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n-Heptane/air combustion in perfectly stirred reactors: Dynamics, bifurcations and dominant reactions at critical conditions

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ABSTRACT

The dynamics of *n*-heptane/air mixtures in perfectly stirred reactors (PSR) is investigated systematically using bifurcation and stability analysis and time integration. A skeletal mechanism of *n*-heptane constructed by entropy production analysis is employed, which is extensively validated for different conditions with respect to the ignition delay time, laminar flame speed, and the typical hysteretic behavior observed in PSRs. The significantly reduced size of the skeletal mechanism, enables the extension of the bifurcation analysis to multiple parameters. In addition to residence time, the effect of equivalence ratio, volumetric heat loss and the simultaneous variation of residence time and inlet temperature on the reactor state are investigated using one- and two-parameter continuations. Multiple ignition and extinction turning points leading to steady state multiplicity and oscillatory behavior of both the strongly burning and the cool flames are found, which can lead to oscillatory (dynamic) extinction. The two-parameter continuations revealed isolas and codimension-two bifurcations (cusp, Bogdanov–Takens, and double Hopf). Computational Singular Perturbation (CSP) and entropy production analysis were used to probe the complex kinetics at interesting points of the bifurcation diagrams.

1. Introduction

The Perfectly Stirred Reactor (PSR) or Continuous Stirred Tank Reactor (CSTR) is commonly used to study complex chemical kinetics and combustion dynamics. In practice, such reactors can be realized by intense mixing using gas reactant jets in a jet-stirred reactor [1]. Efficient mixing provides homogeneous conditions so that the state at the reactor exit is the same as inside, simplifying strongly its numerical modeling.

Since the rigorous analysis of Bilous and Amundson in 1955 [2] and the more comprehensive numerical study of Aris and Amundson [3], the reactor dynamics and stability for the single-step irreversible exothermic reaction $R \rightarrow P$ have been investigated extensively, revealing interesting dynamics which include multiple equilibria and hysteresis loops, super- and subcritical Hopf bifurcations, and complex oscillations (see, for example, [4–6]).

The dependence of the reactor state (indicated for example by its temperature T) on τ, the residence time in the reactor, typically displays an S-shaped curve, connecting the weakly- and strongly burning steady state branches via an unstable steady state branch between the ignition and extinction points [7]. The lower branch of the bifurcation diagram that shows the possible long-term states drawn schematically in Fig. 1 starts from the chemically frozen state at very short residence time and remains weakly reacting up to the residence time of ignition τ_{ign}, where the system state jumps to the strongly burning branch. Starting from a state on the latter branch, the gradual decrease of τ will eventually lead the reactor back to the weakly reacting state at τ_{ext}, the residence time of extinction. Steady state multiplicity exists for $\tau_{ext} \leqslant \tau \leqslant \tau_{ign}$, and the reactor operation becomes sensitive to external perturbations.

More complete pictures of the qualitative features of PSRs and phase portraits for various scenarios of bifurcation diagram have been obtained analytically and numerically for single-step reactions and lumped variables [8–10]. PSRs have also been investigated via Lyapunov's direct method [11], parametric sensitivity [12] as well as from the control and stabilization point of view (e.g. [13]). A discussion of earlier theoretical and experimental studies of ignition and cool flames in CSTRs can be found in the review of Griffiths and Scott [14], the book [6] and the references therein. The ignition and extinction conditions are used for the

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validation and rate constant tuning of detailed and reduced mechanisms by comparison with experimental data (see, for example, [15]).

Although the dynamic behavior of PSRs using generic single- or few-steps reactions has been systematically analyzed, few literature studies have considered detailed reaction mechanisms. Numerical investigations of hydrogen combustion in isothermal PSRs [16–18] revealed complex dynamics which in addition to ignitions and extinctions included oscillations and birhythmicity (coexistence of two stable limit cycles for the same operating conditions). Sensitivity and principal component analysis at the bifurcation points were used to construct minimal reaction mechanisms that can predict state multiplicity [17]. Recent investigations of ignition/extinction behavior of more complex fuels like dimethyl ether [19,20] and *n*-heptane [21] in PSRs focused on the detection of important features with respect to the variation of a single parameter (the residence time) and its effect on the type of extinction (sudden jump to the weakly burning or extinguished state or dynamic extinction via oscillations of increasing amplitude) [20].

The complexity of the reaction mechanism in terms of the number of species and reactions increases dramatically with the size of the fuel molecule [22], and even for ideal homogeneous reactors like the PSR the computational cost becomes high, particularly when a large number of parameters determines the behavior. Thanks to the availability of efficient numerical continuation packages, the analysis of the dynamics of single- or few-steps global reactions can be expanded to detailed mechanisms including hundreds of species and thousands of elementary reactions. The efficient scanning of the dynamics with respect to multiple operating parameters can identify the critical conditions leading to the transition between different reactor states and provide essential information not only to enhance our understanding of the phenomenology of combustion chemistry, but also for the design of experiments to probe different types of kinetics for mechanism validation purposes.

In the present study, we employ a skeletal mechanism constructed using the recently proposed reduction approach that is based on the relative contribution of elementary reactions to the total entropy production [23]. Comparisons with the detailed scheme show that the skeletal mechanism reproduces accurately not only the ignition delay and the laminar flame speed over a wide range of conditions, but it can also accurately capture the complex PSR dynamics including the bifurcation points.

The bifurcation diagram summarizing the possible dynamics as well as the transitions leading from one state to another can be generated by finding the long-time state for the system of equations describing the dynamics for different values of the controlling parameter(s). In a brute force manner, this can be achieved by scanning the parameter space and numerically integrating the transient equations modeling the temporal evolution of the concentration and temperature in the reactor (Section 2) starting from different initial conditions. The dynamics in a PSR is determined by five parameters: the residence time τ, inlet temperature T_0, pressure p, equivalence ratio ϕ and heat loss per unit volume $\dot{Q}_{loss}$, and the brute force method becomes impractical. In addition to the excessive number of integrations that are required, this approach can only identify stable steady or oscillatory states.

Arc-length continuation methods [24] offer an accurate and more efficient way to track changes in the long-term behavior by starting from a particular solution and following it as one or more parameters are varied. Unstable solutions can be computed, and the local stability can be determined by the eigenvalues of the Jacobian matrix obtained by linearization of the governing equations around the desired state: eigenvalues with negative (positive) real parts define stable (unstable) states. In this work, the AUTO-07p package [25,26] is employed to systematically follow the transitions in the observed behavior, first with respect to independent variations of τ and $\dot{Q}_{loss}$ for fixed values of the remaining parameters (one-parameter continuations), and then for the simultaneous variation of τ and T_0 (two-parameter continuation). The effect of equivalence ratio and pressure is assessed by computing the two-parameter diagrams for different values of ϕ and p to partially construct three-parameter diagrams. The observed dynamics include steady and oscillatory strongly burning states and cool flames, multistability over extended ranges of operating conditions and higher codimension bifurcations.

Entropy production analysis can also provide useful information about elementary reactions responsible for bringing the system state to equilibrium. Computational Singular Perturbation (CSP) analysis is also employed to identify the dominant reactions at the bifurcation points. CSP is a time-scale based approach that has been used for the identification of slow and fast processes (e.g. [27]), skeletal and reduced mechanism generation (e.g. [28,29]), analysis of two-stage *n*-heptane ignition [30], as well as flow-chemistry interactions in limiting phenomena [31,32]. The CSP analysis is performed on the so-called explosive mode, i.e. the mode with time scale corresponding to the positive or the least negative eigenvalue of the Jacobian matrix at the state of interest. The corresponding eigenvector, a first-order approximation to the CSP mode, is used to identify the most important reactions at extinction, ignition or oscillatory combustion with the help of the amplitude [33] and time scale participation [34] indices. More detailed CSP-based analyses of autoignition and the multi-stage ignition of *n*-heptane can be found in [35,30,36].

The work presented here is along the lines of the work of Lu and co-workers who studied combustion dynamics in PSRs for *n*-heptane [21], methane [19] and DME [19,20]. One-parameter continuations with respect to the residence time were performed in these works focusing on ignition and extinction, and a variant of the CSP method, the Chemical Explosive Mode Analysis (CEMA) [37], was used to analyze the kinetics.

The paper is organized as follows: Following the presentation of the PSR governing equations in Section 2 and a brief discussion of numerical continuation in Section 3, the skeletal mechanism that was generated using entropy production analysis is presented in Section 4. The CSP analysis tools used are briefly reviewed in Section 5, before turning to the results of numerical calculations both from the chemical kinetics and the dynamical system points of view (Section 6).

2. Governing equations

A system of n_s chemical species $M_i,\ i = 1,\ldots,n_s$ is considered, which reacts according to a mechanism of n_r reversible elementary reactions

$$\sum_{i=1}^{n_s} \nu'_{ik} M_i \rightleftharpoons \sum_{i=1}^{n_s} \nu''_{ik} M_i, \quad k = 1,\ldots,n_r \tag{1}$$

Stoichiometry is defined by ν'_{ik} and ν''_{ik}, the stoichiometric coefficients of species i in reaction k for the reactants and products, respectively. The rate of the elementary reaction k is

$$q_k = q_k^f - q_k^r = k_k^f \prod_{i=1}^{n_s} [X_i]^{\nu'_{ik}} - k_k^r \prod_{i=1}^{n_s} [X_i]^{\nu''_{ik}} \quad k = 1,\ldots,n_r \tag{2}$$

where $[X_i]$ denotes molar concentration of species i and k_k^f and k_k^r are the forward and reverse rate constants of reaction k. The production/consumption rate of the ith species $\dot{\omega}_i$ is the summation of the rates of all reactions involving the species i