Surrogate Fuel Modeling and Uncertainty Quantification

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Outline

- Component Library Approach for transportation fuel surrogates
  - Chemistry reduction techniques
  - Component library approach
  - Application: Jet fuel surrogate
- Chemical mechanism for aliphatic species
- Uncertainty quantification in chemical systems

Reduction Strategies

DRGEP[1]: Directed Relation Graph with Error Propagation

- Removes as many species and reactions as possible while retaining the accuracy of detailed mechanism
- Automatic, fast and efficient
- Generates skeletal mechanisms with consistent chemical pathways

Chemical Lumping[2]

- Replaces chemical isomers by one single representative species
- Very efficient for large hydrocarbons oxidation
- Rate coefficients of the lumped reactions estimated accurately through statistical analysis of the detailed results

Quasi-steady state assumptions

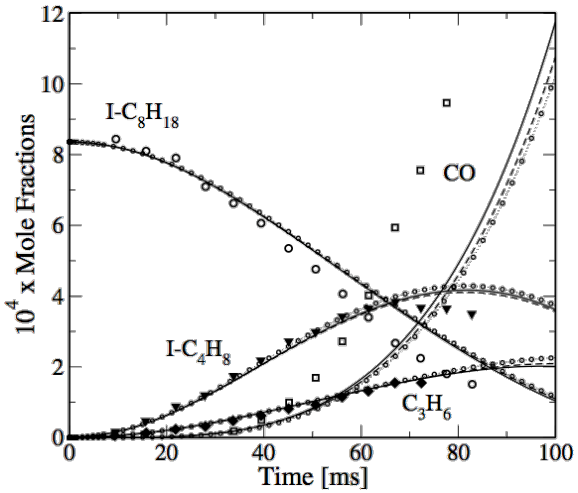
- Replaces differential equations by algebraic expressions

[1] P. Pepiot-Desjardins, H. Pitsch, *Combust. Flame*, 2008.

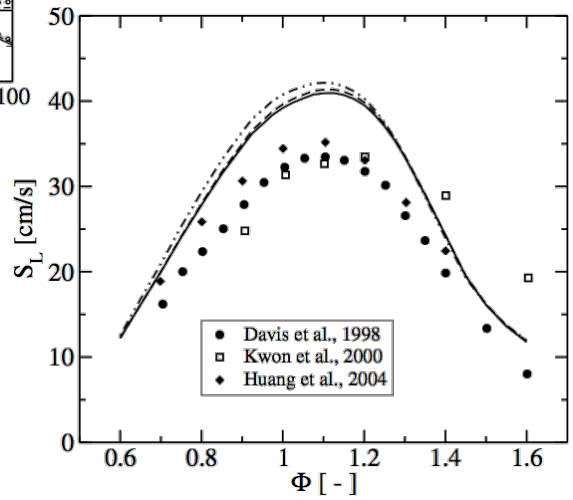
[2] P. Pepiot-Desjardins, H. Pitsch, *Combust. Th. Model.*, 2008.

Integrated Approach

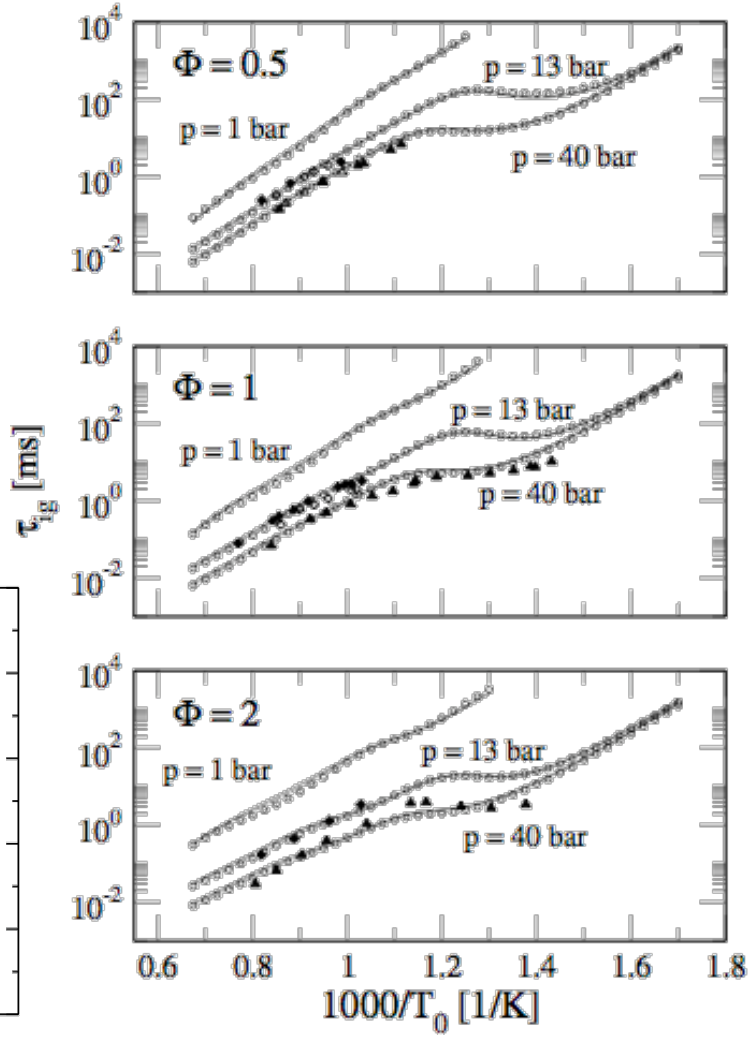
- Highest reduction ratio obtained by combining all techniques
- Example: Iso-octane oxidation mechanism
  - Initial size: 850 species, 7212 reactions
  - Reduced size: 57 species, 504 reactions



Plug Flow Reactor
Very lean I-C_8H_{18}/air
T_0 = 945K

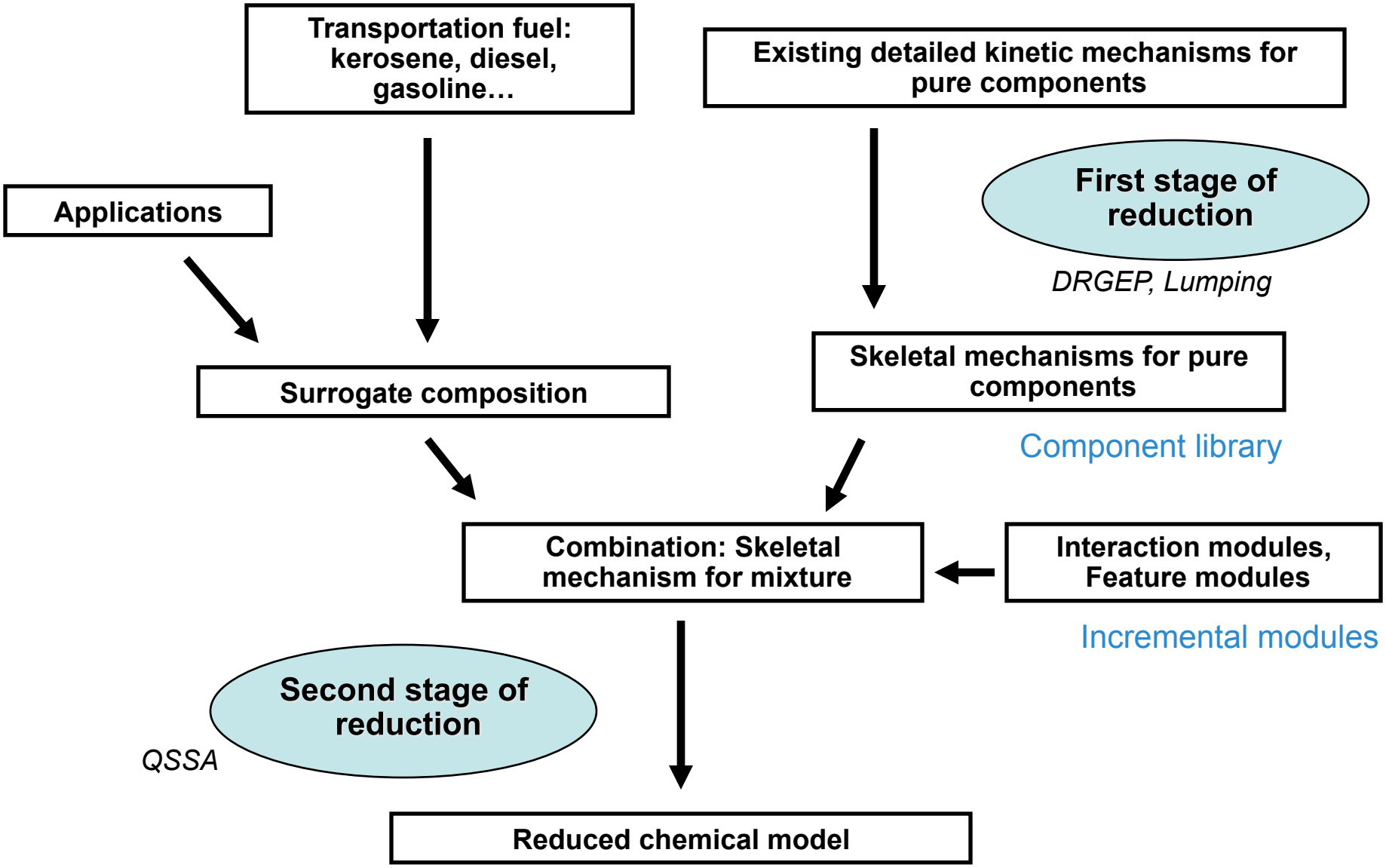


Atmospheric laminar
burning velocities
T_0 = 298K

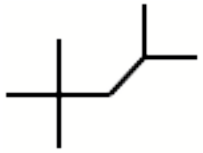
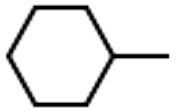
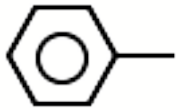


I-C_8H_{18}/air ignition delay times

Component Library Approach



Individual Components and Detailed Kinetic Models

Class	Molecule	Formula	Structure	Comments
Paraffins	Dodecane	$C_{12}H_{26}$		**Mech**: 174 species, *Wang et al.*, 2008 **Exp**: ST, flames
	Iso-octane	C_8H_{18}		**Mech**: 850 species, *LLNL*, 2002 **Exp**: ST, PFR, flames
Naphthenes	Methyl-cyclohexane	C_7H_{14}		**Mech**: 998 species, *LLNL*, 2005 **Exp**: ST, PFR
Aromatics	Toluene	C_7H_8		**Mech**: *Blanquart et al.,* 2008 **Exp**: ST, PFR, flames
	Benzene	C_6H_6		

Base chemistry (C_0-C_4) developed for PAH and soot formation

– Extensively validated
– 151 species, *Blanquart et al.*, 2008.

Possible Jet Fuel Surrogate Compositions

- Automatic composition optimization for any given targets based on group additivity theory

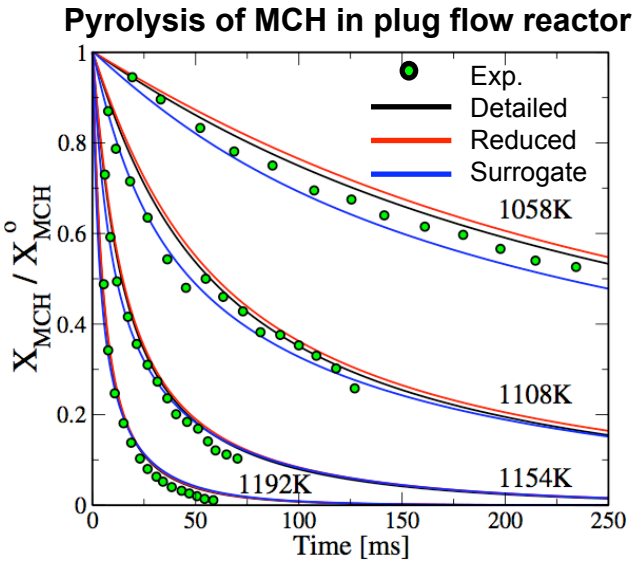
		Average Jet Fuel**	Neat Dodecane	Surrogate 1*	Surrogate 2
Composition [%mol]	Dodecane	N/A	100	73.5	45
	Iso-octane			5.5	
	MCH			10	26.1
	Toluene			10	28.9
	Benzene			1	
H/C ratio		1.91	2.17	2.09	1.91
Formula		$C_{11}H_{21}$	$C_{12}H_{26}$	$C_{10.7}H_{22.3}$	$C_{9.3}H_{17.7}$
Hydrocarbon composition [%vol]	Paraffins	~60	100	88	62
	Naphthenes	~20	0	6.4	20
	Aromatics	~18	0	5.6	18
Cetane Number		~42.7	80	73.4	58
Treshold Sooting Index		~15	5.2	9.3	16.3

*Violi *et al.*, Comb. Sci. Tech. 174:11, 2002

** Edwards *et al.*, J. Prop. Pow., 17:2, 2001

Validation Procedure

- Reduction done for various configurations and over a wide range of pressures, equivalence ratios, and temperatures > 900 K
- Validation performed at each stage of reduction and combination, for each fuel component

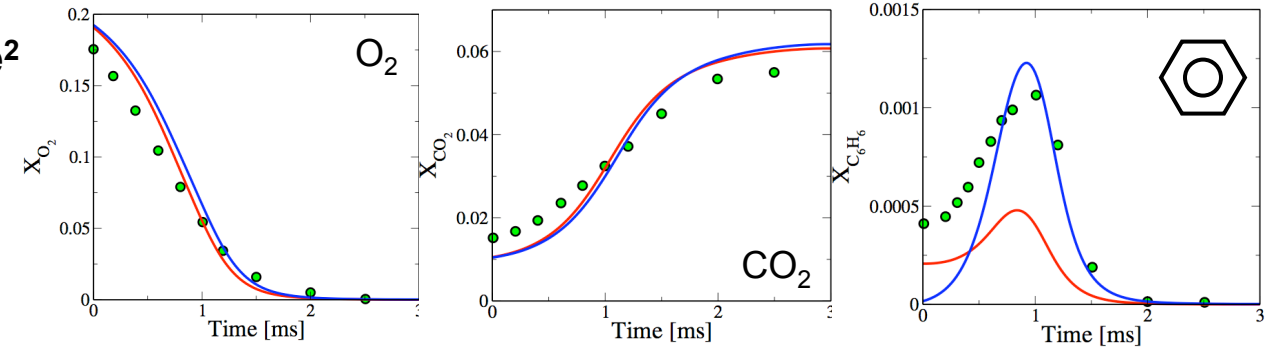


Mechanisms		N_S	N_R
Components	Base Chemistry	151	1658
	Dodecane	174	2625
	Iso-octane	850	7212
	Methyl-cyclohexane	998	8820
Multi-component surrogate		90 + 91 QSS	1197

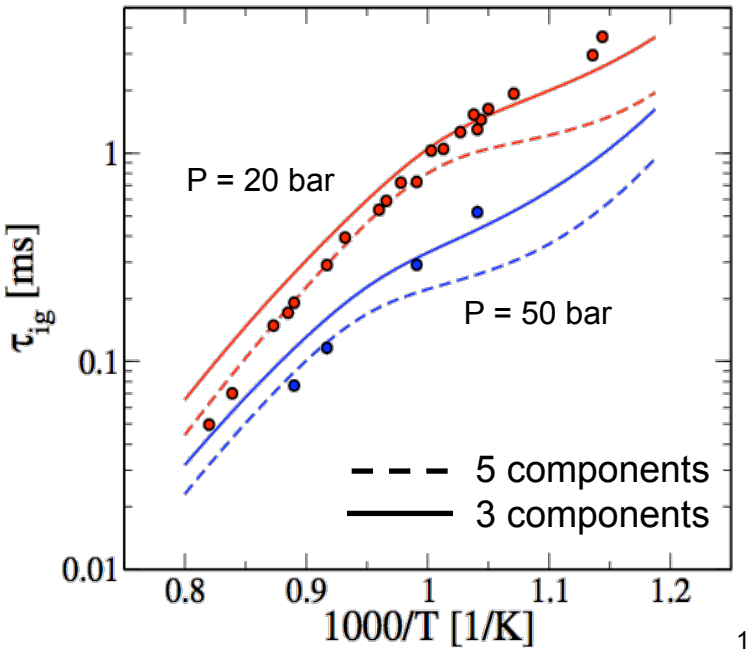
Comparison with Jet Fuel Experiments

Kerosene Premixed Flame[2]

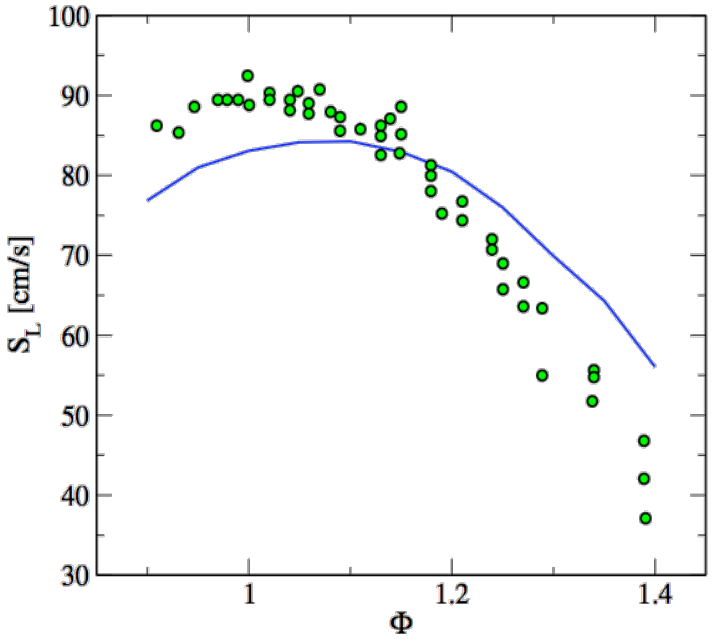
Experiments
5 components
3 components



Jet fuel auto-ignition[1]



Jet fuel laminar burning velocitiy[3]



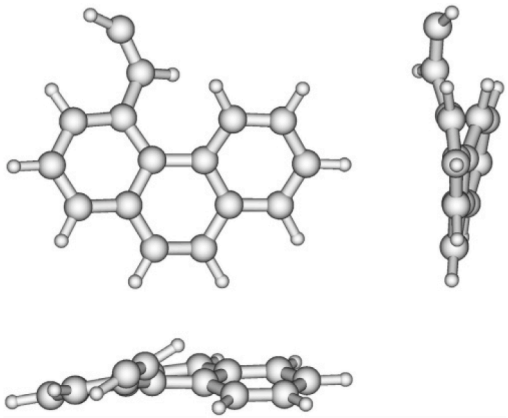
[1] S. S. Vasu, D. F. Davidson, R. K. Hanson - Combust. Flame, 2008
[2] Doute et al, Combust. Sci. Tech. 106, 1995
[3] Eberius et al., 2001

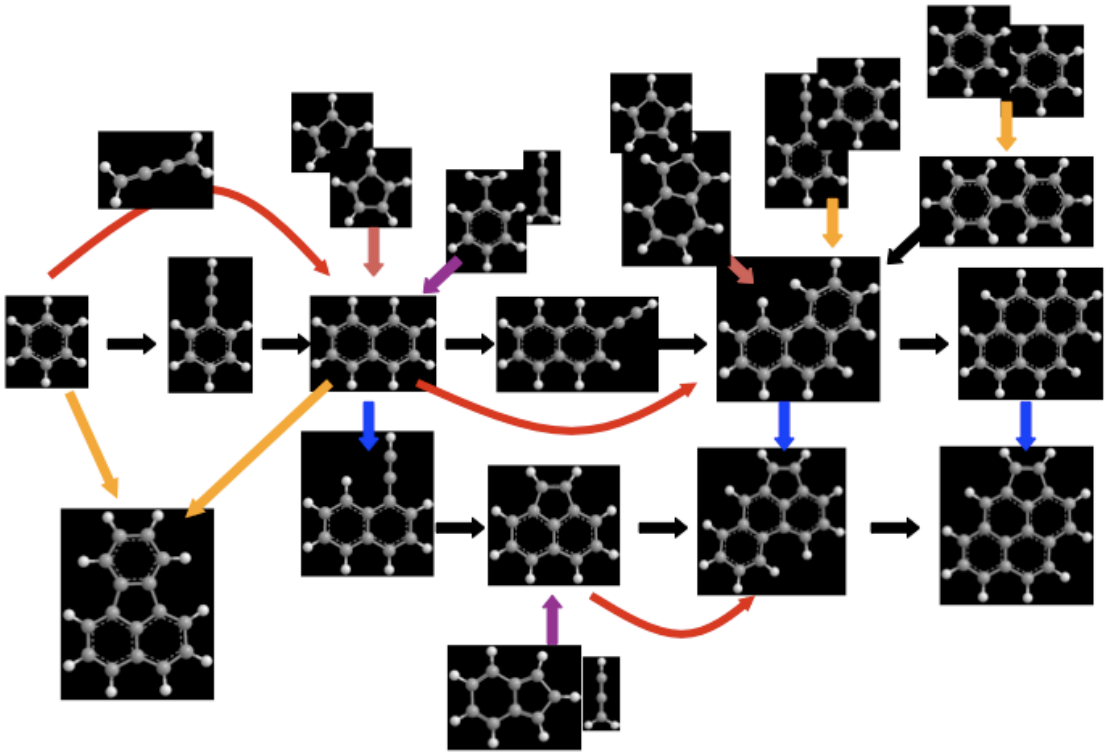
Component Library Infrastructure

- Fully automatic, multi-stage reduction strategy
- Development of an interactive framework for chemical modeling of transportation fuel surrogates
  - Modular and flexible
- Future:
  - Incorporate JetSurF into Component Library
  - Validate multi-component surrogates with experimental data

Chemical Mechanism Development

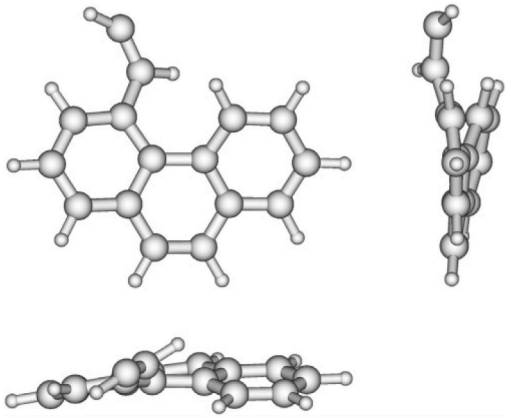
- Objective:
  - Integrate our recent developments for PAH chemical mechanism into JetSurF mechanism





PAH Thermodynamics

- **Thermodynamic Properties**
  - Describe how **stable** each species are
  - Required for *accurate* modeling of combustion
    - Heat capacity
    - Entropy
    - Heat of formation



- **Polycyclic Aromatic Hydrocarbons (PAH)**
  - Formed in *rich premixed* and *diffusion* flames
  - *Intermediates* to soot formation

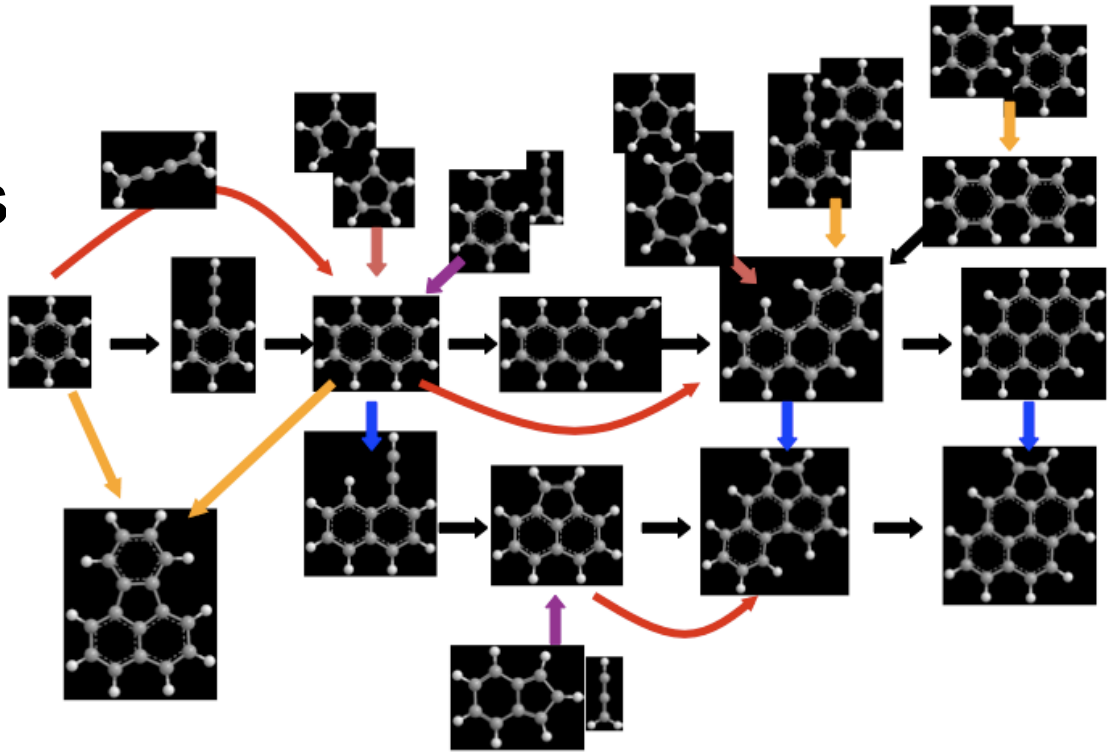
- **New Database of Thermodynamic Properties**
  - *Ab-initio* quantum calculations
    - G3MP2//B3
  - *Internal degree of rotation*
    - *Hindered* rotors
  - Group Corrections (GC)

		G3MP2//B3	
species	exp.	orig.	GC
	Aromatic Species		
benzene	82.93 ± 0.5	76.95	82.99
naphthalene	150.3 ± 1.5	134.89	148.83
anthracene	226.7 ± 3.5	208.28	230.11
phenanthrene	201.7 ± 2.9	185.18	201.76
pyrene	225.7 ± 1.2	200.69	226.09
chrysene	263.5 ± 4.5	240.64	259.86
perylene	306.0 ± 0.8	283.32	306.11
coronene	302.0 ± 8.0	251.99	292.43
avg. error		22.11	2.34
	Substituted Aromatics and Radicals		
phenyl	339.7 ± 2.0	341.14	
phenylacetylene	306.6 ± 1.7	307.97	
styrene	146.9 ± 1.0	138.38	
styryl	393.5 ± 7.0	402.80	
acenaphthylene	259.7 ± 4.6	244.18	
biphenyl	182.0 ± 0.7	163.33	

⇒ Blanquart, G., Pitsch, H. « Thermochemical properties of Polycyclic Aromatic Hydrocarbons (PAH) from G3MP2B3 calculations » *Journal of Physical Chemistry A* (**2007**)

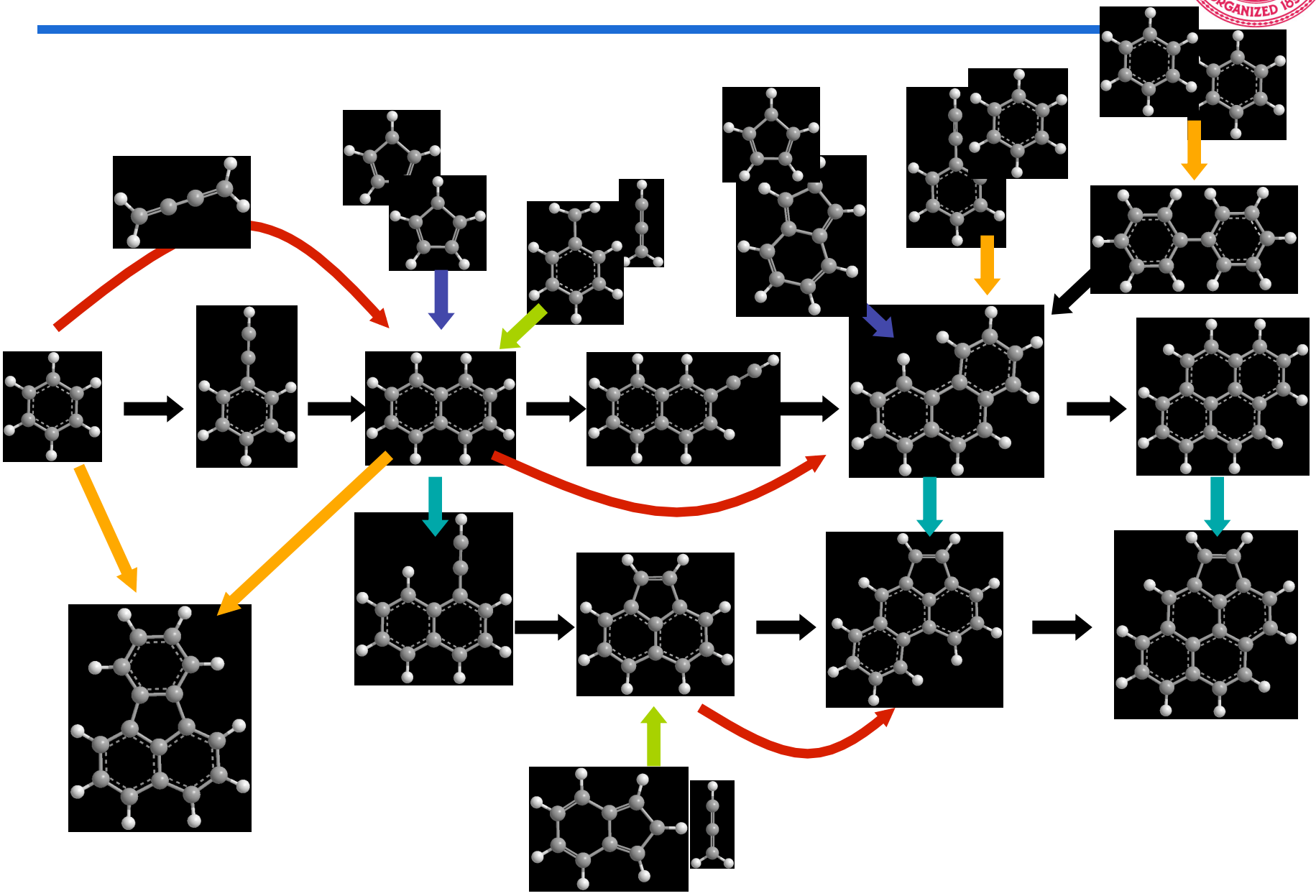
Chemical Mechanism

- Based Blanquart et al. mechanism
- PAH part starts from Wang, Frenklach mechanism
- Updated with new rates and pathways



⇒ Blanquart, G., Pepiot-Desjardins, P., Pitsch, H. « Chemical mechanism for high temperature combustion of engine relevant fuels with emphasis on soot precursors » *Combustion and Flame* (**2008**) submitted

PAH Growth



Chemical Mechanism

- **Small Hydrocarbon Chemistry**
- **C3 & C4 Chemistry**
- **Aromatic Chemistry**
- **Chemistry of Alkanes**
- **PAH Chemistry**

Results

- **1** Detailed chemical mechanism
- **13** fuels
- **149** species
- **1651** reactions

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#=====================================================================#
#                                                                     #
#       Curran, H. J., P. Gaffuri, W. J. Pitz, and C. K. Westbrook    #
#        "A Comprehensive Modeling Study of iso-Octane Oxidation"     #
#              Combustion and Flame 129:253-280 (2002).               #
#                                                                     #
#=====================================================================#


# ------------------- HIGH TEMPERATURE -------------------- #
# ---------------------- 15 Species ----------------------- #
# --------------------- 73 Reactions --------------------- #

# Reactions of I-C8H18

IC00 : I-C8H18 -> Y-C7H15 + CH3                 { A = 1.02E+49 n = -9.38 E = 404.10 }
IC01 : I-C8H18 -> I-C4H8 + I-C3H7 + CH3         { A = 5.75E+49 n = -9.66 E = 410.20 }
IC02 : I-C8H18 -> 2 T-C4H9                      { A = 1.94E+57 n =-11.84 E = 414.13 }

IC03 : I-C8H18 + H     -> C-C8H17 + H2          { A = 5.15E+01 n =  3.92 E =  10.16 }
IC04 : I-C8H18 + O     -> C-C8H17 + OH          { A = 1.25E+04 n =  3.07 E =   5.82 }
IC05 : I-C8H18 + OH    -> C-C8H17 + H2O         { A = 1.03E+07 n =  1.99 E =  -1.19 }
IC06 : I-C8H18 + O2    -> C-C8H17 + HO2         { A = 1.03E+11 n =  0.84 E = 196.29 }
IC07 : I-C8H18 + CH3   -> C-C8H17 + CH4         { A = 1.14E-18 n =  9.25 E =  -8.89 }
IC08 : I-C8H18 + HO2   -> C-C8H17 + H2O2        { A = 9.85E+10 n =  0.73 E =  70.89 }
IC09 : I-C8H18 + CH3O2 -> C-C8H17 + CH3O + OH   { A = 9.85E+10 n =  0.73 E =  70.89 }

# Reactions of C-C8H17

IC10 : C-C8H17 -> I-C4H8  + T-C4H9              { A = 4.28E+22 n = -2.81 E = 127.70 }
IC11 : C-C8H17 -> Y-C7H14 + CH3                 { A = 2.55E+39 n = -7.47 E = 189.48 }
IC12 : C-C8H17 -> I-C4H8 + CH3 + C3H6           { A = 4.22E+24 n = -3.34 E = 158.66 }

IC13 : C-C8H17 + HO2   -> D-C8H17O + OH         { A = 7.00E+12 n =   .00 E =  -4.18 }
IC14 : C-C8H17 + CH3O2 -> D-C8H17O + CH3O       { A = 7.00E+12 n =   .00 E =  -4.18 }

# Reactions of D-C8H17O

IC15 : D-C8H17O -> I-C4H8 + CH3 + CH3COCH3      { A = 1.33E+23 n = -2.98 E =  64.44 }
IC16 : D-C8H17O -> T-C4H9 + I-C3H7 + HCO        { A = 7.95E+33 n = -6.00 E =  97.57 }
IC17 : D-C8H17O -> Y-C7H15 + CH2O               { A = 2.69E+20 n = -2.08 E =  62.99 }

# Reactions of Y-C7H15

IC18 : Y-C7H14 + H -> Y-C7H15                   { A = 7.92E+16 n = -1.01 E =  15.98 }
IC19 : Y-C7H15 -> Y-C7H14 + H                   { A = 1.83E+17 n = -0.90 E = 165.71 }
IC20 : Y-C7H15 -> I-C4H8  + I-C3H7              { A = 1.94E+18 n = -1.49 E = 136.77 }
IC21 : Y-C7H15 -> T-C4H9  + C3H6                { A = 1.12E-44 n = 15.73 E = -65.59 }

# Reactions of Y-C7H14

IC22 : Y-C7H14 -> I-C4H7 + I-C3H7               { A = 6.53E+59 n =-12.99 E = 394.69 }
IC23 : Y-C7H14 -> T-C4H9 + A-C3H5               { A = 2.09E+65 n =-14.94 E = 384.52 }

IC24 : Y-C7H14 + H  -> X-C7H13 + H2             { A = 2.38E-13 n =  7.67 E = -47.65 }
IC25 : X-C7H13 + H2 -> Y-C7H14 + H              { A = 3.93E+06 n =  2.36 E =  92.29 }

IC26 : Y-C7H14 + OH  -> X-C7H13 + H2O           { A = 7.76E-09 n =  6.18 E = -41.33 }
IC27 : X-C7H13 + H2O -> Y-C7H14 + OH            { A = 1.92E+05 n =  2.76 E = 159.33 }

# Reactions of X-C7H13

IC28 : X-C7H13 + HO2 -> I-C3H5CHO + I-C3H7 + OH { A = 1.00E+13 n =  .00 E =    .00 }

# Reactions of T-C4H9O

IC29 : T-C4H9O -> I-C3H7 + HCO + H              { A = 1.78E+39 n = -7.30 E = 156.05 }
IC30 : T-C4H9O -> CH2O + I-C3H7                 { A = 7.25E+39 n = -7.59 E = 140.03 }
IC31 : T-C4H9O -> CH3COCH3 + CH3                { A = 3.09E+13 n =  0.03 E =  58.87 }
```

⇒ Blanquart, G., Pepiot-Desjardins, P., Pitsch, H. « Chemical mechanism for high temperature combustion of engine relevant fuels with emphasis on soot precursors » *Combustion and Flame* (**2008**) submitted

Validation Results

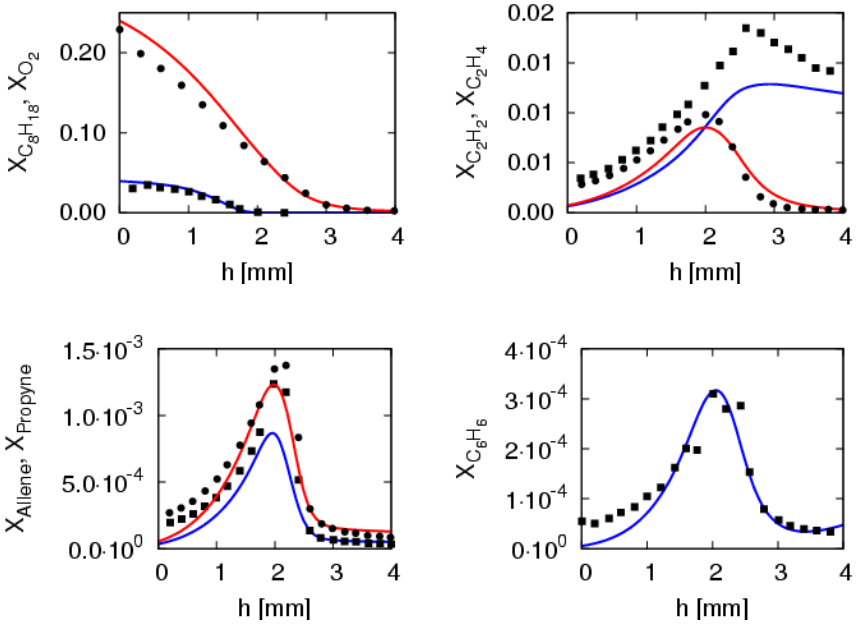
- **Entire mechanism validated with large database of experimental data**
  - **Ignition** delay times
    - Lean
    - Stoichiometric
    - Rich
  - Laminar **Burning Velocities**
    - Atmospheric
    - Moderate pressure (3bar - 5bar)
    - *High* pressure (up to 25bar)

- **Soot precursors in flames**
  - **Premixed** flames
    - n-heptane
    - iso-octane
  - Counterflow **diffusion** flames
    - acetylene
    - n-heptane

Soot Precursors

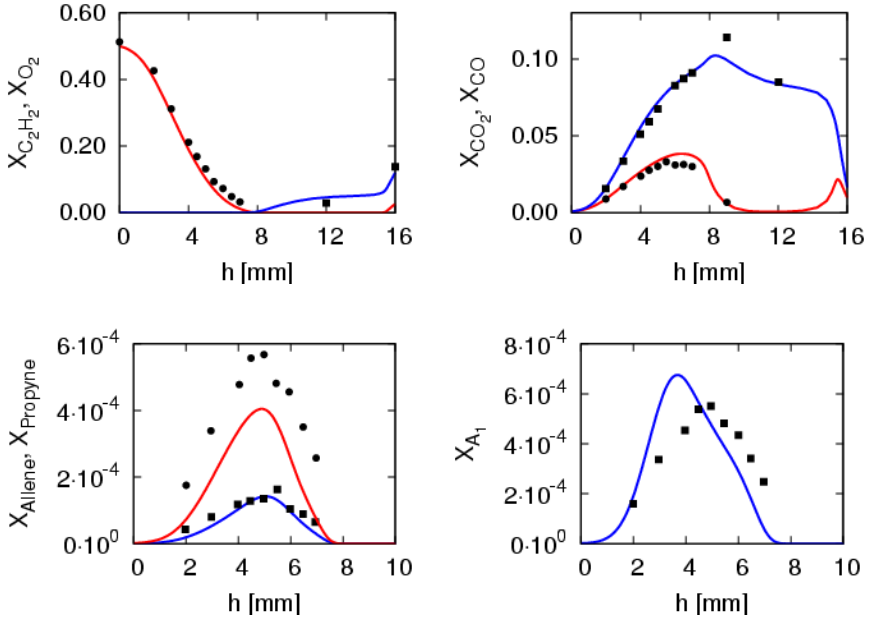
Laminar Premixed Flames

Iso-Octane / Air flame
Rich mixture (φ=1.9)
Atmospheric

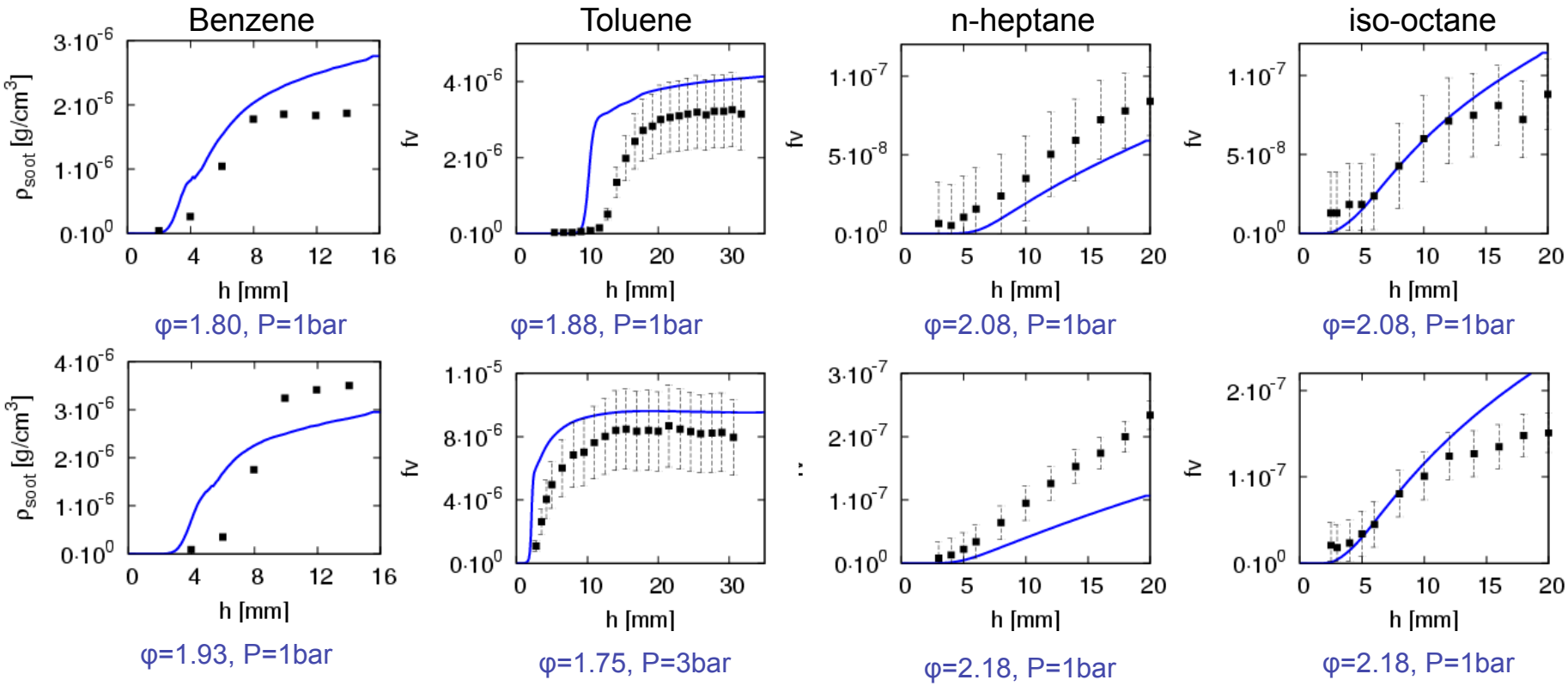


Laminar Diffusion Flames

Acetylene counterflow flame
Partially premixed (φ=0.63)
Atmospheric



Fuel Components



- **Results Analysis**
  - **Accurate prediction** of soot concentration in premixed flames
  - Soot volume fraction *increases with equivalence ratio* (φ)

Uncertainty Quantification for Reactive Flow Simulations

- Uncertainty in numerical solution can be classified into
  - Aleatory: Uncertainty due to randomness in system, e.g. uncertainty in operating conditions of system or physical properties
  - Epistemic: Uncertainty due to lack of knowledge
- Monte Carlo (MC) simulations can be used for propagation of parametric uncertainty
  - MC simulations for complex models are very inefficient
  - No information about sensitivity of model to parametric uncertainty
- Polynomial chaos (PC) expansions can be used for stochastic representation of uncertainty

Polynomial Chaos Expansion Approach

- Uncertain model parameter (α) can be represented as spectral expansion given its PDF
- Spectral expansions called Polynomial Chaos expansions can be constructed using
  - Orthogonal polynomials (Hermite, Legendre, Laguerre etc.)
  - Weights associated with PDF

$$\alpha = \sum_{k=0}^{\infty} \alpha_k \Psi_k$$

- If Hermite polynomials are used then $\Psi_0=1, \Psi_1=\xi, \Psi_2=\xi^2-1$ etc.

Non-Intrusive Polynomial Chaos

- MC sampling of stochastic parameters is done to compute deterministic solution
- Coefficients of PC expansion are computed by projecting solutions onto PC basis

- Advantage: No need to modify trusted deterministic codes
- Disadvantage: Expensive for computationally intensive problem

- Intrusive method can be used for efficient solution

Intrusive Polynomial Chaos

- Variable u(x,t,ξ) is expressed in form of PC expansion

$$u(x,t,\xi) = \sum_{k=0}^{N} u_k(x,t)\Psi_k$$

- The expansion is substituted in the deterministic equation
- Orthogonality is used to get N+1 equations for u_k's
- Nonlinear models involve operations on multiple stochastic parameters
- Pseudospectral approach is used to simplify function evaluation of stochastic parameters

Uncertainty Quantification

- Objective:
  - Uncertainty propagation in LES
    - E.g.: Effect of uncertain rates on NOx emissions from aircraft engine
  - Intrusive PC too expensive and complicated
    - ➡ New UQ method with greatly reduced cost based on direct solution of uncertainty PDF equation
    - ➡ New method didn't work!
  - Focus on
    - Intrusive PC in laminar chemistry code
    - Epistemic uncertainty
      - Uncertainty caused by chemistry reduction

Pseudospectral Approach

- Intrusive PC leads to high order polynomials in non-linear terms
  - Pseudospectral approach

Multiplication

- Product of two PC expansions having order P result in PC expansion of order 2P
- Expansion of order 2P is projected on PC expansion of order P
- Thus if w=u$\times$v then

$$w = \sum_{k=0}^{P} w_k \Psi_k \quad \text{where} \quad w_k = \sum_{i=0}^{P} \sum_{j=0}^{P} u_i v_j \frac{< \Psi_i \Psi_j \Psi_k >}{< \Psi_k^2 >}$$

Implementation

- Overloaded mathematical operators and functions were implemented in a library
- Can be used in chemical kinetic calculations to propagate uncertainty in initial conditions, reaction rate parameters, thermodynamic properties etc.
- E.g. Knowing PC expansions of A, T, E_a, evaluation of reaction rate $k=AT^n\exp(-E_a/T)$ can be done as

$$k = A \star exp(n \star ln(T) - E_a \oslash T)$$

Where $\star$ and $\oslash$ are overloaded multiplication and division operators

Future Work

- Incorporation of JetSurF into Component Library
- Validate surrogates based on JetSurF
- Integration of PAH chemistry into JetSurF mechanism
- UQ
  - Intrusive PC in laminar chemistry code
  - Model uncertainty caused by chemistry reduction