and limitations with large-scale mechanisms and share what made our efforts successful. AUTO-07p's model equations need to be coded into a C or Fortran-90 subroutine, which allows easy connection to Cantera's Fortran-90 interface. Using Cantera as mechanism interpreter makes very simple to define AUTO's model equations as the code for defining reaction rates and source-terms can be replaced by a single-line call to the appropriate Cantera function. A simple perfectly stirred reactor (PSR) model was implemented using mass and energy balances as detailed in Cantera's manual (http://www.cantera.org/docs/sphinx/html/reactors.html). This is the most common reactor type for bifurcation analysis studies due to its simplicity and value in approximating important sections of complex reactive flows, like recirculation zones in a reactor. As the continuation code updates solution variables and parameters, Cantera is called to calculate chemistry source terms, rate of change of enthalpy, and heat capacities, which are used to fully specify the differential equations. We provide the PSR model's example source code as Supplementary material.

For efficient bifurcation analysis, it is necessary to discuss how to reduce or eliminate numerical problems arising when large-scale kinetics mechanisms are involved. Each of the factors listed below appear to be important for success when we combine AUTO-07p and Cantera. We also tested the combination of CONT [1] and Cantera; however, we report result produced by AUTO-07p as this appears to be more flexible, faster, better documented and currently supported package. Nevertheless, factors discussed in (a) and (c) below applies to both bifurcation analysis packages.

(a) When differential and/or algebraic equations of large-scale mechanisms are solved numerically, solvers may predict very small but negative concentrations of redundant species originating from round-off errors. This may lead to spurious solutions, especially when bifurcation analysis codes are involved. Even if this problem is avoided, the ratio of small and large concentrations could easily span 15–20 orders of magnitude. It is easy to see that formulating the differential equation system in the usual textbook fashion creates great difficulties for solvers to find reliable step-sizes. The problem is general for numerical integrators, algebraic solvers, and pseudo-