A Kinetic Model for Limit Phenomena Prediction Based on Bifurcation Analysis

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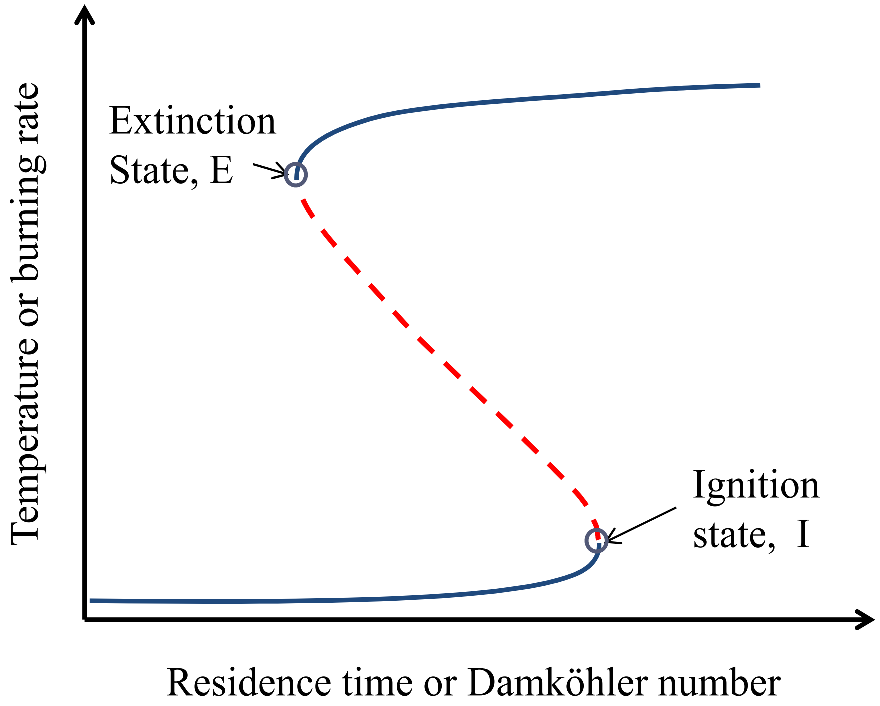
Outline

- Background
- Methodology and results
  - Bifurcation analysis for limit phenomena (e.g. ignition, extinction, onset of flame instabilities) with detailed chemistry for dimethyl ether (DME) in perfectly stirred reactors (PSR)
  - A bifurcation Index (BI) to identify controlling reactions for limit phenomena
  - A simplified DME kinetics model based on BI, with tuned rate parameters
- Summary

Background

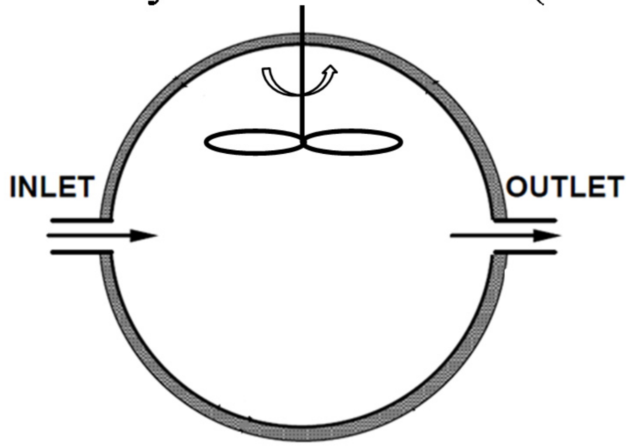
- Limit flame phenomena, e.g. ignition, extinction and onset of flame instabilities, are important in combustion applications
- Near-limit combustion complicated by complex couplings
  - Chemical-physical, e.g. chemistry-turbulence
  - Chemical-chemical, e.g. in detailed chemistry
- Identification of controlling processes in limit phenomena
  - Theoretical analysis with simple chemical & transport models, (Ju et al. 1998, Chen & Ju 2008, Sivashinsky 1977, Joulin & Clavin 1979, Creta & Matalon 2011 …)
  - Sensitivity analysis (Turanyi 1990, Tomlin 2013 …)
  - Computational singular perturbation (CSP) (Lam & Goussis 1994, Kazakov et al, 2006, …)
  - Chemical explosive mode analysis (CEMA) (Lu et al. 2010, Luo et al. 2011, Shan et al. 2012 …)

Limit Phenomena in Steady Flames: The "S"-Curve



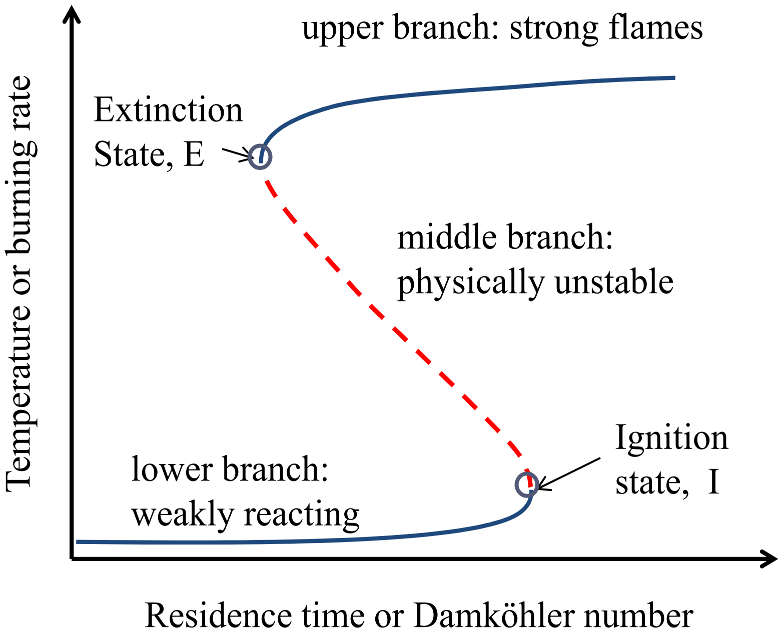
An example:

Perfectly Stirred Reactor (PSR)



- "S"-curve featured by steady state combustion
- Turnings points typically known as "extinction" or "ignition" states
  - Lower (ignition) turning: HCCI engines, jet engine startup, …
  - Upper (extinction) turning: flame stabilization, lean blow-out …
  - Controlled by different reaction pathways

Bifurcation Points and Ignition/Extinction



- Governing equations

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) = \underset{\text{chemical source term}}{\underset{\swarrow}{\boldsymbol{\omega}(\mathbf{y})}} + \underset{\text{mixing}}{\underset{\searrow}{\mathbf{s}(\mathbf{y})}} = \mathbf{0} \qquad \mathbf{y} = \begin{pmatrix} y_1 \\ \cdots \\ y_K \\ T \end{pmatrix}$$

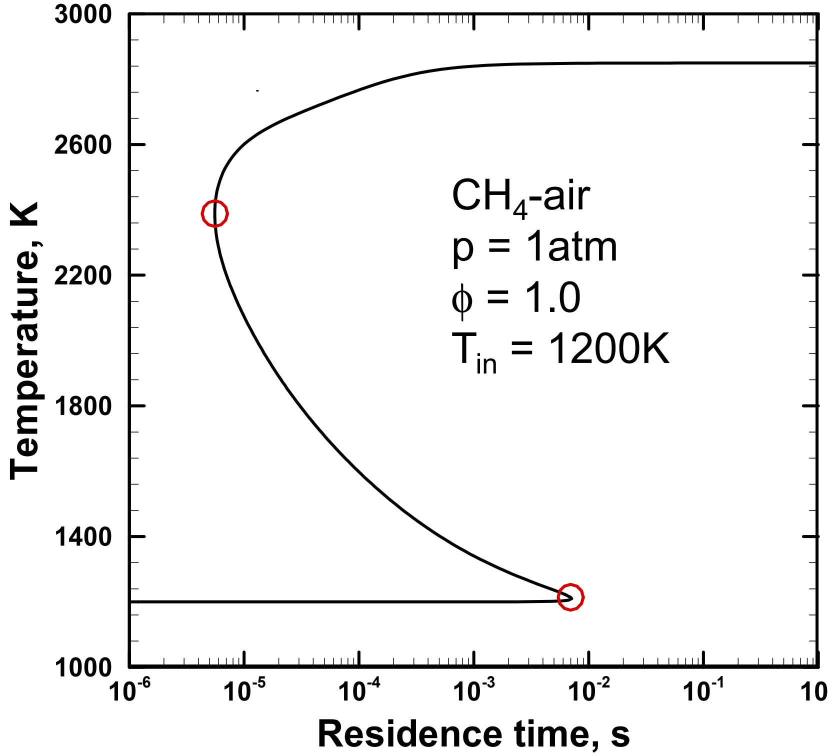
- The Jacobian $\mathbf{J}_{\mathbf{g}} = \dfrac{\partial \mathbf{g}}{\partial \mathbf{y}}$

- Ignition/extinction states (turning point) are bifurcation points:

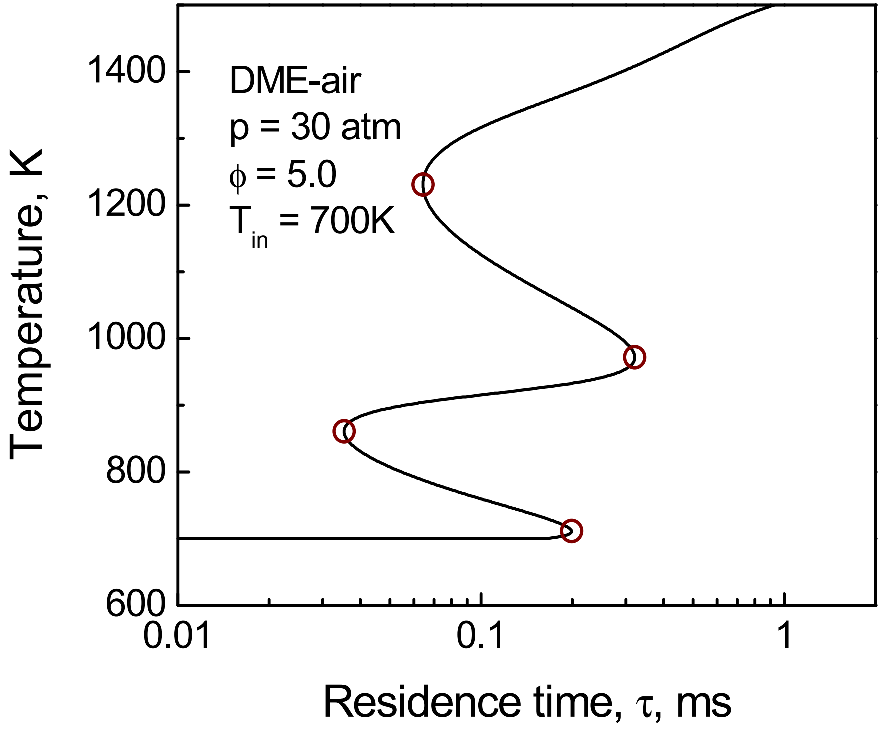
$\mathbf{J}_{\mathbf{g}}$ is singular, or $\boxed{\lambda=0}$

“S”-Curves for Practical Fuels in PSR

CH_4-air, no NTC
GRI-Mech 3.0

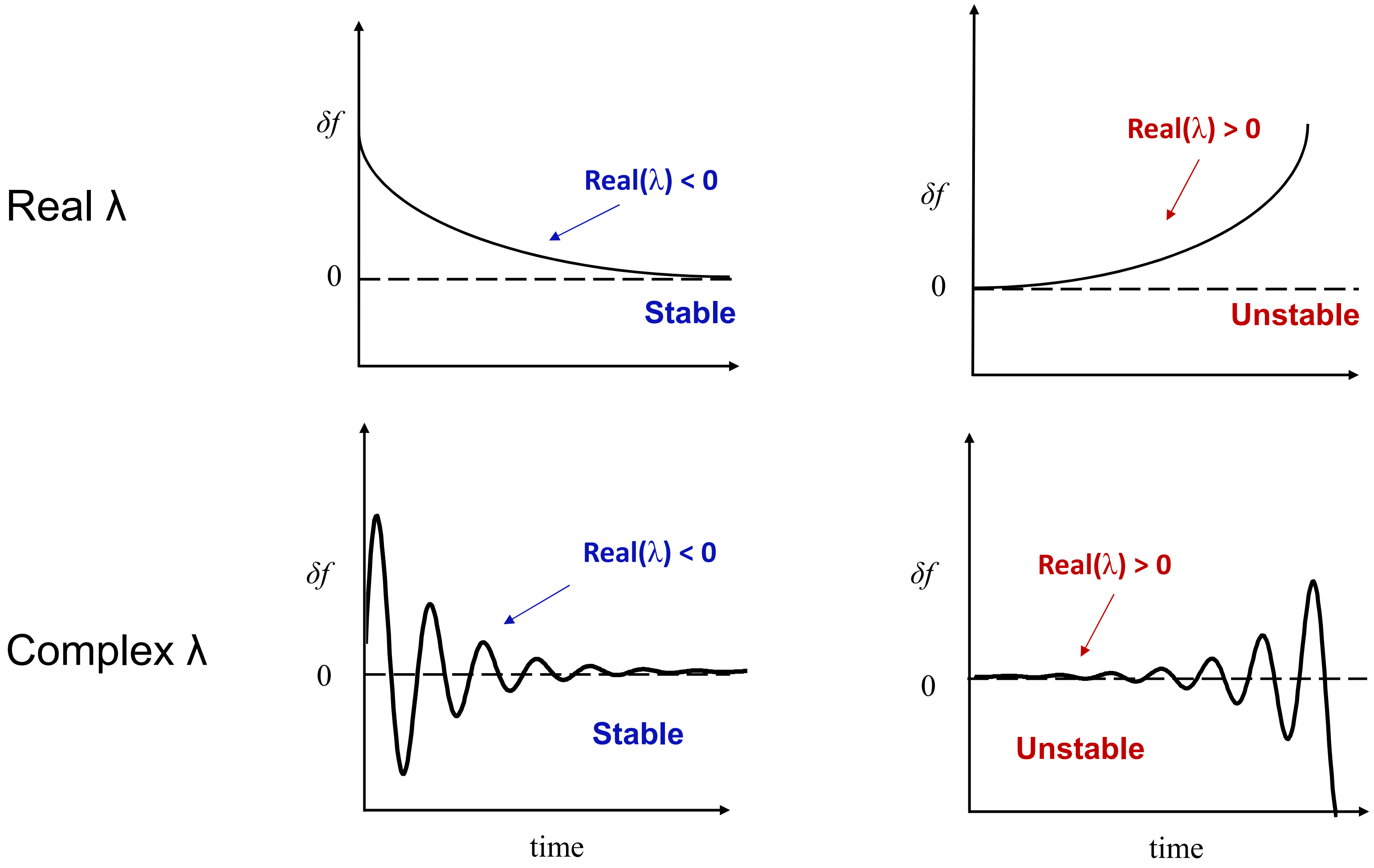


DME-air, with NTC
(Mech: Zhao et al, 2008)



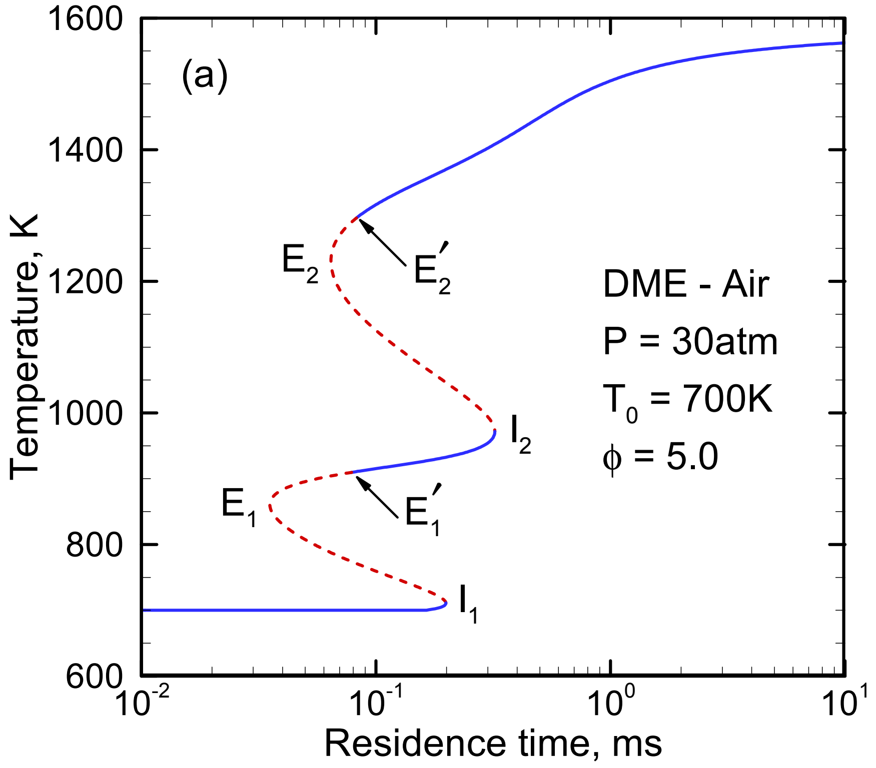
- Fuels with NTC can feature multiple criticalities
- Are all the turning points physical ignition/extinction states?

Eigenvalue λ_l of the Jacobian and Stability

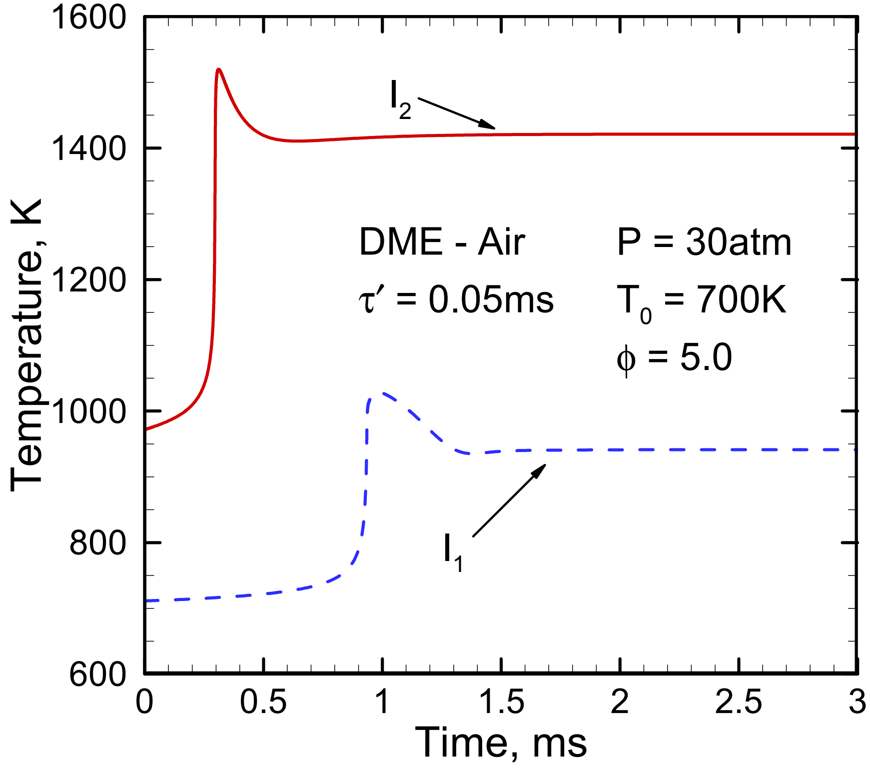


- Real(λ_l): system stability, λ_l: the eigenvalue with largest (least negative) real part
- Imag(λ): oscillation frequency

Ignition Points I_1 & I_2



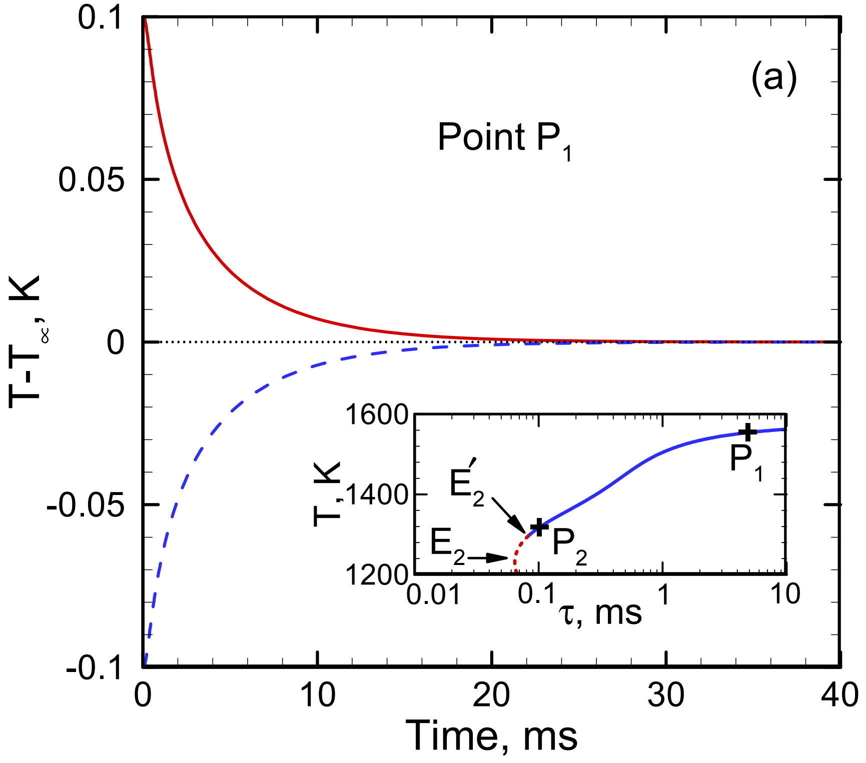
Steady state PSR



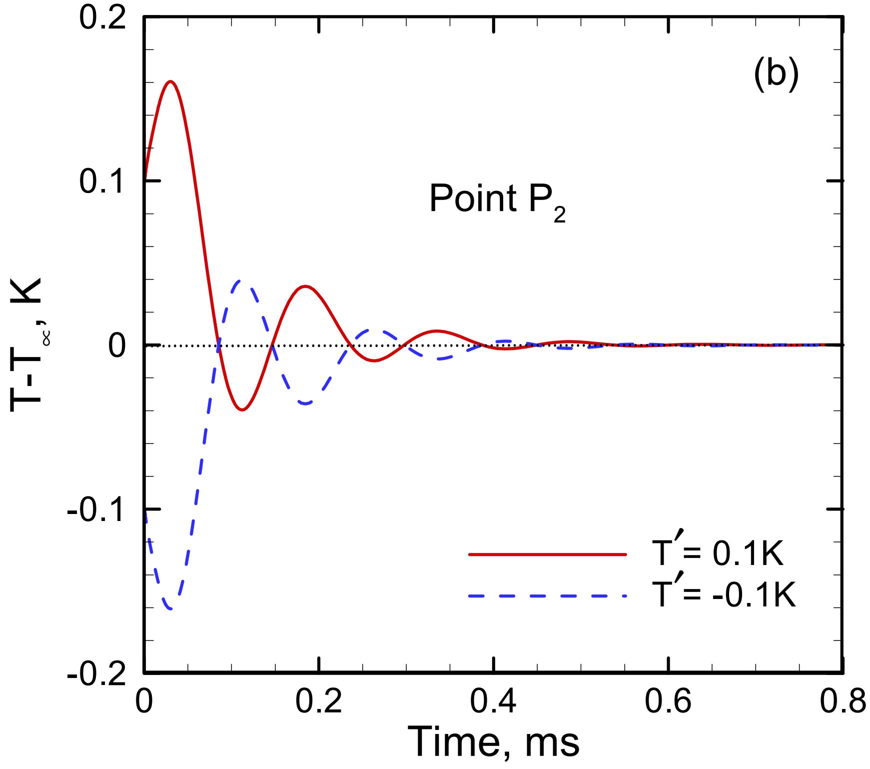
Unsteady PSR

- I_1: Cool flame ignition
- I_2: Strong burning ignition

Points P_1 & P_2 on Upper Branch: $\mathrm{Re}(\lambda_1)<0$, Stable



$\tau = 4.9\text{ms}, \lambda_1 = -0.21\ \text{ms}^{-1}$

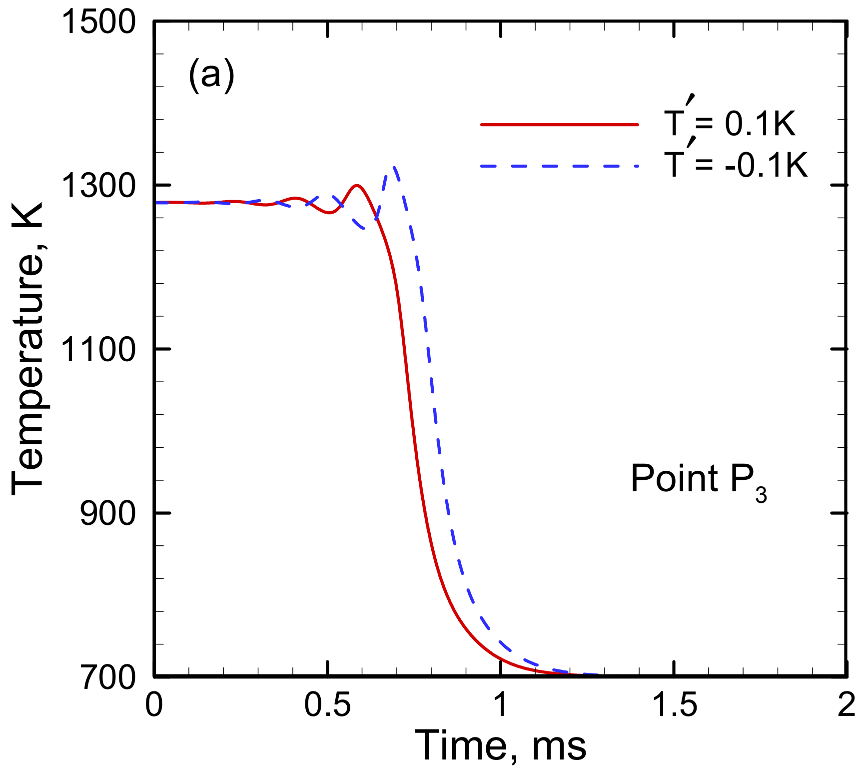


$\tau = 0.1\text{ms}, \lambda_1 = -9.5+42i\ \text{ms}^{-1}$

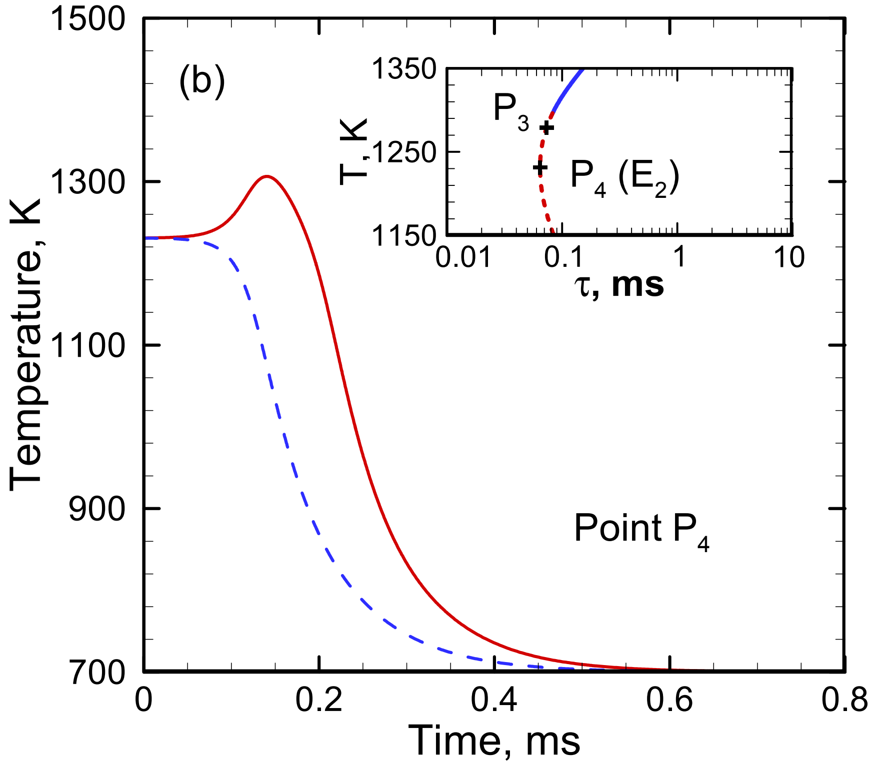
- P_1 and P_2 are both stable

Point P_3 & P_4 on Upper Branch: $Re(\lambda_1)>0$, Unstable

$\tau = 0.07\text{ms}, \lambda_1=7.8 + 35i \text{ ms}^{-1}$



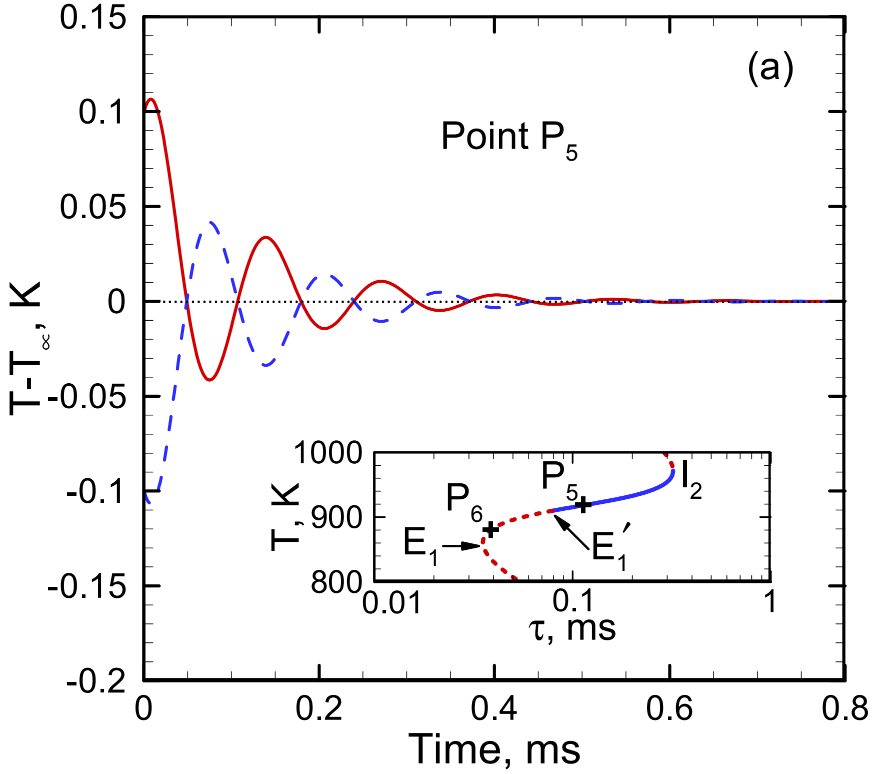
$\tau = 0.06\text{ms}, \lambda_1=50 \text{ ms}^{-1}, \lambda_2=0$



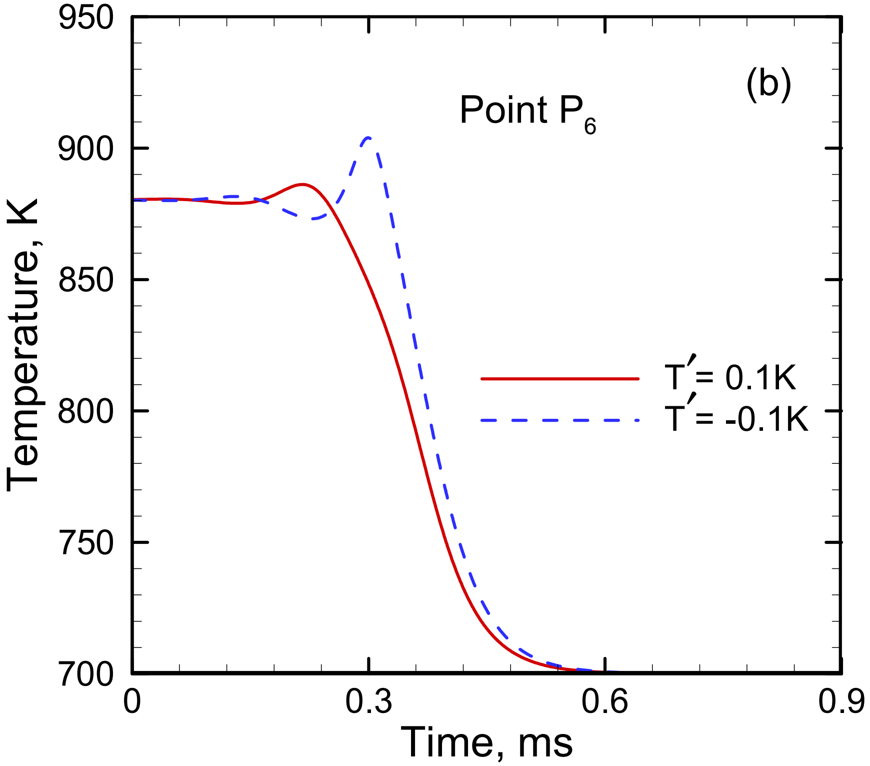
- P_3 and P_4 are both unstable
- Extinction occurs at E_2', before reaching the turning point E_2

Points P_5 & P_6 on the Cool Flame Branch

$\tau = 0.1\text{ms}, \lambda_1 = -8.5 + 35i\ \text{ms}^{-1}$



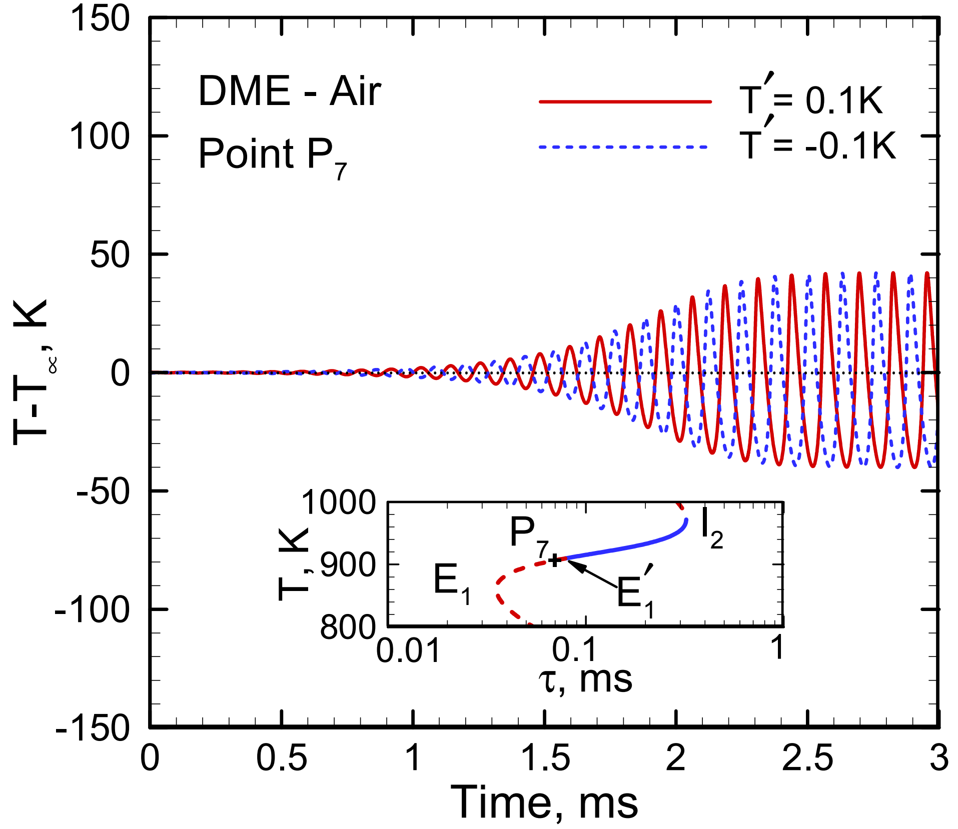
$\tau = 0.04\text{ms}, \lambda_1 = 1.8 + 35i\ \text{ms}^{-1}$



- P_5 is stable
- P_6 is unstable, perturbations lead to extinction

Point P_7 on the Cool Flame Branch

$\tau = 0.07\text{ms}, \lambda_1 = 3.0 + 56i \text{ ms}^{-1}$

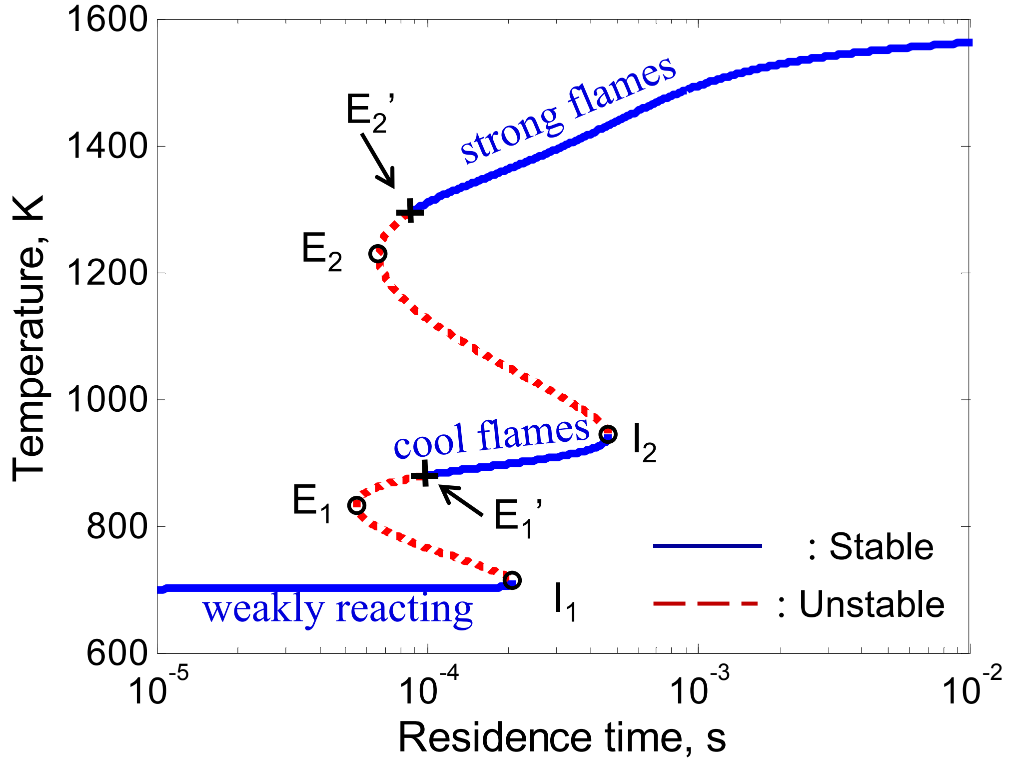


- Perturbations evolve to limit-cycle oscillation
- E_1’ can be considered the extinction point for the cool flames

Summary of Limit Phenomena of DME/Air in PSR

DME-Air

(p = 30atm, T_{in} = 700K, ϕ = 5.0)



- Multiple branches and turnings
- Negative temperature coefficient (NTC) chemistry leads to cool flame branches
- Stable and unstable branches separated by bifurcation points: $Re(\lambda) = 0$
- The turning points: $\lambda = 0$
- I_2/E_2': ignition/extinction of strong flames
- I_1/E_1': ignition/extinction of cool flames

Bifurcation Index (BI) : Identification of Controlling Reactions at the Bifurcation Points

- The governing equation and Jacobian matrix:

$$\frac{d\mathbf{y}}{dt} = \boldsymbol{\omega}(\mathbf{y}) + \mathbf{s}(\mathbf{y}) = \sum_{r=1}^{I} \underset{\substack{\downarrow \\ r\text{th reaction}}}{\boldsymbol{\omega}_r} + \underset{\substack{\searrow \\ \text{mixing}}}{\mathbf{s}(\mathbf{y})} \qquad \mathbf{J}_{\mathbf{g}} = \mathbf{J}_{\boldsymbol{\omega}} + \mathbf{J}_{\mathbf{s}} = \sum_{r=1}^{I} \underset{\substack{\downarrow \\ \partial\boldsymbol{\omega}_r/\partial\boldsymbol{y}}}{\mathbf{J}_r} + \underset{\substack{\searrow \\ \partial\boldsymbol{s}/\partial\boldsymbol{y}}}{\mathbf{J}_{\mathbf{s}}}$$

$$\lambda = \mathbf{b}\cdot\mathbf{J}_{\mathbf{g}}\cdot\mathbf{a} = \sum_{r=1}^{I} \mathbf{b}\cdot\mathbf{J}_r\cdot\mathbf{a} + \mathbf{b}\cdot\mathbf{J}_{\mathbf{s}}\cdot\mathbf{a} = \sum_{r=1}^{I} \lambda_r + \lambda_{I+1} = 0$$

(**b, a**: eigenvectors associated with λ)

- **Bifurcation Index (BI):**

$$\boxed{\mathrm{BI}^r = \frac{\lambda_r}{\max\left|\lambda_r\right|_{r=1,I+1}}}$$

Contribution of the rth reaction (or mixing) to the bifurcation (ignition/extinction)

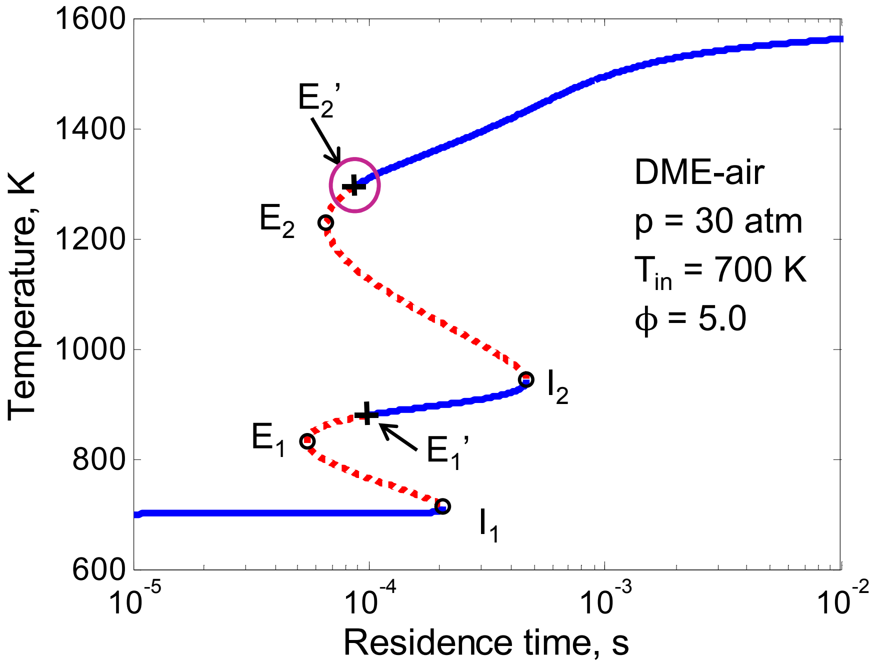
Analytic Jacobian Evaluation

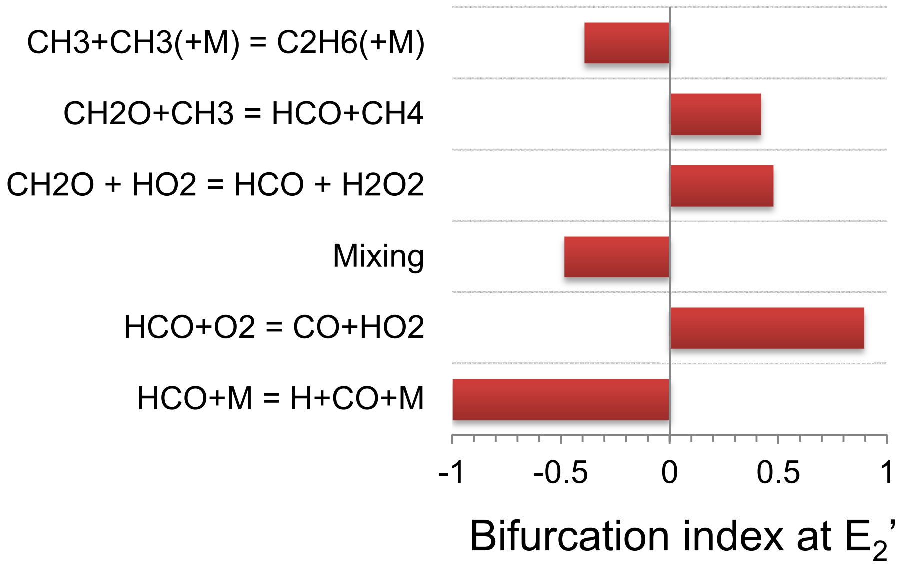
$$\mathbf{J}_{\boldsymbol{\omega}} = \frac{\partial \boldsymbol{\omega}}{\partial \mathbf{y}} = \frac{\partial}{\partial \mathbf{y}} \sum_{r=1,I} \boldsymbol{\omega}_r = \sum_{r=1,I} \mathbf{J}_r, \quad \mathbf{J}_r = \frac{\partial \boldsymbol{\omega}_r}{\partial \mathbf{y}} = \mathbf{S}_r \frac{\partial R_r}{\partial \mathbf{y}} + R_r \frac{\partial \mathbf{S}_r}{\partial \mathbf{y}}$$

- $\mathbf{S}_r$: Stoichiometric coefficients for the rth reaction
  R_r: Net rate of the rth reaction

- Analytic Jacobian should be used for bifurcation analysis: Numerical Jacobian may not have sufficient significant digits
- Analytic Jacobian automatically generated for different mechanisms with a in-house code

Bifurcation Index for Strong Flame Extinction of DME/Air in PSR





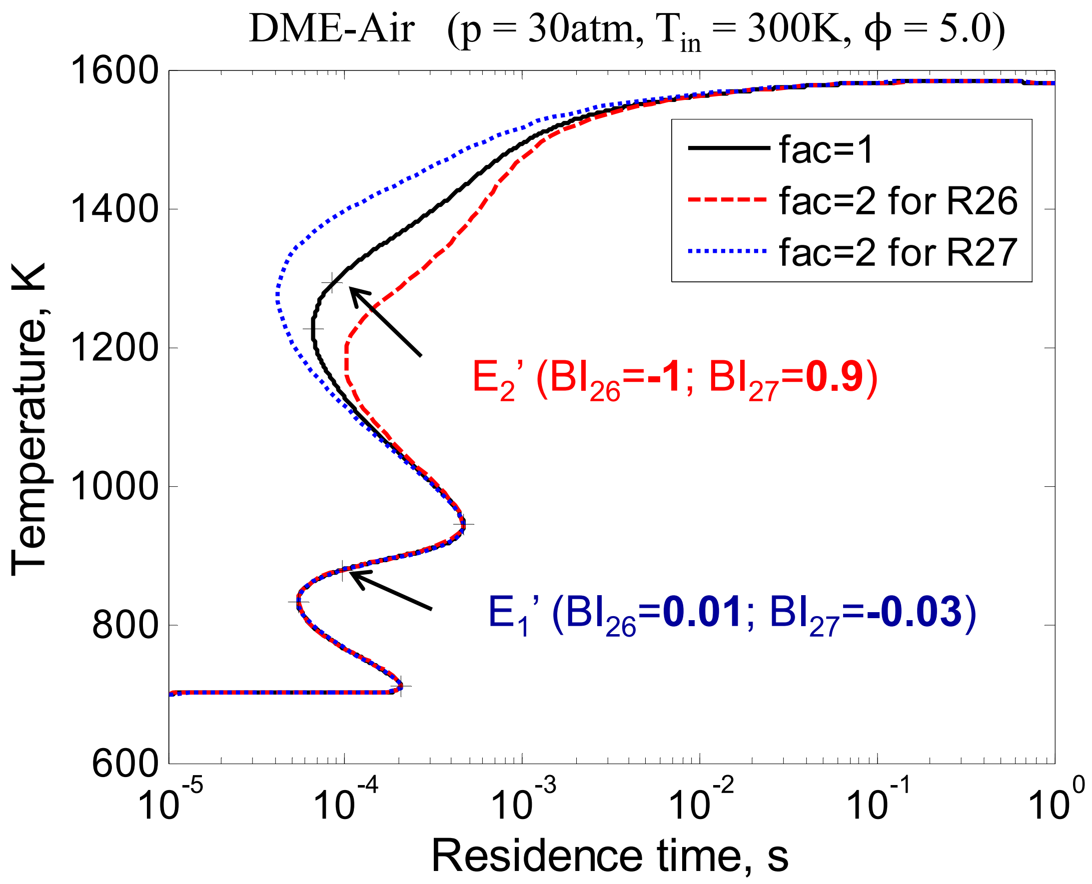
- Strong flame extinction point (E_2') involves small molecules, e.g. those related to CO formation

Effects of Reactions with Large BIs on Strong Flame Extinction

Perturbed A-factors in k = A T^n exp(-E/RT) for

R26: HCO+M = H+CO+M

R27: $HCO+O_2=CO+HO_2$



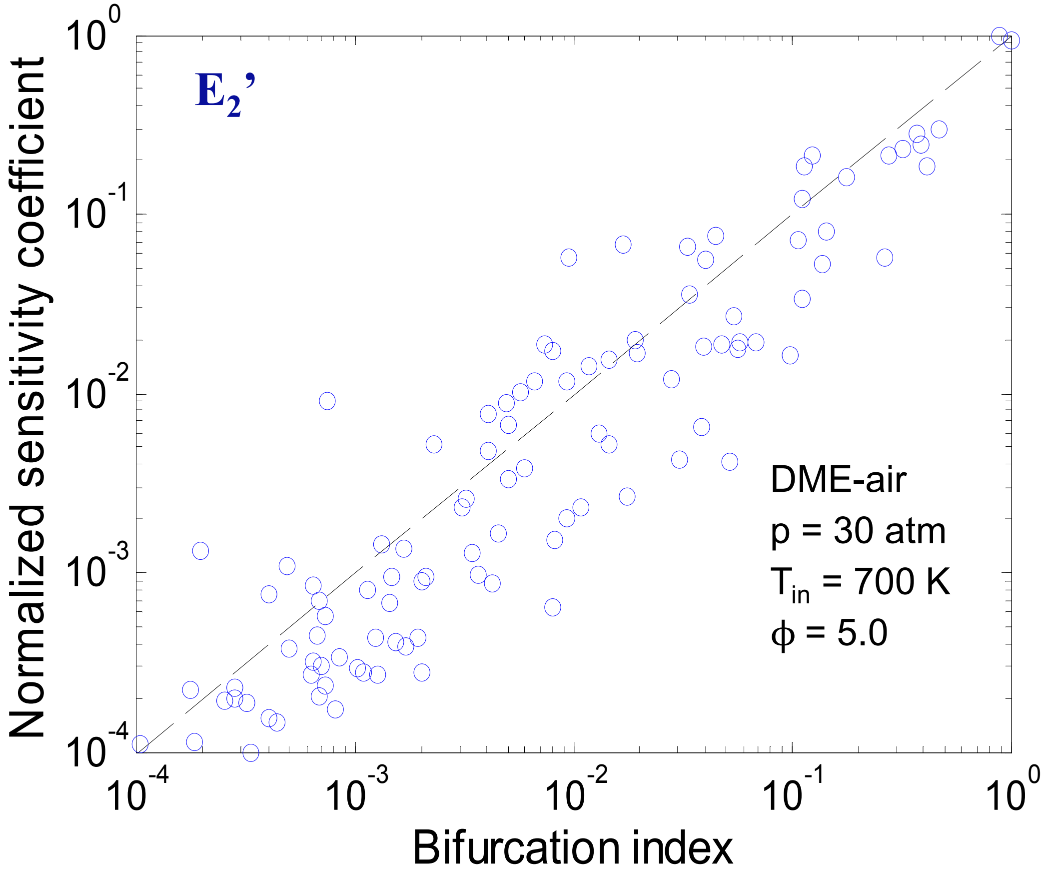
Perturbed A-factors by a factor of 2

Large BI at E_2': significant effects

Small BI at E_1': minor effects

BI vs. Global Sensitivity Analysis for Strong Flame Extinction

Sensitivity of residence time τ with respect to each reaction rate at E_2'

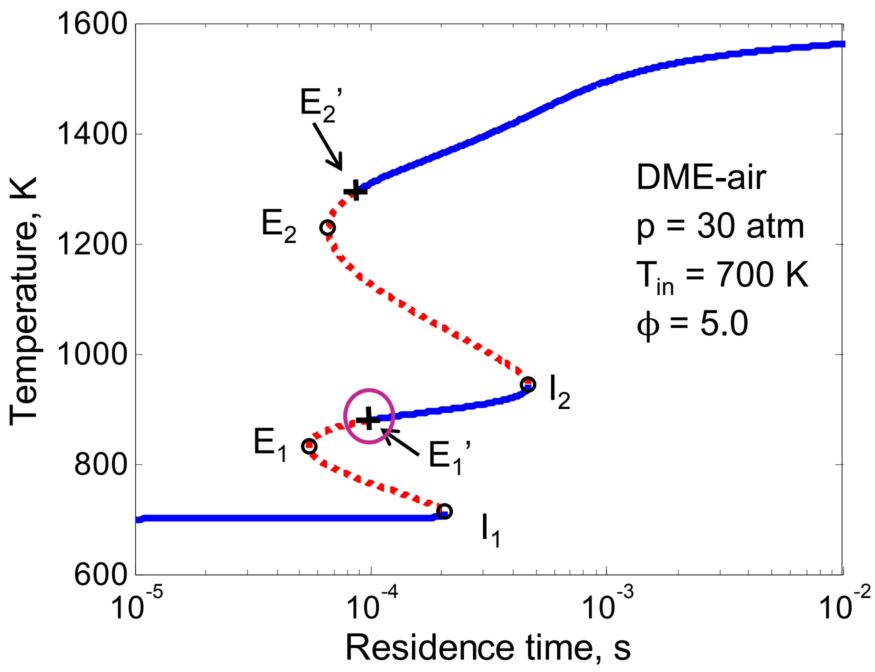


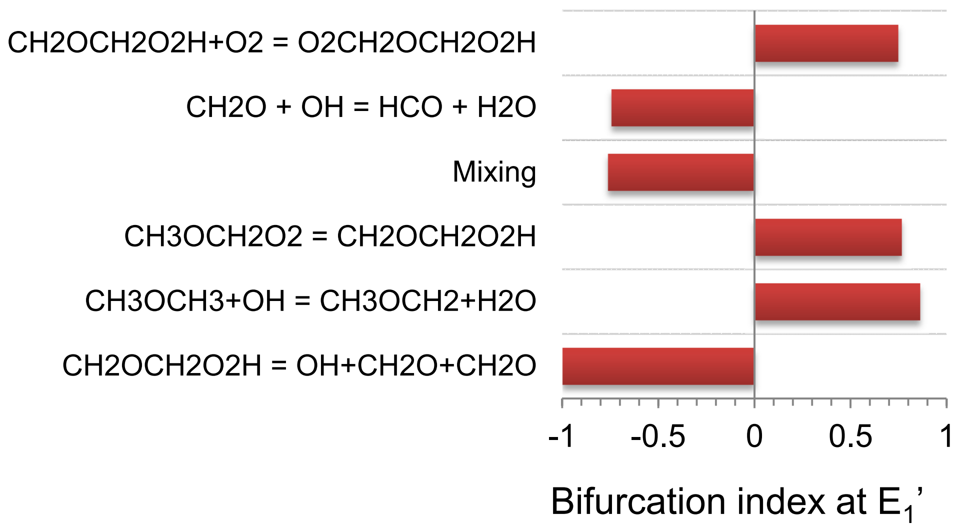
- Sensitivity coefficient:

$$\frac{|d \ln \tau / d \ln A|}{\max|d \ln \tau / d \ln A|}$$

- Sensitivity is overall linearly correlated with BI
- Pros of BI:
  - Simple to implement
  - Computationally efficient
  - Directly indicates physical extinction & ignition

Bifurcation Index for Cool Flame Extinction of DME/Air in PSR





- Cool flame extinction point (E_1') involves larger molecules, e.g. peroxides, related to the NTC chemistry

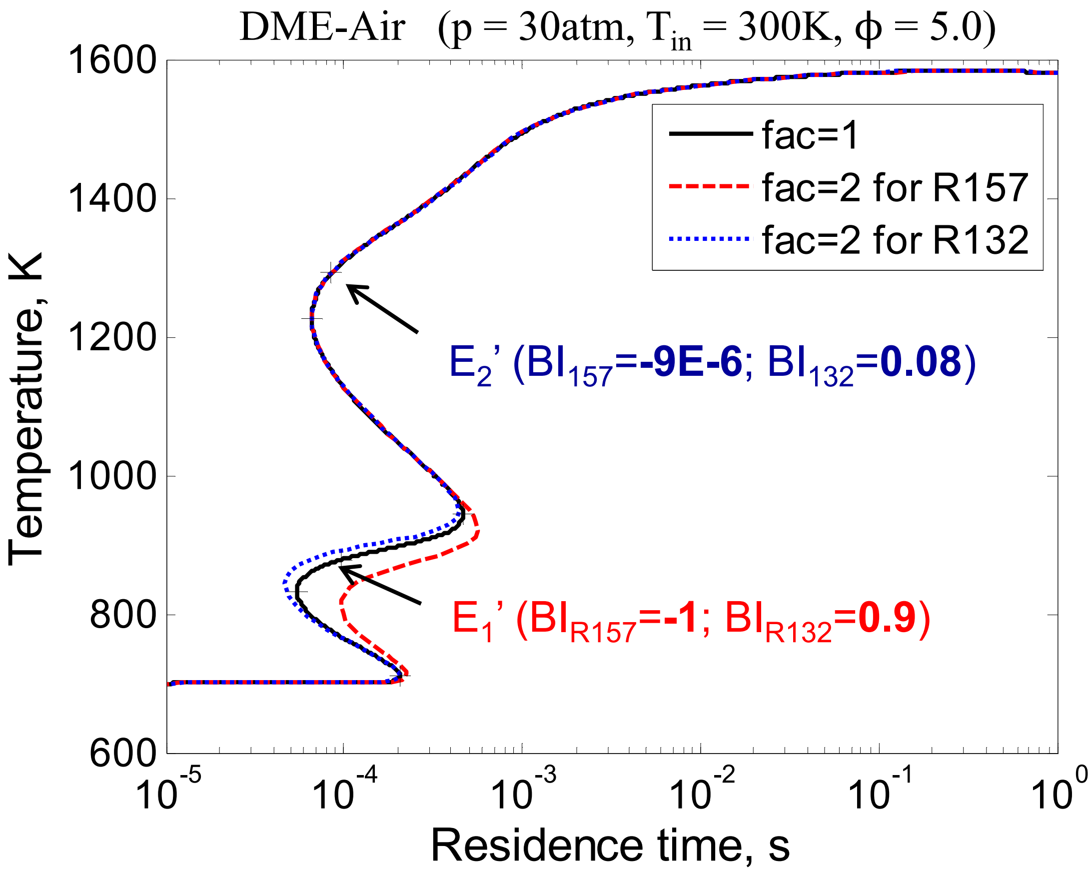
Effects of Reactions with Large BIs on Cool Flame Extinction

Perturbed A-factors in $k = A\,T^n \exp(-E/RT)$ for

R157: $CH_2OCH_2O_2H = OH+CH_2O+ CH_2O$

R132: $CH_3OCH_3+OH = CH_3OCH_2+H_2O$

DME-Air (p = 30atm, T_{in} = 300K, ϕ = 5.0)



E_2' (BI_{157}=**-9E-6**; BI_{132}=**0.08**)

E_1' (BI_{R157}=**-1**; BI_{R132}=**0.9**)

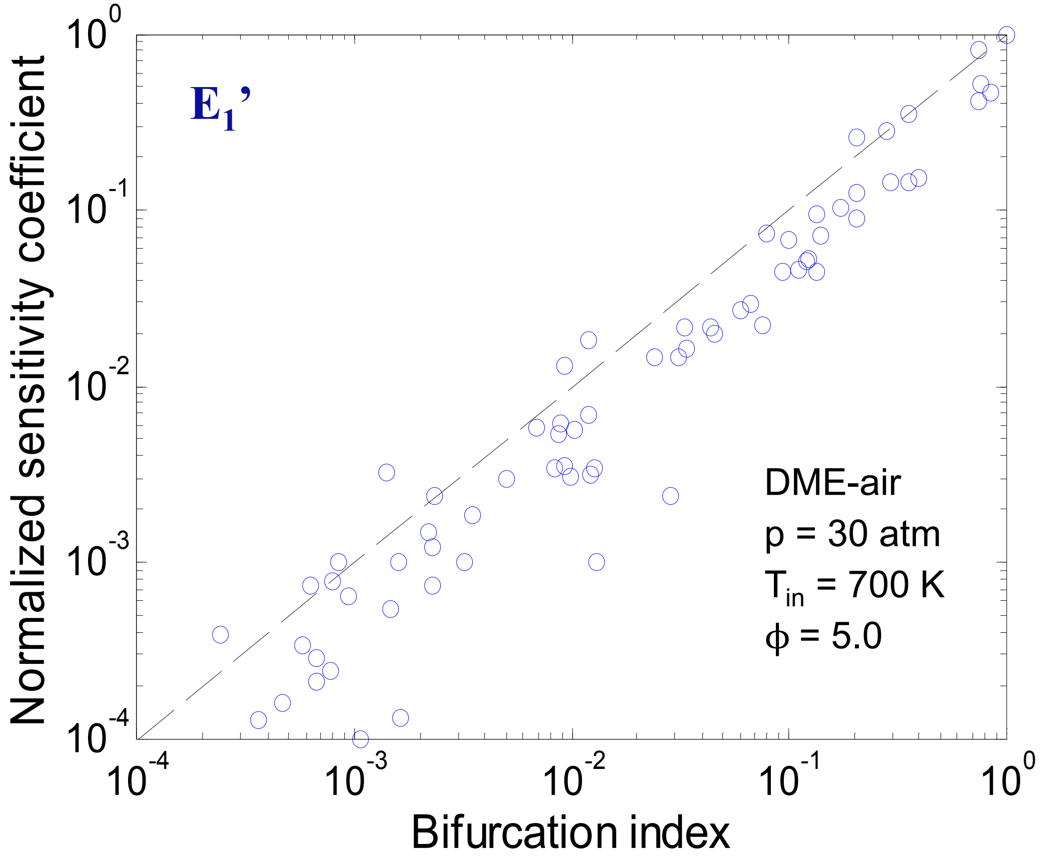
Perturbed A-factors by a factor of 2

Small BI at E_2': minor effects

Large BI at E_1': significant effects

BI vs. Global Sensitivity Analysis at Cool Flame Extinction

Sensitivity of residence time τ with respect to each reaction rate at E_1'

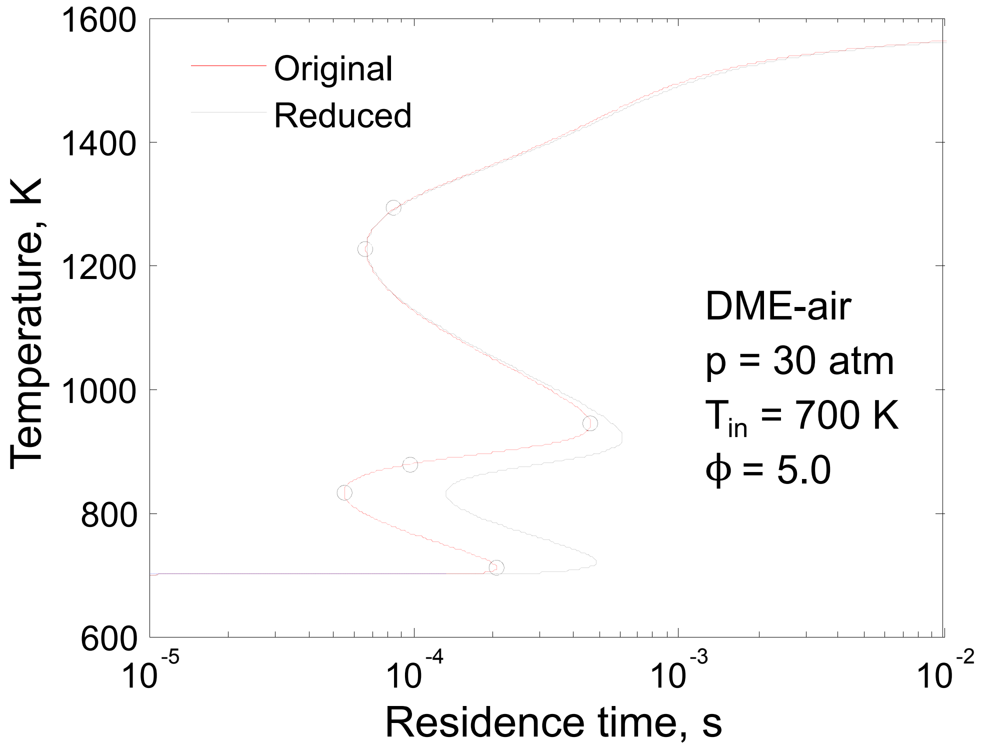


- Sensitivity coefficient :

$$\frac{\left|d\ln\tau/d\ln A\right|}{\max\left|d\ln\tau/d\ln A\right|}$$

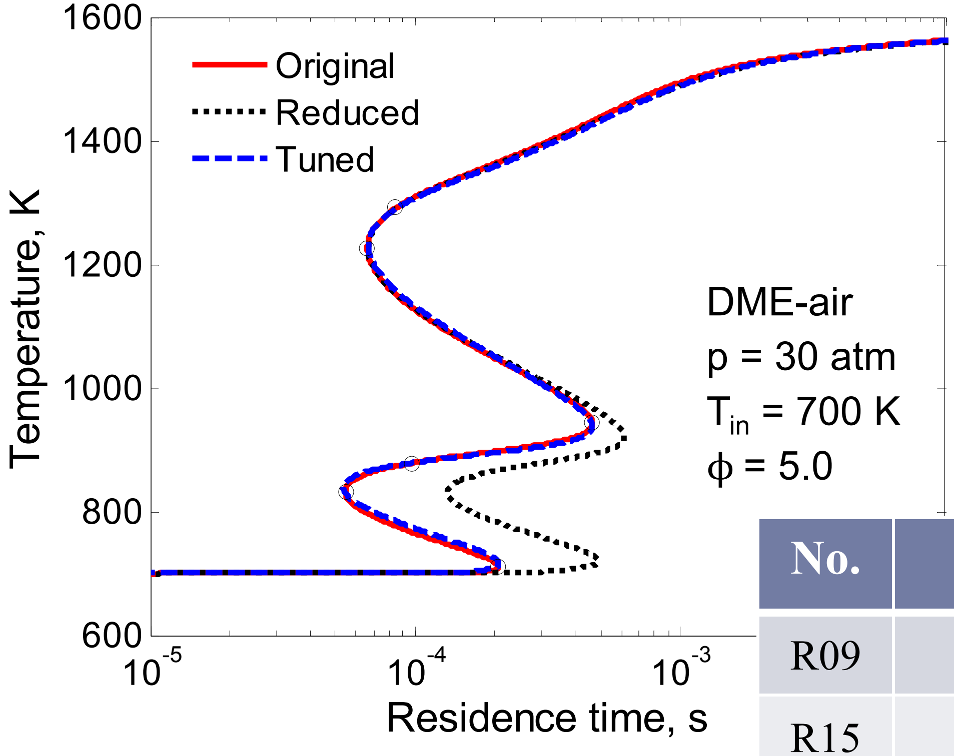
- Sensitivity is overall linearly correlated with BI
- BIs can quantify the importance of each reaction

Mechanism Reduction Based on BI



- Starting skeletal mechanism (derived from Zhao et al. 2008)
  - 39 species, 175 reactions
- A compact reduced model
  - Reactions removed if |BI|<0.01 at the all the 6 bifurcation points
- Reduced
  - 37 species, 103 reactions

Reactions with Tuned A-Factors Based on BI



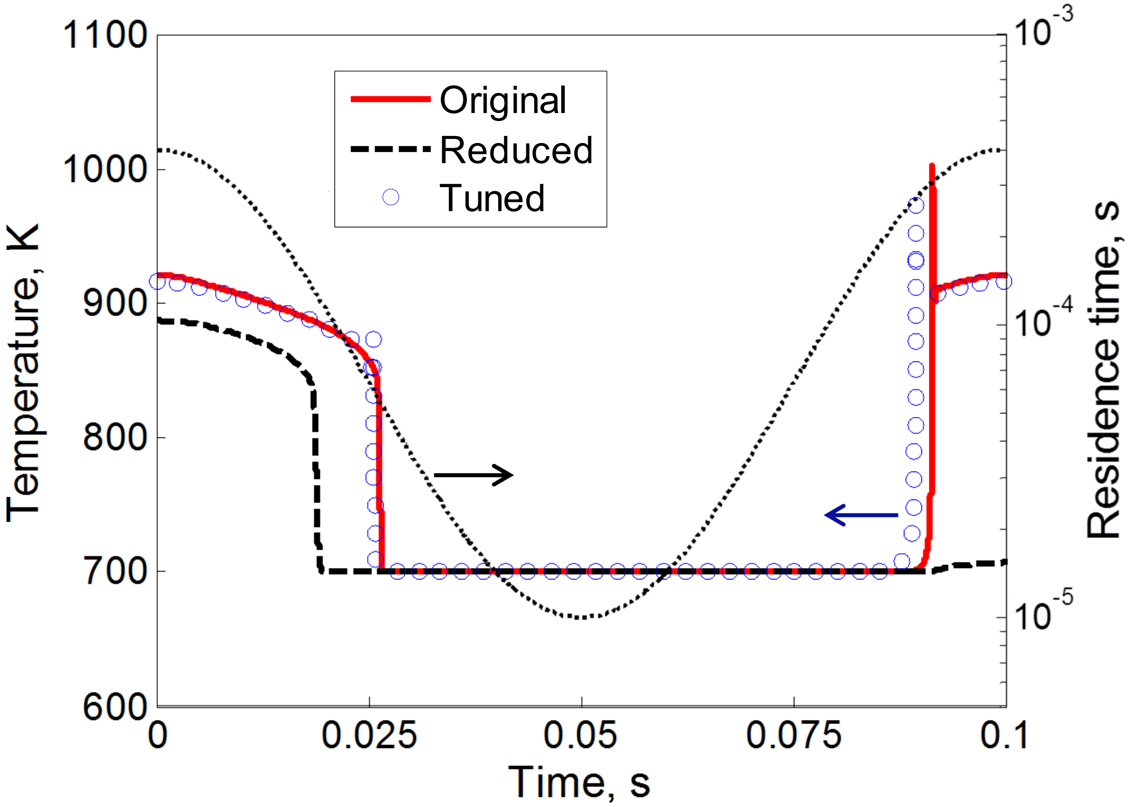
A-factors tuned for 6 reactions

- With large BI values
- Linearly independent BI values at the 6 bifurcation points

No.	Reaction	A’/A
R09	H2O2(+M) = OH+OH(+M)	0.81
R15	HCO+M = H+CO+M	1.46
R16	HCO+O2 = CO+HO2	1.44
R84	CH3OCH3+OH = CH3OCH2+H2O	3.00
R96	CH3OCH2O2 = CH2OCH2O2H	1.94
R97	CH2OCH2O2H = OH+CH2O+CH2O	1.29

Validation in Unsteady PSR

DME-air (p=30atm, Tin=700K, ϕ=5.0)
Original Mechanism : 39 species, 175 reactions
Tuned Mechanism: 37 species, 103 reactions



- The tuned model agrees well with the original mechanism

Conclusions

- Multiple criticalities observed for DME/air mixtures with NTC chemistry
- Physical extinction states may not occur at turning points, can be identified with a bifurcation analysis
- Bifurcation index (BI) defined to quantify controlling reactions for limit phenomena
- BI strongly correlate to global sensitivities, but are much easier to compute
- Reduced model constructed based on BI, and tuned to accurately predict ignition/extinction

Acknowledgement

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