Continuation Analysis of Complex Chemical Mechanisms for Jet-Fuels Combustion in PSR

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1 Introduction

Limit combustion phenomena, such as ignition, are rather sensitive to chemical kinetics and these properties are therefore used to physically characterize the behaviour of different fuels. In the framework of bifurcation theory, the ignition and extinction correspond to saddle-node bifurcation points in a classical S-shaped steady-state curve [11, 18]. Then, the location of ignition and extinction conditions and their dependence on the main parameters (like pressure, equivalence ratio, residence time or inlet temperature in reactors) can be reformulated as a problem of bifurcation analysis. However, this approach represents a computationally difficult task when reaction mechanisms with several hundreds of species and thousands of chemical reactions are considered. In the past, a full bifurcation analysis has been successfully conducted adopting detailed schemes for some elementary fuels like hydrogen [7, 13] or methane with the simpler versions of the GRI mechanism [14, 15] by using software written specifically for modelling combustion reactions. Nowadays, the need to face with dynamic combustion phenomena and the widening of fuels composition is leading to the adoption of very large chemical mechanisms, with several hundreds of species and thousands of chemical reactions. Even considering the increased computer power, the methods of bifurcation theory are computationally very challenging. To speed-up the computations and preserve the accuracy required, an approach based on analytical Jacobian evaluation was recently proposed by Shan and Lu [18]. These authors presented the complete bifurcation map for methane, Di-Methyl Ether (DME) and Jet Fuels (JF) [18–20] by using computer code that automatically generate mechanism-specific subroutines for analytical Jacobian evaluation from mechanisms described in CHEMKIN format. In this work an alternative approach is proposed to construct the bifurcation diagram without any need of a further preprocessing of the chemical mechanism given in CHEMKIN format. Cantera [6], a suite of object-oriented software tools is adopted for the management of kinetic mechanism (including thermodynamic and transport properties) and the computation of the properties derived from the state variables (e.g. density, heat capacity). It is then coupled with a predictor-corrector pseudo-arclenght continuation algorithm [8]. In order to overcome the computational difficulties arising when dealing with large chemical mechanisms, some basic elements of this algorithm are chosen specifically, as illustrated in the paper. The proposed approach has been then applied to compare ignition

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and extinction of three JF mixtures. They are complex mixtures of hundreds of hydrocarbons spanning a wide range of carbon numbers and chemical classifications [4], posing a significant test case for the developed method.

2 Methodology

The equations of unsteady adiabatic constant pressure PSR can be written as:

$$\frac{dY_j}{dt} = \frac{Y_{j,f} - Y_j}{\tau} + \frac{W_j r_j}{\rho V}, \qquad j = 1, 2, \dots, N_s$$
(1)

$$\frac{dT}{dt} = \sum_{j=1}^{N_s} \left(\frac{Y_{j,f}(h_{j,f} - h_j)}{c_p \tau} - \frac{h_j W_j r_j}{\rho V c_p} \right)$$
(2)

where $Y, t, W, r, N_s, T, h, c_p, V$ are, respectively, the mass fraction, the time, the molecular weight, the net production rate, the number of chemical species, the mass specific enthalpy, constant pressure specific heat and the volume of reactor. The subscripts j and f refer, respectively, to species index and to feed conditions. The stationary solutions curve [17], including ignition and extinction states, has been identified by using a one-parameter continuation technique. Let

 $\mathbf{F}(\mathbf{x},p)$

denotes the augmented system formed by the r.h.s. of the Eq.(1) and Eq.(2) and an additional scalar equation representing the chosen parameterization. The pseudo arc-length continuation algorithm [8] is used to numerically solve the steady state vector system:

$$\mathbf{F}\left(\mathbf{x},p\right) = 0\tag{3}$$

where x is the state vector, $\mathbf{x} = [Y_1, \dots, Y_{N_s}, T]$ and p the chosen parameter that is, in all the computations here reported, the residence time τ in the PSR. An appropriate choice of the following sub-modules is required for a successful continuation algorithm:

- predictor;

- corrector;
- step-size control.

The first two of these three items can be chosen independently of each other. Instead the step-size control depends on the choice of the parametrization strategy, the predictor and the corrector [17]. There is not an ideal choice for all these items but the choice is problem dependent. The corrector step is the most computationally expensive. Therefore, for the sake of brevity, this paper briefly illustrate the method adopted only for this task. It is usually performed by means of a Newton-like method thus requiring the Jacobian matrix evaluation of Eq.(3). The number of entries of this matrix increases by increasing the number of species while the computational cost, matrix factorization should be avoided together with a significant reduction of function \mathbf{F} evaluations. This is achieved by adopting the so-called Broyden's method [1, 2, 9] that constructs a sequence of states that converge to the solution of Eq.(3) by using the iterative scheme:

$$\mathbf{Y}_{k+1} = \mathbf{Y}_k - \mathbf{B}_k^{-1}(\mathbf{Y}_k)\mathbf{F}(\mathbf{Y}_k)$$

that correspond to a secant update, in conjunction with the formula [2]:

$$\mathbf{B}_{k+1}^{-1} = \mathbf{B}_{k}^{-1} + \frac{\Delta \mathbf{Y} - \mathbf{B}_{k}^{-1} \Delta \mathbf{F}}{\Delta \mathbf{Y}^{T} \mathbf{B}_{k}^{-1} \Delta \mathbf{F}} \Delta \mathbf{Y}^{T} \mathbf{B}_{k}^{-1}$$

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Table 1: Composition of selected surrogates.					
Jet Fuel	Reference	Formula	MW	Surrogate	
			[kg/kmol]	Species	[mol %]
JET-A	[4]	C _{8.60} H _{17.27}	120.67	n-decane	42.67
				iso-octane	33.02
				toluene	24.31
Shell [™] GTL	[10]	C _{9.81} H _{21.62}	139.3	n-decane	90.6
				iso-octane	9.4
Sasol TM CTL	[10]	C _{9.59} H _{19.98}	135.1	n-decane	72.0
				iso-octane	13.0
				n-propylbenzene	15.0

The cost of every Broyden step is approximatively equal to the cost of a vector function evaluation. It is locally superlinearly convergent [9]. The solutions stability and then ignition and extinction states are identified by proper test functions based on the numerical eigenvalues of the Jacobian of \mathbf{F} . The continuation algorithm and the description of the governing equations have been implemented by using the Matlab© programming environment. The CANTERA open source library [6] are used in conjunction to manage the kinetic scheme and to compute c_p , h, W, r as function of the state of the system. The overall tool is very flexible and general and it makes the continuation analysis viable even on desktop class computers.

3 Application to Jet-Fuels

The code developed has been adopted to study the chemical stability of three different JF, respectively:

- JET-A POSF 4658;
- Shell GTL (Gas-To-Liquid);
- Sasol CTL (Coal-To-Liquid);

These fuels are complex mixture of several hundreds hydrocarbons including alkanes, aromatics, and cycloalkanes or naphtenes [3], that does not permit the complete development of a detailed reaction model [10]. Therefore the surrogates reported in Table 1 have been defined to study their combustion behaviour. Obviously, in order to describe the conversion of reactants to products, a detailed kinetic scheme is needed. To allow a consistent comparison of the different fuels, a single chemical mechanism should be adopted for all the three fuels. Such a scheme must be able at least to describe the combustion of any hydrocarbon that constitutes the surrogates, if not a specific validation for the adopted surrogate is available. A detailed scheme suitable for this purpose has been proposed by the Chemical Reaction Engineering and Chemical Kinetics (CRECK) group, ver. 1212 [5, 16]. It consists of 466 species and 14631 reactions. The one-parameter continuation of the stationary solution from cold conditions to ignited ones in a PSR with the residence time as parameter and inlet temperature of 900 K has been performed at two different pressures (10 atm and 50 atm) and varying mixture composition (air/fuel equivalence ratios Φ_A ranging from 0.6 to 1.4 by 0.1). Figure 1 shows the equilibrium state temperature in the reactor as function of residence time for the three selected JF under pressure of 50 atm and inlet temperature of 900 K. The curves are typical folded S-curves with multiple solutions and distinct ignition and extinction states (Law, 2006). Figure 1 confirms that the three fuels have a similar behaviour. This result was expected, because the alternative fuels have been designed to replace the traditional jet fuels without any change of engine technology. The most relevant difference between the three jet fuels is at ignition and extinction states. In particular JET-A has ignition and extinction residence times greater than that of the alternative jet fuels.



Figure 1: Reactor Temperature vs. Residence Time for a non-isothermal CSTR, at 50 atm, stoichiometric conditions, and 900 K inlet temperature. The circles represent the location of the fold bifurcations, the solid lines indicating stable branches, and dotted lines indicating unstable branches solutions. Symbols are reported every 50 computed points.

The effect of mixture composition and pressure on extinction and ignition conditions can be estimated by collecting results from several one-parameter continuations. Figure 2, left, reports the obtained map of ignition and extinction limit points in the two parameters space residence time τ - air/fuel equivalence ratio Φ_A . The ignition residence time slowly (almost linearly) grows with Φ_A for all the different fuels, with larger differences for the JET-A at 10 atm. Both ignition and extinction residence times decrease by increasing pressure. The ignition reactor temperature, reported in Figure 2 right, is slightly sensitive to mixture composition. Therefore a longer residence time is required to allow the activation of the reaction for leaner mixtures, and ignition happens when a critical temperature is reached, which is almost independent from mixture composition.

The extinction temperature is very sensitive to mixture composition, with a maximum at $\Phi_A = 0.7$ for p = 10 atm and at $\Phi_A = 0.8$ for p = 50 atm (fuel rich mixtures). Among the different fuels, these temperatures clearly diverge by decreasing Φ_A , i.e. moving towards reach mixtures.

The extinction residence time and reactor temperature behave almost mirror, i.e. when extinction residence time grows the extinction reactor temperature decrease and vice-versa. However, the minimum of extinction residence time does not correspond to the maximum of extinction temperature. Indeed, the extinction residence time is minimum at air/fuel ratio $\Phi_A = 0.9$ (slightly fuel rich mixtures) for both values of pressure considered.

The substantial chemical equivalence of the traditional fuels and the new synthetic fuels is confirmed: appreciable differences arise especially at higher values of the pressure.

4 Conclusions

A predictor-corrector continuation method suitable for the parametric study of fuel-air mixtures combustion modelled with large detailed kinetic mechanisms has been presented. In particular, we have shown the potential of the Broyden's method as corrector in the continuation of system of ODE arising

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Figure 2: Left: extinction and ignition limit points in the $(\tau - \Phi_A)$ parameters space. Right: reactor temperature in the same limit points reported othe left. Pressure 10 atm and 50 atm and mixture inlet temperature 900 K.

from 0-dimensional models adopting complex chemical schemes. The numerical code has been developed in Matlab and coupled with the CANTERA libraries for the prompt inclusion of the chemical and thermodynamic data of the mixtures. The overall code results very compact and highly customizable, offering the opportunity of an easy extension to different reactor configurations or to the investigation of different mixtures compositions and chemical mechanisms. Actually, it has proven to be effective also in application to parametric continuation of problems governed by PDE equations [12]. Finally, we have applied this code to the study of ignition and extinction of conventional and alternative JF-air mixtures in a non-isothermal adiabatic PSR. Several one-parameter continuations have been performed at different pressure conditions and with different air/fuel equivalence ratios by using the residence time as bifurcation parameter. Ignition and extinction points have been collected over a single map to show that, even if the general trends of conventional fuels are equally reproduced by the alternative fuels, some differences exist especially close to ignition and extinction conditions and that these differences are sensitive to pressure and, close to extinction, to air/fuel equivalence ratio.

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