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EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

DATA COLLECTION AND MINING TOWARD VIRTUAL CHEMISTRY OF SMART ENERGY CARRIERS

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Continuation tools as a virtual test bench for chemical reaction mechanisms

Luigi Acampora[a], Francesco S. Marra[b]

[a] *Università degli Studi del Sannio, Dipartimento di Ingegneria, Benevento, ITALY*

[b] *Istituto di Ricerche sulla Combustione – CNR, Napoli, ITALY*

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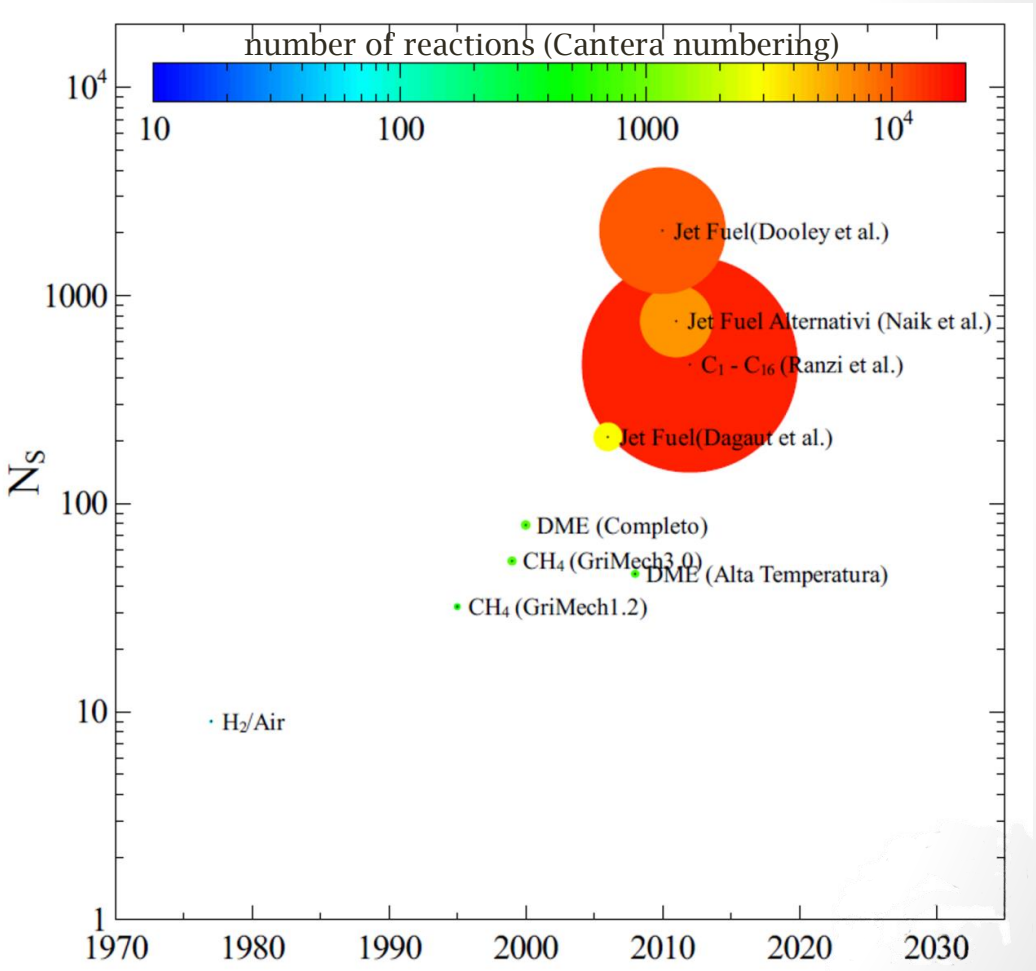
Istituto di Ricerche sulla Combustione

Introduction - I

Increasing interest into the use of detailed chemical mechanisms with hundreds of species and thousands of reactions or more:

- Accuracy of predictions
- Prediction of pollutants

- Fuel composition flexibility
- Widening of sources (biofuels, synthetic fuels, by-product fuels, solar fuels, …)
- Widening of combustion processes (LPP, gasification, pyrolysis, catalytically enhanced conversion, detonation engines, …)



Some representative mechanisms with their dimensions

Introduction - II

Explore the behaviour of chemical mechanisms

Obtain a rapid characterization:

- Over a wide range of conditions changing:
  - pressure,
  - composition,
  - temperature,
  - residence time
  - …
- Identify critical conditions:
  - ignition and extinction
  - oscillations (harmful stable unsteady regimes)

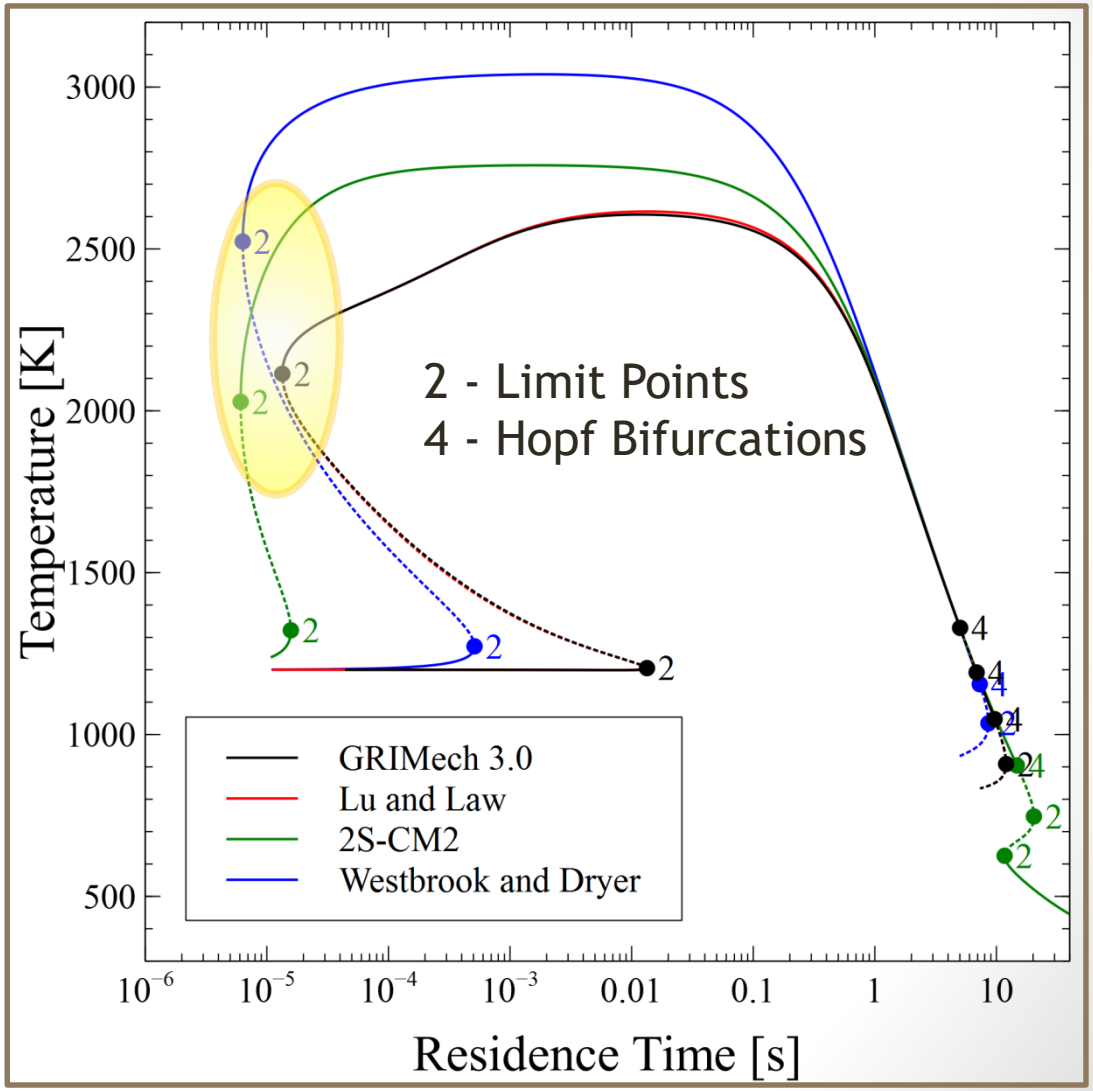
PSR with heat transfer:
Bifurcation map $\phi = 1$

Methane oxidation
$\phi = 1$
$p = 1$ atm
$T_{in} = 1200\ K$

Heat transfer to the wall:
$T_{env} = 300K$
$\alpha A/V = 125.4\ W/m^3K$

(Acampora et al. 2015; Acampora et al., 2016)

with heat transfer



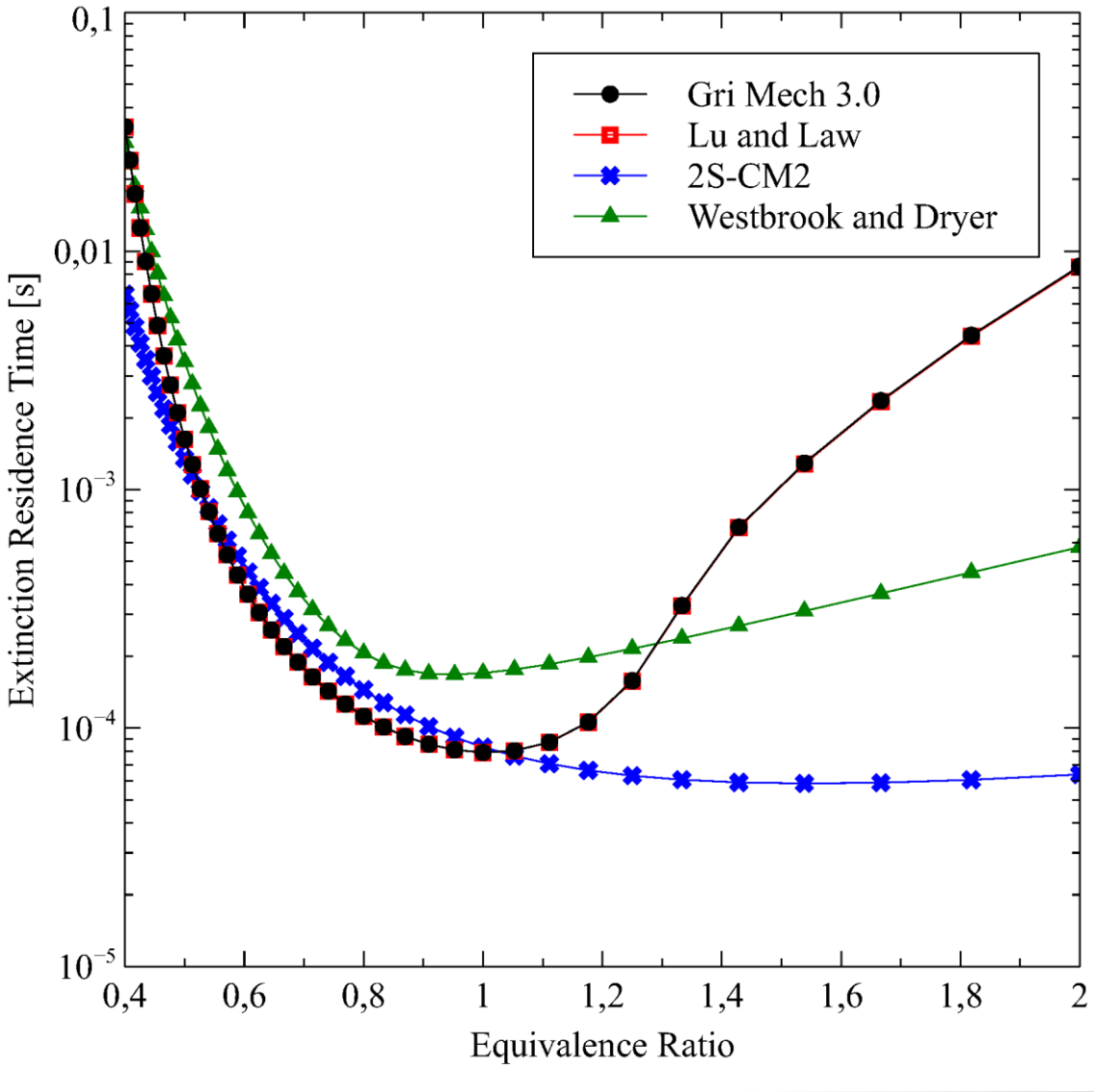
PSR with heat transfer:
Bifurcation map: limit points at varying ϕ

Methane oxidation
ϕ varying
$p = 1$ atm
$T_{in} = 300\ K$

Heat transfer to the wall:
$T_{env} = 300K$
$\alpha A/V = 125.4\ W/m^3K$

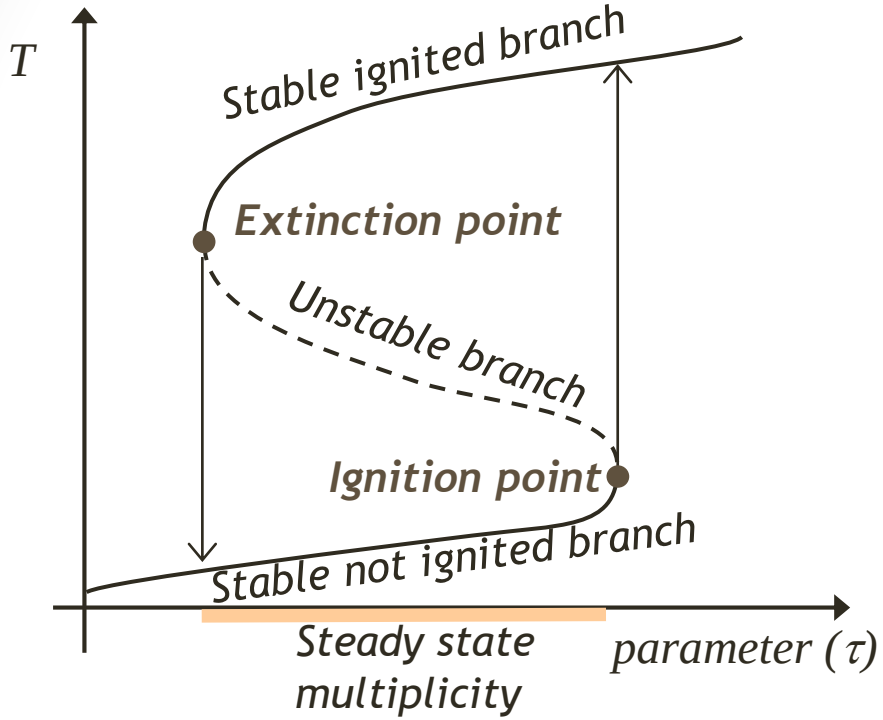
(Acampora et al. 2015; Acampora et al., 2016)

Extinction points varying the equivalence ratio collected from bifurcation maps



Introduction - III

S-shaped curve



Map of steady states (stable and unstable) of the system

Extinction and ignition points mathematically exactly defined

Detection of Bifurcation Points as function of the parameter

- Ignition and extinction correspond to turning points (fold/saddle-node bifurcation points) in a classical S-shaped steady-state curve (Law, 2006).
- Their location 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***.

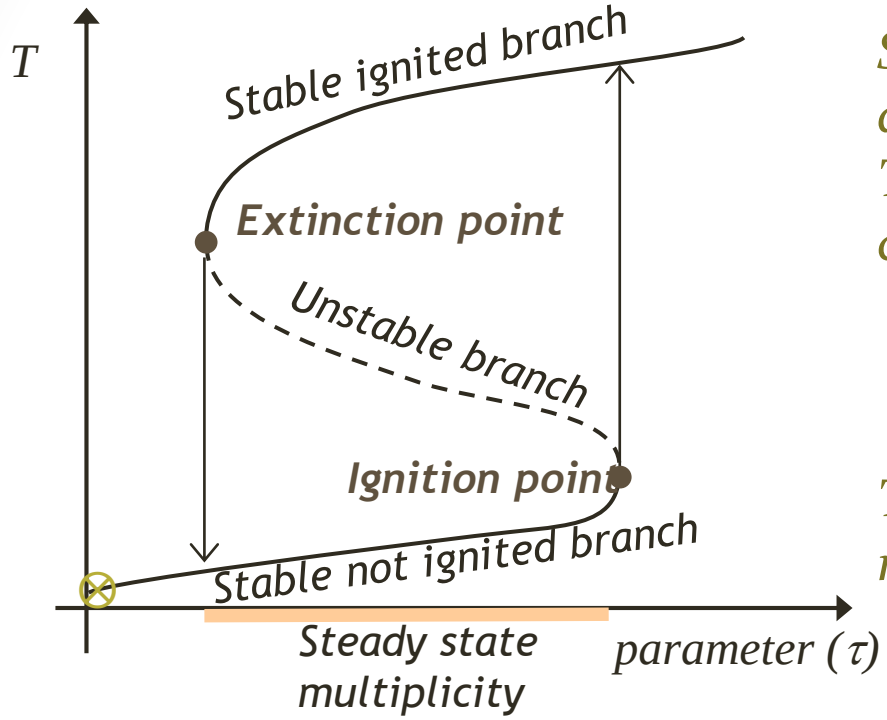
Introduction - IV

This approach results in a **computationally difficult task** when reaction mechanisms with several hundreds of species and thousands of chemical reactions are considered because:

- **large database**: in addition to the mathematical model, the thermodynamic, transport and kinetic data and the subroutines to compute physical and chemical properties of the reacting mixture must be provided.

- **computational effort**: the large number of species and chemical reactions increases dramatically the computational effort already high in the bifurcation analysis of a simple PSR model.

Introduction - V



Continuation analysis

Starting from a stable solution ⊗, determine the next point of the map. This is done with a predictor-corrector algorithm

$$X_i \xrightarrow{predictor} \tilde{X}_{i+1} \xrightarrow{corrector} X_{i+1}$$

The curve is implicitly defined by a non linear equation:

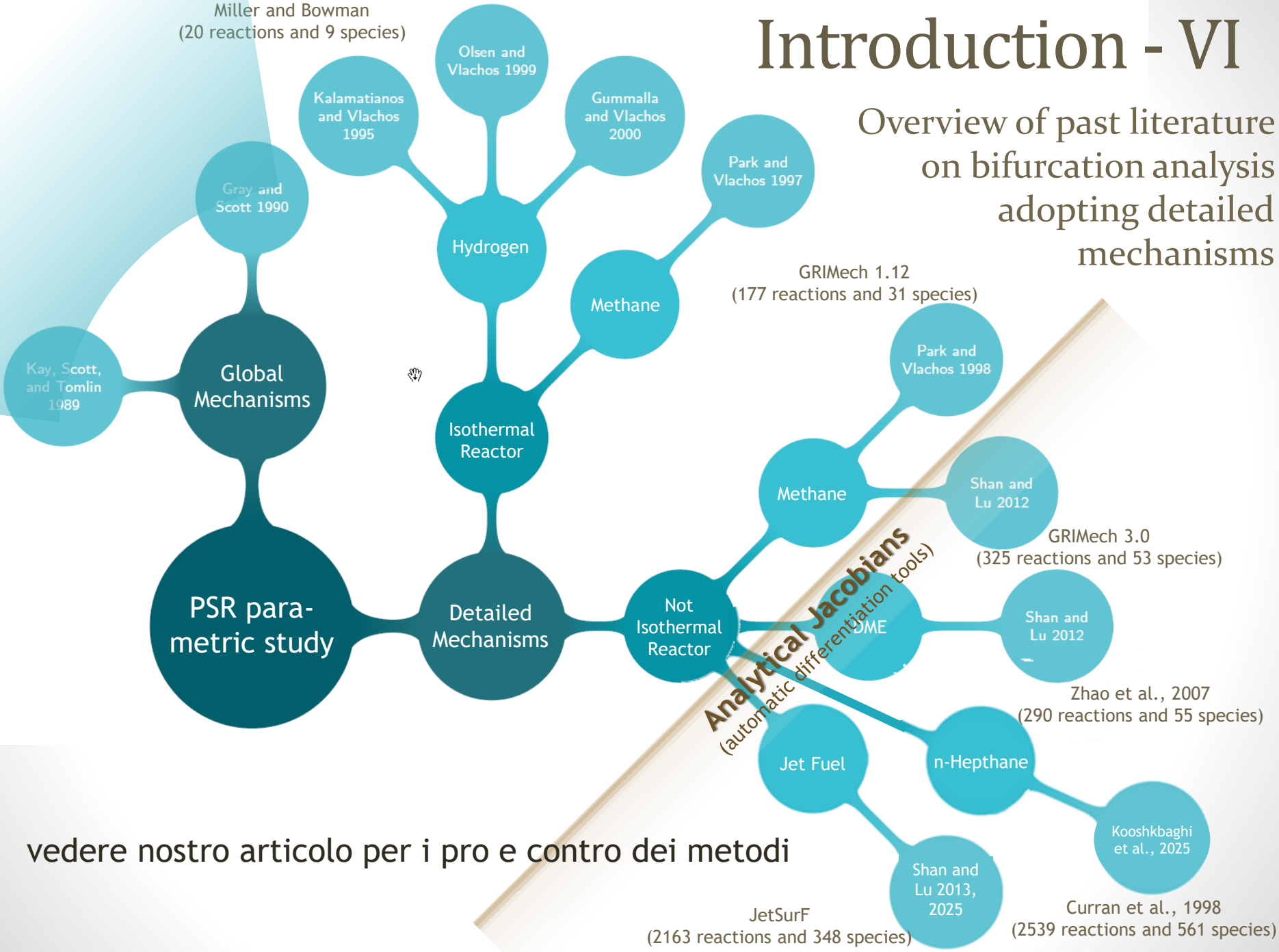
$$\mathrm{F}(X) = 0$$

Where is the problem ?

Solution of this equation is usually done adopting Newton-like methods, that requires the ***computation and inversion*** *of the Jacobian matrix* $\partial \mathrm{F}(\tilde{X}_{i\ k})/\partial X_i$ *at each point and inner iteration. This leads to a* ***formidable numerical problem***.

Introduction - VI

Overview of past literature on bifurcation analysis adopting detailed mechanisms



vedere nostro articolo per i pro e contro dei metodi

Aim of the work

Build a general continuation tool able perform the bifurcation analysis of PSRs (or other relatively simple models) with detailed chemical mechanisms.

The basic elements of the continuation tool are chosen specifically to overcome the difficulties in dealing with reaction mechanisms with several hundreds of species and thousands of chemical reactions.

Matlab is used to program and solve the bifurcation algorithm.

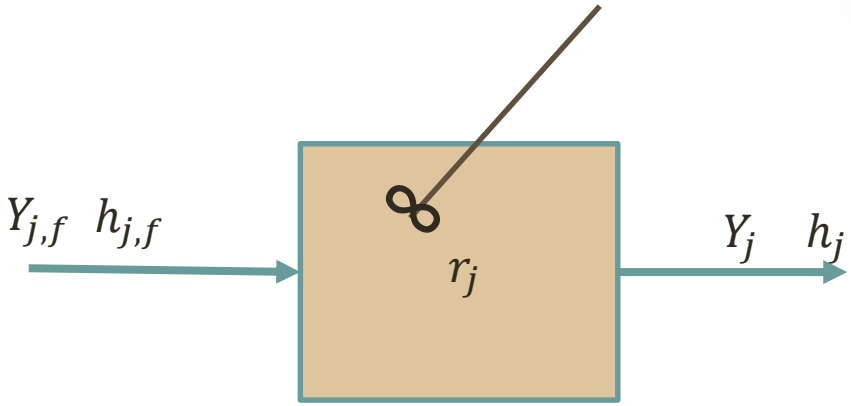
Cantera (Goodwin et al., 2003) is adopted to: manage kinetic mechanisms (including thermodynamic and transport properties); compute the mixture properties (e.g. density, heat capacity).

(Acampora et al. 2014; Acampora and Marra, 2015)

Reactor Model: Perfectly Stirred Reactor (PSR)

Hypothesis

- Constant Volume
- Constant Pressure
- Adiabatic
- Ideal Gas



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

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

Symbols:

- Y mass fraction
- τ residence time
- T Temperature [K]
- r reaction rates
- t time [s]
- W molecular weight [Kg/kmol]
- ρ density [Kg/m^3]
- N_s number of chemical species
- h mass specific enthalpy [J/Kg]
- c_p constant pressure specific heat [J/Kg K]
- V reactor volume [m^3]

Bifurcation Analysis

The bifurcation analysis of a system means:

1. determining its steady state solutions also known as the equilibrium points and studying the dependence of these points on the parameter (**continuation problem**);
2. locating the bifurcation points, i.e. the equilibria in which qualitative changes in the dynamics of the system occur.

Bifurcation Analysis - I

The bifurcation analysis of a system means:

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Recast the PSR equations in the form:

$$\frac{dx}{dt} = f(x, \alpha) \qquad x = [Y_1, \dots, Y_{Ns}, T]$$

step 1 is equivalent to find the curve implicitly defined by:

$$F(X) = 0 \quad F: \mathbb{R}^{n+1} \rightarrow \mathbb{R}^n$$

$$X = (x, \alpha)$$
$$F = f(x, \alpha)$$
$$n = N_s + 1$$

The number of equations is lower than the number of the unknowns. An extra scalar equation has to be added to the system to obtain a **well-posed problem**. We seek a numerical solution as a sequence of points (starting from a known equilibrium point) that describes the solution map with desired accuracy:

$$X_1, X_2, \cdots, X_i, \dots$$

Bifurcation Analysis - II

The bifurcation analysis of a system means:

1. determining its steady state solutions also known as the equilibrium points and studying the dependence of these points on the parameter (**continuation problem**);
2. locating the bifurcation points, i.e. the equilibria in which qualitative changes in the dynamics of the system occur.

Adopting a predictor corrector method:

$$X_i \xrightarrow{predictor} \tilde{X}_{i+1} \xrightarrow{corrector} X_{i+1}$$

a common choice for an extra scalar equation is the equation of a hyper-plane passing through $\tilde{X}_{i+1}$ and orthogonal to the normalized vector v_i tangent to the equilibrium curve in the point X_i (Keller, 1987; Kuznetsov, 1998):

$$p(X) = \langle X - \tilde{X}_{i+1}, v_i \rangle = 0$$

Addition of this equation to the system, leads to the **well-posed problem**:

$$F(X) = \begin{bmatrix} \mathrm{F}(X) \\ p(X) \end{bmatrix} = 0$$

Bifurcation Analysis - III

The bifurcation analysis of a system means:

1. determining its steady state solutions also known as the equilibrium points and studying the dependence of these points on the parameter (**continuation problem**);
2. locating the bifurcation points, i.e. the equilibria in which qualitative changes in the dynamics of the system occur.

The **location of the bifurcation points** is addressed by studying the eigenvalues $\lambda = a + ib$ of the Jacobian matrix:

$$J_f = \frac{\partial f(x, \alpha)}{\partial x}$$

For the model presented, only two different bifurcations can be detected:

- a **Fold bifurcation** (or Saddle-Node bifurcation or Turning Point), associated with the existence of a **null eigenvalue**;
- a **Hopf bifurcation** (or Andronov-Hopf bifurcation), corresponding to the presence of a pair of **purely imaginary eigenvalues** (Kuznetsov, 1998).

These bifurcations are detect by monitoring **test functions** (ψ). Evaluation of these functions must be possible in each equilibrium point.

The computational effort

The bifurcation analysis of a system means:

1. determining its steady state solutions also known as the equilibrium points and studying the dependence of these points on the parameter (**continuation problem**); Newton's methods are used to solve:

$$F(X) = 0 \quad \longrightarrow \quad J = \frac{\partial F}{\partial X} \approx \frac{\Delta F}{\Delta X} \dashrightarrow J^{-1}$$

2. locating the bifurcation points, i.e. the equilibria in which qualitative changes in the dynamics of the system occur.

$$J_f = \frac{\partial f(x,\alpha)}{\partial x} \approx \frac{\Delta f(x,\alpha)}{\Delta x} \dashrightarrow L\Lambda R$$

To keep the computational effort affordable, the capabilities of automatic differentiation tools have been exploited, by rewriting the problem in the form (*Shan and Lu, 2012*; *Kooshkbaghi et al., 2015*):

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

$$\frac{dT}{dt} = \sum_{j=1}^{N_S} \left(\frac{Y_{j,f}\left(h_{j,f} - h_j\right)}{\bar{c}_p\, \tau} - \frac{h_j W_j r_j}{\rho\, V\, \bar{c}_p} \right)$$

$$\rightarrow \quad \frac{dx}{dt} = L(x) + P(x)$$

The computational effort

The bifurcation analysis of a system means:

1. determining its steady state solutions also known as the equilibrium points and studying the dependence of these points on the parameter (**continuation problem**); Newton's methods are used to solve:

$$F(X) = 0 \quad \longrightarrow \quad J = \frac{\partial F}{\partial X} \approx \frac{\Delta F}{\Delta X} \dashrightarrow J^{-1}$$

2. locating the bifurcation points, i.e. the equilibria in which qualitative changes in the dynamics of the system occur.

$$J_f = \frac{\partial f(x,\alpha)}{\partial x} \approx \frac{\Delta f(x,\alpha)}{\Delta x} \dashrightarrow L\Lambda R$$

To make the approach general, the adoption of numerical perturbation method (instead of analytical evaluation) is here proposed to obtain the Jacobian matrices.

Increasing the number of species and the number of reaction the cost of the evaluation of Jacobian matrices increases dramatically because both the size of the system $f(x,\alpha)$ and the complexity of its source terms increases and consequently the computational cost of the evaluation of the vector functions $F(X)$ and $f(x)$ and matrix operations.

Predictor-Corrector Method - I

The Predictor-Corrector Method consists of three basic steps:

- prediction;
- correction;
- step-size control.

The algorithms that avoid the evaluation of Jacobian matrix or minimize the number of evaluation of $F(X)$ must be preferred.

Predictor-Corrector Method - II

The Predictor-Corrector Method consists of three basic steps:

- prediction;
- correction;
- step-size control.

Tangent predictor

$$\tilde{X}_{i+1} = X_i + \bar{h}_{i+1} \mathrm{v}_i \qquad with \quad \mathrm{v}_i : \begin{cases} \dfrac{\partial \mathrm{F}_i}{\partial X_i} \cdot \mathrm{v}_i = 0 \\ \mathrm{v}_{i-1} \cdot \mathrm{v}_i = 1 \end{cases}$$

Secant predictor

$$\tilde{X}_{i+1} = X_i + \bar{h}_{i+1} \frac{X_i - X_{i-1}}{\|X_i - X_{i-1}\|}$$

The algorithms that avoid the evaluation of Jacobian matrix or minimize the number of evaluation of $F(X)$ must be preferred.

Predictor-Corrector Method - III

The Predictor-Corrector Method consists of three basic steps:

- prediction;
- correction;
- step-size control.

Newton's method

$$X_{k+1} = X_k - J^{-1}(X_k)F(X_k)$$

Broyden's method (Broyden, 1965)

Broyden's iterative scheme: $X_{k+1} = X_k + B_k^{-1}(X_k)F(X_k)$

Shermann-Morrison formula: $B_{k+1}^{-1} = \frac{\Delta X - B_k^{-1}\Delta F}{\Delta X^T B_k^{-1}\Delta F}\Delta X^T B_k^{-1}$

with $\Delta X = X_k - X_{k-1}$,$\Delta F = F(X_k) - F(X_{k-1})$ and $B_0^{-1} = J^{-1}(X_0 = X_i)$ or equal to any satisfactory approximation of the Jacobian matrix inverse.

The algorithms that avoid the evaluation of Jacobian matrix or minimize the number of evaluation of $F(X)$ must be preferred.

Predictor-Corrector Method - IV

The Predictor-Corrector Method consists of three basic steps:

- prediction;
- correction;
- step-size control.

Dhooge et al., 2003

$$\bar{h}_{i+1} = \begin{cases} c_{dec}\bar{h}_i & no\ convergence \\ \bar{h}_i & N_{iter} \geq N_{thr} \\ c_{inc}\bar{h}_i & otherwise \end{cases}$$

where $c_{dec} = 0.5$, $c_{inc} = 1.5$ and N_{thr} is a constant integer problem dependent (fuel, reaction mechanism and correction step tolerances).

The algorithms that avoid the evaluation of Jacobian matrix or minimize the number of evaluation of $F(X)$ must be preferred.

Test Functions - I

The test functions can be defined in such a way to have a zero at the bifurcation points.

From the definition of these points, they can be expressed as:

$$\psi_F(X) = \prod_{i=1}^{n} \lambda_i(X) = \det(J(X))$$

$$\psi_H(X) = \prod_{1 \le i \le j \le n} (\lambda_i(X) + \lambda_j(X)) = \det(2J(X) \odot I)$$

These popular smooth test functions are not suitable for the problem at hand because:

- the products of sequences, or the determinants, can be too large to be represented by conventional floating-point values (overflow) when large reaction mechanisms are adopted.
- the test function for Hopf bifurcations introduces a limit on the size of the reaction mechanism linked to memory resources: the bialternate product $\odot$ is a square matrix M with size $m = n(n-1)/2$ and $N_{nz} = O(n^3)$ nonzero elements. In a 64-bit system environment, $(8 + 8)N_{nz} + 8(m + 1)$ bytes are needed to store M as sparse while $8n^2$ bytes are required to store only J as dense.

Test Functions - II

The test functions can be defined in such a way to have a zero at the bifurcation points.

To avoid these issues we introduce the test functions:

$$\psi_F(X) = \prod_{i=1}^{n} \operatorname{sign} \lambda_i(X)$$

$$\psi_H(X) = \prod_{1 \le i \le j \le n} \operatorname{sign}(\lambda_i(X) + \lambda_j(X))$$

The bifurcation is detected when:

$$\psi\,(X_i)\psi\,(X_{i+l}) \le 0$$

To further reduce the computational effort we select $l > 1$ (generally $l = 5$) thus decreasing the number of test functions evaluations.

The proposed test functions are not continuous, therefore the location of bifurcation points is obtained by a sort of bisection method. The equilibrium points X_i and X_{i+l} define a search interval. The midpoint of this interval is used as initial guess in order to solve the system $F(X) = 0$. In the resulting equilibrium point the test function is evaluated and according to the results a new search interval is selected. This process is repeated until the search interval has become sufficiently small.

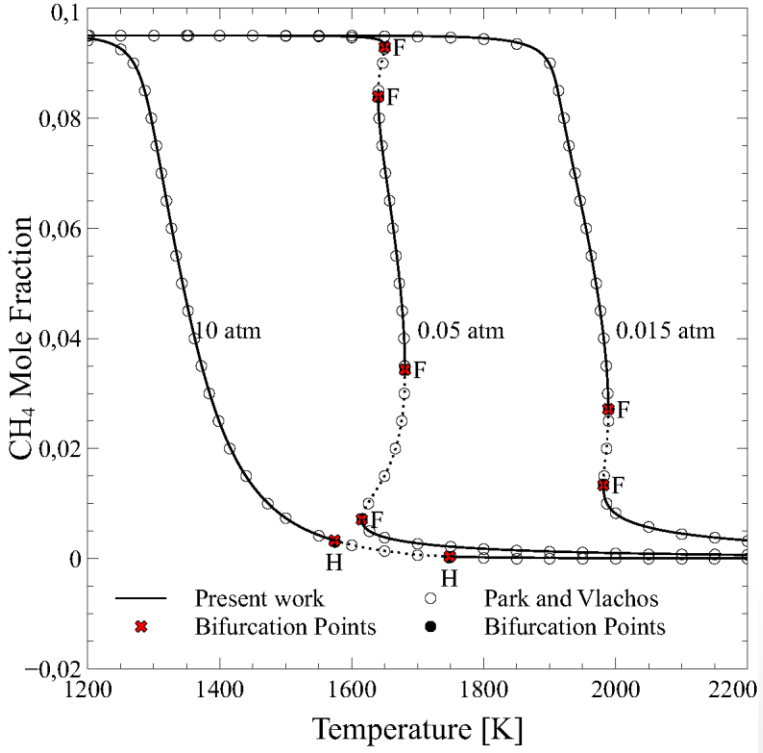
Validation: Test 1

Park and Vlachos, 1998

Park and Vlachos performed a one parameter continuation in order to determine the effect of the temperature of the feed mixture (continuation parameter) on the bifurcation behavior of methane/air mixtures in an **isothermal** PSR.

The methane oxidation is described by using the GRI-Mech 1.2 reaction mechanism (32 species and 177 reactions).

The reactor operates at $\tau = 0.001\ s$ and it is fed with methane-air mixture (9.5% CH_4 - 90.5% air by volume, defined as 21% O_2 and 79% N_2).



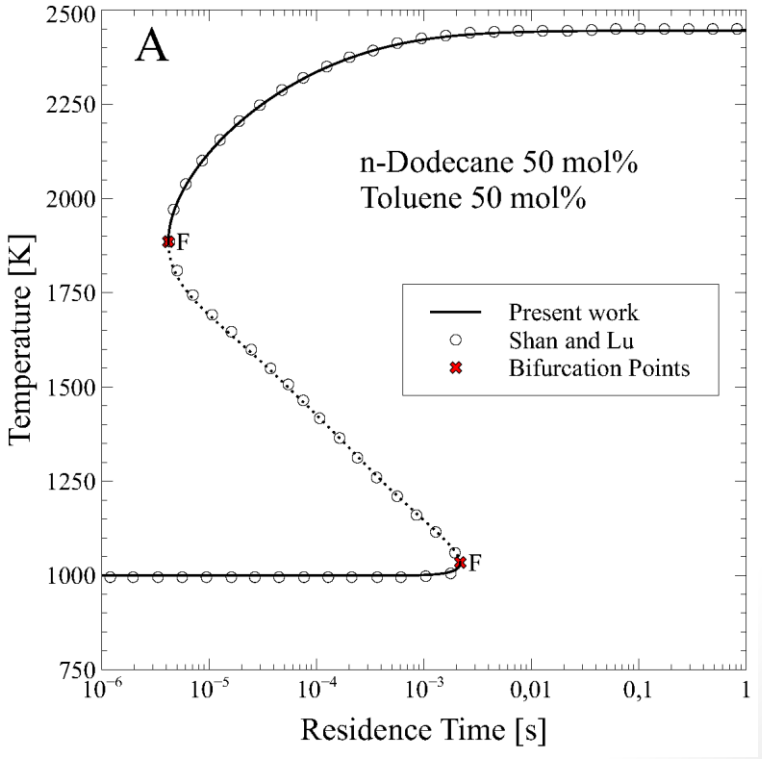
Validation: Test 2

Shan and Lu, 2013

Shan and Lu investigate the effects of surrogate composition on ignition and extinction. They study n-alkanes, n-butyl-cyclohexane and toluene and their blends in order to verify which component or blend can be adequate for reproducing ignition and extinction in **adiabatic**, **non-isothermal PSR**.

The fuels combustion is described by the JetSurF 2.0 mechanism (348 species and 2163 reactions).

The reactor operates at 1013250 Pa (10 atm) and it is fed with a fuel-air mixture at 1000 K with equivalence ratio 0.7.



Scalability: Application to Jet Fuels

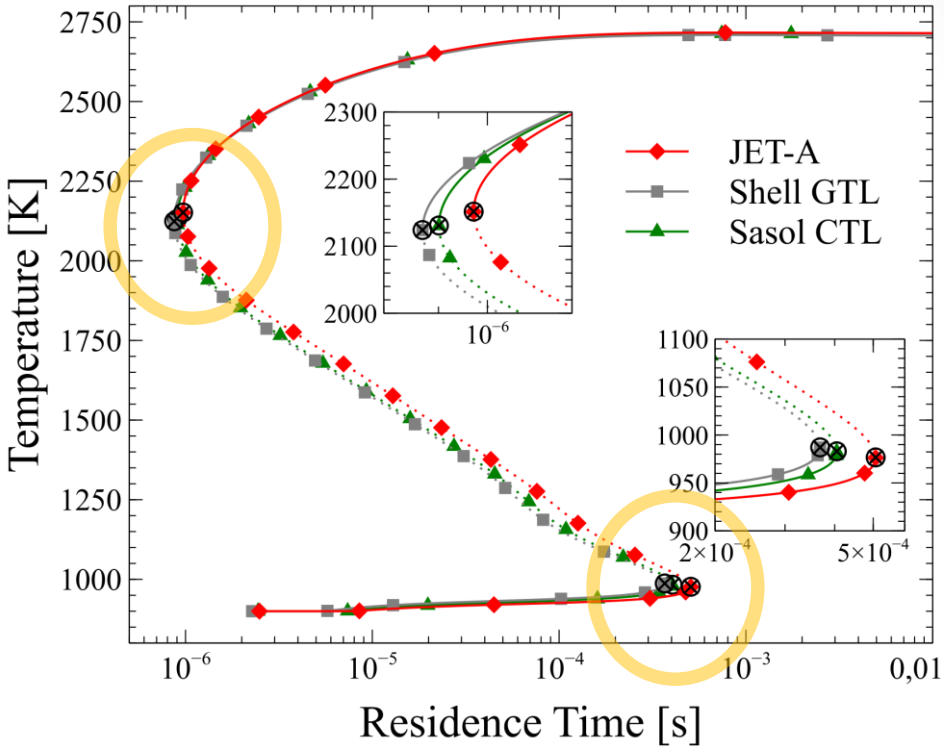
The procedure illustrated has been adopted to study ignition and extinction of three different JF-air mixture in a PSR.

Name	Surrogate Reference	Formula	MW	Surrogate	
			[kg/kmol]	species	mol%
JET-A POSF4658	Dooley et al., (2010)	$C_{8.60}H_{17.27}$	120.67	n-decane	42.67
				iso-octane	33.02
				toluene	24.31
Shell™ GTL	Kick et al., (2012)	$C_{9.81}H_{21.62}$	139.3	n-decane	90.60
				iso-octane	9.40
Sasol™ CTL	Kick et al., (2012)	$C_{9.59}H_{19.98}$	135.1	n-decane	72.00
				iso-octane	13.00
				n-propylbenzene	15.00

The combustion for all fuels is described by the Chemical Reaction Engineering and Chemical Kinetics (CRECK) mechanism (Frassoldati et al., 2010; Ranzi et al., 2012), ver. 1212 (**466 species and 14631 reactions**).

Results - I

- Pressure: 50 atm
- Temperature of the inlet mixture: 900 K
- Stoichiometric conditions



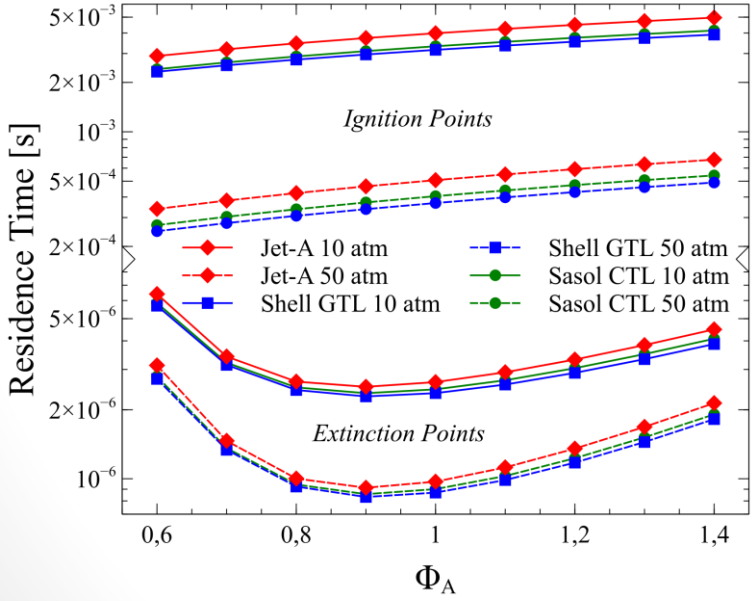
The three fuel surrogates have similar behavior.
This result was expected, because the alternative fuels have been designed to replace the traditional jet fuels without any change of engine technology.

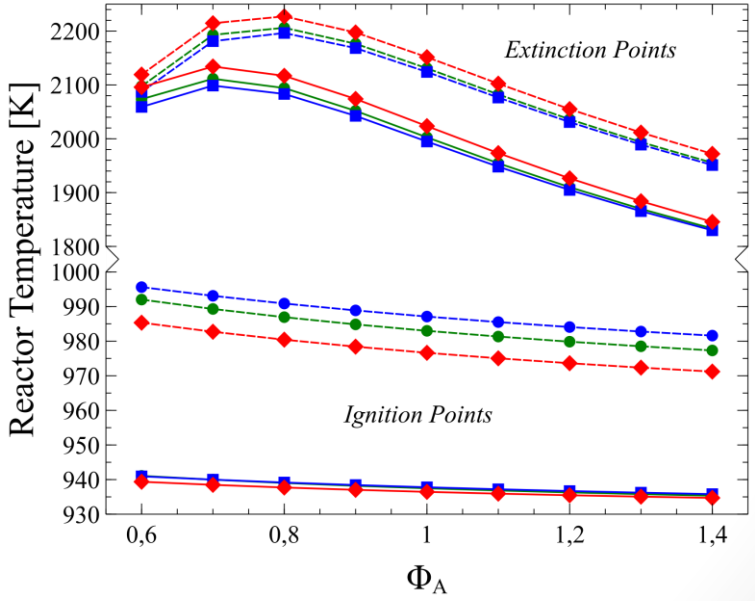
The most relevant difference between the three jet fuel surrogates is at ignition and extinction states. In particular JET-A has ignition and extinction residence times greater than that of the alternative jet fuels.

Results - II

To further investigate the differences at ignition and extinction points, several one-parameter continuations were performed at **air/fuel equivalence ratios** Φ_A from 0.6 to 1.4 and at two different **pressure** 10 atm and 50 atm.

The effect of mixture composition and pressure on extinction and ignition was estimated by ***collecting results*** from the performed one-parameter continuations.





Scalability Results

Table 1: CPU time required for the three different study cases presented.

Fig.	N_S	N_R	Curve	N_{EP}	θ_C	θ_C/N_{EP}	θ_S	$\frac{\theta_C+\theta_S}{N_{EP}N_S}$	$\frac{\theta_C+\theta_S}{N_{EP}N_R}$
1	32	177	10 atm	1000	10.93	0.011	2.94	4.3e-4	7.8e-5
			0.05 atm	1000	14.17	0.014	2.94	5.3e-4	9.7e-5
			0.015 atm	1000	12.29	0.012	2.51	4.6e-4	8.4e-5
2	348	2163	100% Dodecane	3000	1385.66	0.462	159.02	1.5e-3	2.4e-4
			50% Dodecane 50% Toluene	3000	1324.22	0.441	164.79	1.4e-3	2.3e-4
3	482	19072	Res. Time	2500	1954.01	0.782	588.30	2.1e-3	5.3e-5

times in seconds

θ_C time to compute equilibrium curve

θ_S time to compute bifurcation points

N_S number of species

N_R number of reactions

N_{EP} number of computed equilibrium points

Conclusions

- A predictor-corrector continuation method for the parametric study of fuel-air mixtures with combustion modelled by large detailed kinetic mechanisms has been presented.
- We have shown the importance of:
  - a suitable correction algorithm (Broyden's method);
  - the adoption of modified test functions for this class of problem;
  - coupling the numerical code with CANTERA in order to manage chemical and thermodynamic data.
- The resulting bifurcation analysis tool remain efficient in the case of large reaction mechanisms, allowing the computation of a full bifurcation diagram on desktop computers.
- The approach has been validated against two test cases from scientific literature. His capability has been proven by studying ignition and extinction of conventional and alternative JF-air mixtures in a non-isothermal adiabatic PSR.
- Ignition and extinction points have been collected over single maps to show that, even if alternative fuels reproduce the qualitative behavior of the conventional fuel, differences exist especially close to ignition and extinction. These differences are sensitive to pressure and, close to extinction, to Φ_A.

Thank you for your kind attention

For contacts and info:
marra@irc.cnr.it