A Method for Generating Reduced Kinetic Mechanisms used for Numerical Modeling of Reactive Flows

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OUTLINE

Motivation

Differential Entropy Inequality (DEI)

Theorem

- Finite-Rate Chemistry

Method For Creating Reduced Kinetics Models

- Linear and Nonlinear Least Square Fitting

Results

Conclusions & Future Work

MOTIVATION

WHY USE
REDUCED KINETIC MECHANISMS?

Need to reduce computational cost

- number of species
- number of reactions

Uncertain that all reactions are included

MOTIVATION

Results of any numerical simulation must satisfy

- mass, momentum and energy conservation

Is this enough?

Differential Entropy Inequality

DIFFERENTIAL ENTROPY INEQUALITY

$$-\mathrm{tr}[(\mathbf{T}+P\mathbf{I})\cdot\mathbf{D}]+\frac{1}{T}\epsilon\cdot\nabla T+cRT\sum_{B=1}^{N}\mathbf{j}_{(B)}\cdot\frac{\mathbf{d}_{(B)}}{\rho_{(B)}}+\sum_{j=1}^{K}\sum_{B=1}^{N}\mu_{(B)}r_{(B,j)}\leq 0$$

$\mathbf{T}$ - stress tensor

$\mathbf{D}$ - rate of deformation

ϵ - energy flux corrected for mass transfer effects

c - total molar density

$\mathbf{j}_{(B)}$ - mass flux of species B

$\mathbf{d}_{(B)}$ - driving force for mass transfer of species B corrected for temperature and pressure gradients

$\mu_{(B)}$ - chemical potential of species B

$r_{(B,j)}$ - rate of production

TERMS OF ENTROPY INEQUALITY

Compressible Newtonian fluid

$$-tr[(\mathbf{T} + P\mathbf{I}) \cdot \mathbf{D}] \leq 0$$

Fourier's law of heat conduction

$$\frac{1}{T}\boldsymbol{\epsilon} \cdot \nabla T \leq 0$$

Fick's first law for dilute gases

$$cRT \sum_{B=1}^{N} \mathbf{j}_{(B)} \cdot \frac{\mathbf{d}_{(B)}}{\rho_{(B)}} \leq 0$$

FLUIDIZED BED GASIFIER[1]

$$\begin{aligned} VM \rightarrow\ & 0.132CO_2 + 0.116CO + 0.019H_2 + 0.107CH_4 \\ & + 0.302H_2O + 0.013H_2S + 0.012C_3H_6 \\ & + 0.023C_2H_4 + 0.004C_2H_6 + 0.064TAR + 0.005HCN \end{aligned}$$

$$C + H_2O \rightarrow CO + H_2$$

$$C + CO_2 \rightarrow 2CO$$

$$C + 1/2O_2 \rightarrow CO$$

$$CO + 1/2O_2 \rightarrow CO_2$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

[1] SHAHNAM ET AL., JOURNAL OF VERIFICATION, VALIDATION AND UNCERTAINTY QUANTIFICATION, DEC. 2016, VOL.1

THEOREM

FINITE-RATE CHEMISTRY

$$\sum_{n=1}^{N_s} \nu'_{(n)(r)} \mathcal{M}_{(n)} \to \sum_{n=1}^{N_s} \nu''_{(n)(r)} \mathcal{M}_{(n)}, \quad r = 1, \ldots, N_r$$

$\mathcal{M}_{(n)}$ - chemical symbol for species n
$\nu'_{(n)(r)}$ and $\nu''_{(n)(r)}$ - stoichiometric coefficients for species n in reaction r

Law of mass action

$$\omega_{(r)} = k_{(r)} \prod_{n=1}^{N_s} c_{(n)}^{\nu'_{(n)(r)}}, \quad r = 1, \ldots, N_r$$

$\omega_{(r)}$ - volumetric molar progress of reaction r
$k_{(r)}$ - reaction-rate constant
$c_{(n)}$ - molar concentration of species n

FINITE-RATE CHEMISTRY (2)

Arrhenius expression (empirical)

$$k_{(r)} = A_{(r)} T^{\beta_{(r)}} \exp\left[\frac{-E_{a,(r)}}{\hat{R}T}\right], \quad r = 1, \dots, N_r$$

Molar rate of production of species n in reaction r

$$R_{(n)(r)} = \left(\nu''_{(n)(r)} - \nu'_{(n)(r)}\right)\omega_{(r)}, \qquad \begin{matrix} n = 1, \dots, N_s \\ r = 1, \dots, N_r \end{matrix}$$

Net molar production rate of species n

$$R_{(n)} = \sum_{r=1}^{N_r} R_{(n)(r)} = \sum_{r=1}^{N_r} \left(\nu''_{(n)(r)} - \nu'_{(n)(r)}\right)\omega_{(r)}, \quad n = 1, \dots, N_s$$

ASSUMPTIONS FOR FOURTH TERM

- Dilute solution or ideal gas
- All reactions conform to the law of mass action

$$R_{(B,j)} = \left(\nu''_{(B,j)} - \nu'_{(B,j)}\right)\left(k_{(f,j)}\Pi_B c_{(B)}^{\nu'_{(B,j)}} - k_{(b,j)}\Pi_B c_{(B)}^{\nu''_{(B,j)}}\right)$$

- All reactions are reversible

$$\sum_{B=1}^{N}\mu_{(B)}r_{(B,j)} = XRT\left[\prod_B\left(y_{(B)}/y^{\star}_{(B)}\right)^{\nu'_{(B,j)}} - \prod_B\left(y_{(B)}/y^{\star}_{(B)}\right)^{\nu''_{(B,j)}}\right]\ln\left\{\frac{\prod_B\left(y_{(B)}/y^{\star}_{(B)}\right)^{\nu''_{(B,j)}}}{\prod_B\left(y_{(B)}/y^{\star}_{(B)}\right)^{\nu'_{(B,j)}}}\right\}$$

$$X \equiv k_{(f,j)}\prod_B {c^{\star}_{(B)}}^{\nu'_{(B,j)}} = k_{(b,j)}\prod_B {c^{\star}_{(B)}}^{\nu''_{(B,j)}}$$

THEOREM[†]

The differential entropy inequality (1) is automatically satisfied for dilute gases, if all the reactions are both reversible and conform to the law of mass action, that is, the exponents of the molar concentrations used to calculated the progress of reaction variables are the stoichiometric coefficients.

[†] Role of differential entropy inequality in chemically reacting flows, *Chemical Engineering Science* **66** (2011), 5236-43, 2011

LEAST SQUARE FITTING

$$r_i = y_i - f\left(x_i, \vec{\eta}\right), \quad i = 1, \ldots, N_p. \tag{1}$$

r_i - residual at point i of a data set containing N_p points
x_i and y_i - independent and dependent coordinates
f - function of the independent variable and the solution vector $\vec{\eta}$; $\vec{\eta} \in \mathbb{R}^{N_\eta}$
N_η - number of parameters

$$\vec{r} = \vec{y} - \vec{f}\left(\vec{x}, \vec{\eta}\right). \tag{2}$$

Minimization of the square of the residual over all the data points yields

$$\sum_{i=1}^{N_p} J_{ij} r_i = 0, \quad j = 1, \ldots, N_\eta, \tag{3}$$

or in matrix form

$$\overline{\overline{J}}^T \vec{r} = 0 \tag{4}$$

where the elements of the Jacobian $\overline{\overline{J}}$ are

$$J_{ij} = -\frac{\partial r_i}{\partial \eta_j} = \frac{\partial f\left(x_i, \vec{\eta}\right)}{\partial \eta_j}, \qquad \begin{matrix} i = 1, \ldots, N_p \\ j = 1, \ldots, N_\eta \end{matrix} \tag{5}$$

LINEAR AND NONLINEAR LEAST SQUARE FITTING

Linear

$$\overline{\overline{J}}^T \overline{\overline{J}} \vec{\eta} = \overline{\overline{J}}^T \vec{y}$$

Nonlinear

$$\vec{\eta}^{k+1} = \vec{\eta}^k + \Delta \vec{\eta}^k .$$

$$\overline{\overline{J}}^{T,k} \overline{\overline{J}}^k \Delta \vec{\eta}^k = \overline{\overline{J}}^{T,k} \vec{r}^k$$

LEAST SQUARES METHOD FOR FITTING ARRHENIUS PARAMETERS

Example: Westbrook and Dryer two-step mechanism for methane combustion

Reaction	Equation
I	$\mathrm{CH_4 + 1.5O_2 \rightarrow CO + 2H_2O}$
II	$\mathrm{CO + 0.5O_2 \rightleftharpoons CO_2}$

$$
\begin{aligned}
R_{(\mathrm{CH_4})} &= -\omega_{(1)} \\
R_{(\mathrm{H_2O})} &= 2\omega_{(1)} \\
R_{(\mathrm{O_2})} &= -1.5\omega_{(1)} - 0.5\omega_{(2f)} + 0.5\omega_{(2b)} \\
R_{(\mathrm{CO})} &= \omega_{(1)} - \omega_{(2f)} + \omega_{(2b)} \\
R_{(\mathrm{CO_2})} &= \omega_{(2f)} - \omega_{(2b)}
\end{aligned}
$$

LEAST SQUARES METHOD FOR FITTING ARRHENIUS PARAMETERS (2)

Linear Least Squares

$$\vec{R} = \overline{\overline{\nu}}\vec{\omega}, \quad \overline{\overline{\nu}} \in \mathbb{R}^{N_s \times N_r}$$

$$\vec{\omega} = \left(\overline{\overline{\nu}}^T \overline{\overline{\nu}}\right)^{-1} \overline{\overline{\nu}}^T \vec{R}$$

Nonlinear Least Squares

$$r_{(r),i} = \omega_{(r),i} - f_{(r),i}\left(T_i, \vec{\eta}_{(r)}\right), \quad i = 1, \dots, N_p$$

$$f_{(r),i}\left(T_i, \vec{\eta}_{(r)}\right) = A_{(r)} T_i^{\beta_{(r)}} \exp\left[\frac{-E_{a,(r)}}{\hat{R}T_i}\right] \prod_{n=1}^{N_s} c_{(n),i}^{q'_{(n)(r)}}, \qquad \begin{array}{l} i = 1, \dots, N_p \\ r = 1, \dots, N_r \end{array}$$

$$\vec{\eta}_{(r)} = \begin{bmatrix} A_{(r)} & \beta_{(r)} & E_{a,(r)} \end{bmatrix}^T, \quad r = 1, \dots, N_r$$

LEAST SQUARES METHOD FOR FITTING ARRHENIUS PARAMETERS (3)

$$\overline{\overline{J}}_{(r)} = \begin{bmatrix} \frac{\partial f_{(r),1}}{\partial A_{(r)}} & \frac{\partial f_{(r),1}}{\partial \beta_{(r)}} & \frac{\partial f_{(r),1}}{\partial E_{a,(r)}} \\ \vdots & \vdots & \vdots \\ \frac{\partial f_{(r),N_p}}{\partial A_{(r)}} & \frac{\partial f_{(r),N_p}}{\partial \beta_{(r)}} & \frac{\partial f_{(r),N_p}}{\partial E_{a,(r)}} \end{bmatrix}, \quad r = 1, \ldots, N_r$$

$$\frac{\partial f_{(r)}}{\partial A_{(r)}} = \frac{f_{(r)}}{A_{(r)}}, \quad r = 1, \ldots, N_r,$$

$$\frac{\partial f_{(r)}}{\partial \beta_{(r)}} = f_{(r)} \ln\left(T\right), \quad r = 1, \ldots, N_r,$$

$$\frac{\partial f_{(r)}}{\partial E_{a,(r)}} = \frac{-f_{(r)}}{\hat{R}T}, \quad r = 1, \ldots, N_r$$

$$\Delta \vec{\eta}^k = \left(\overline{\overline{J}}^{T,k} \overline{\overline{J}}^k \right)^{-1} \overline{\overline{J}}^{T,k} \vec{r}^k$$

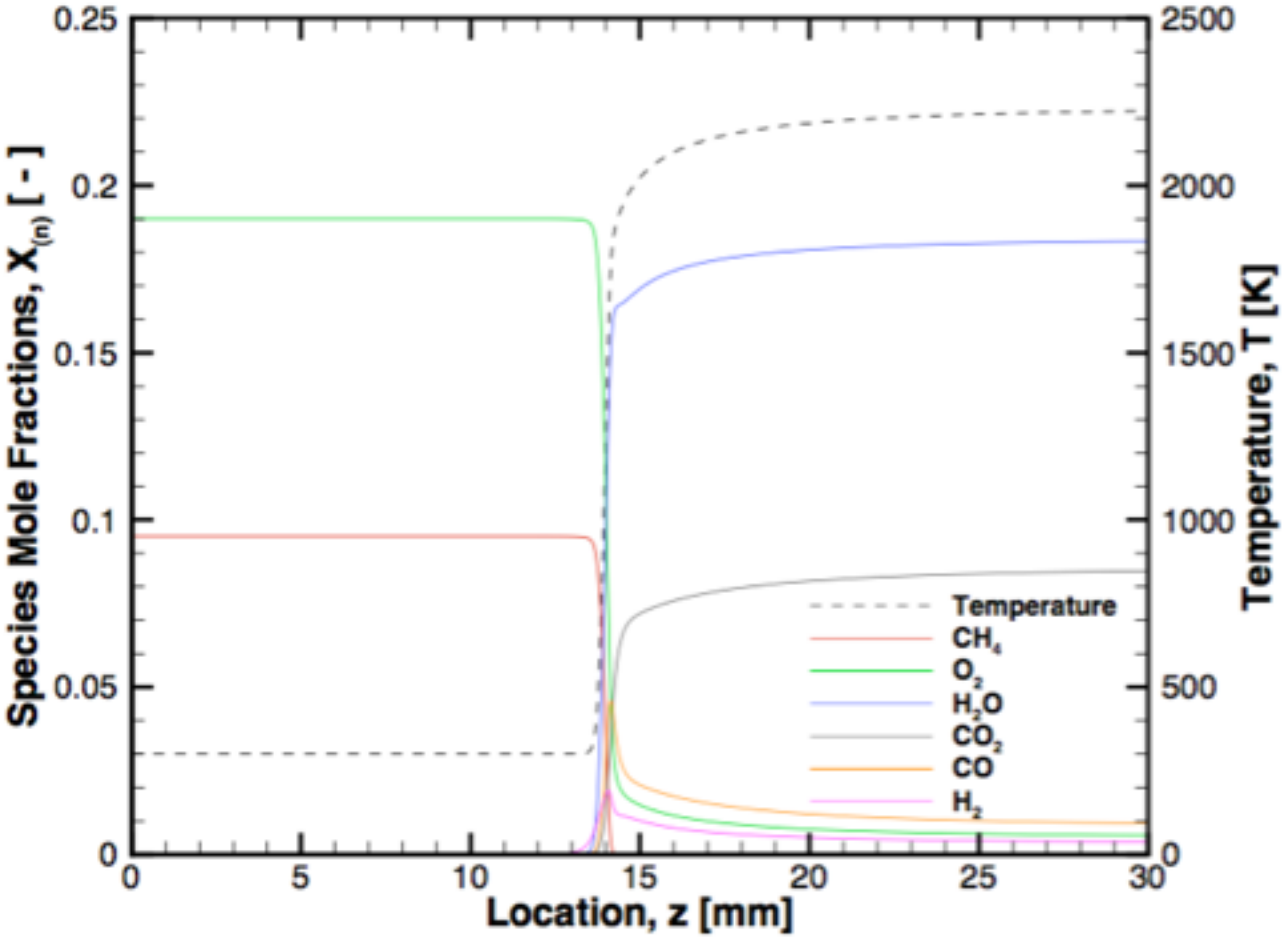
LEAST SQUARES METHOD FOR FITTING ARRHENIUS PARAMETERS (4)

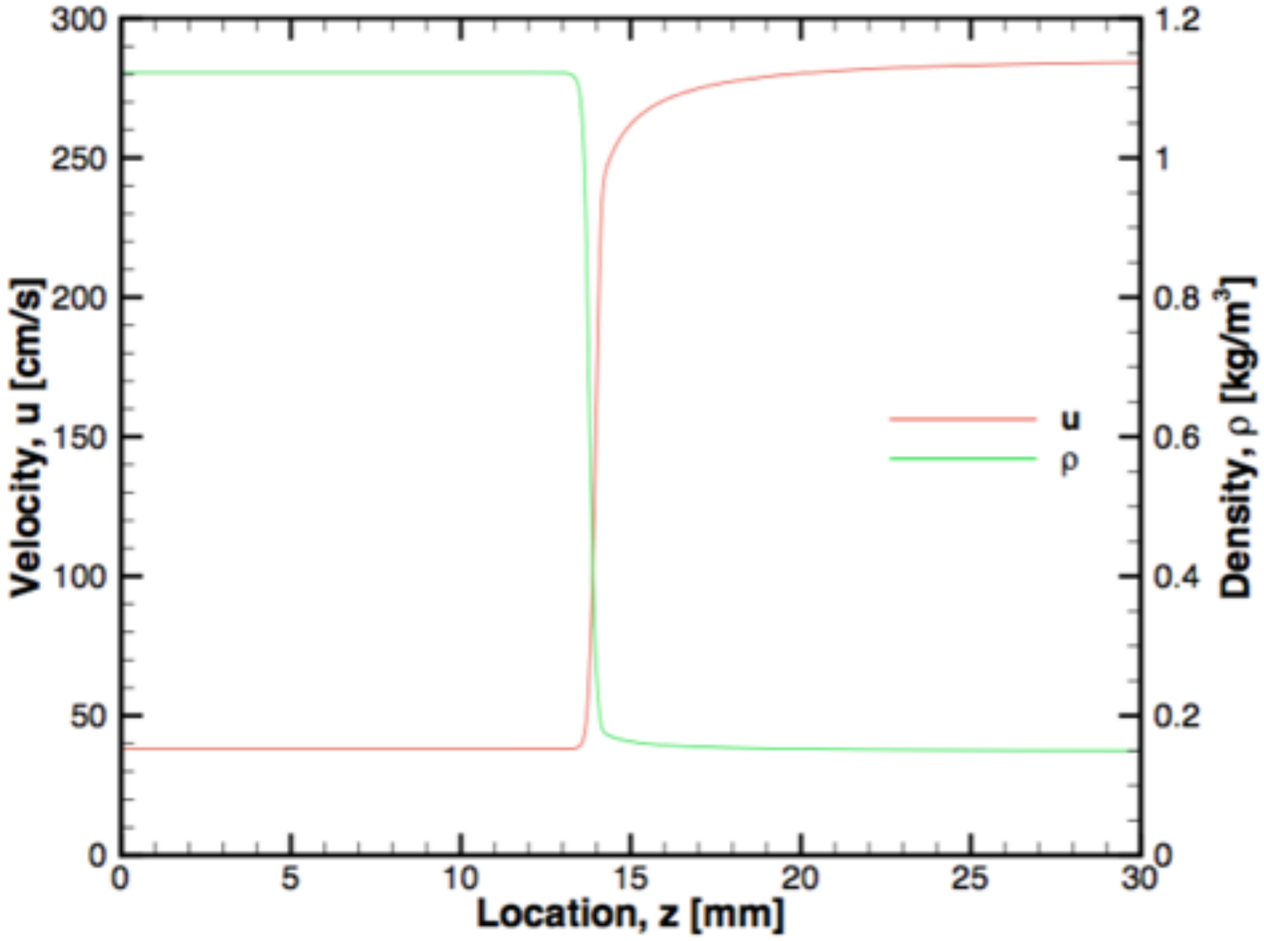
Steps:

1. A detailed mechanism simulation is run to generate a data set containing temperature, species concentration, and species production rate through a flame front.
2. Progresses of reaction are approximated at each data point from the species production rates using linear least squares.
3. The Arrhenius parameters are found for each reaction by performing a non-linear least squares curve fit of the approximated progresses of reaction.
    (a) The form of function $f_{(r)}$ is found by using the Arrhenius rate equation;
    (b) An initial guess of the solution vector for each reaction r is found by testing an assortment of combinations of the Arrhenius parameters;
    (c) The residual and Jacobian are calculated for each reaction r;
    (d) The solution vector is updated for each reaction r;
    (e) If a convergence criterion is met the solution has been found. If not, the guess of the solution vector is updated and the residual and Jacobian are recomputed for the new guess.

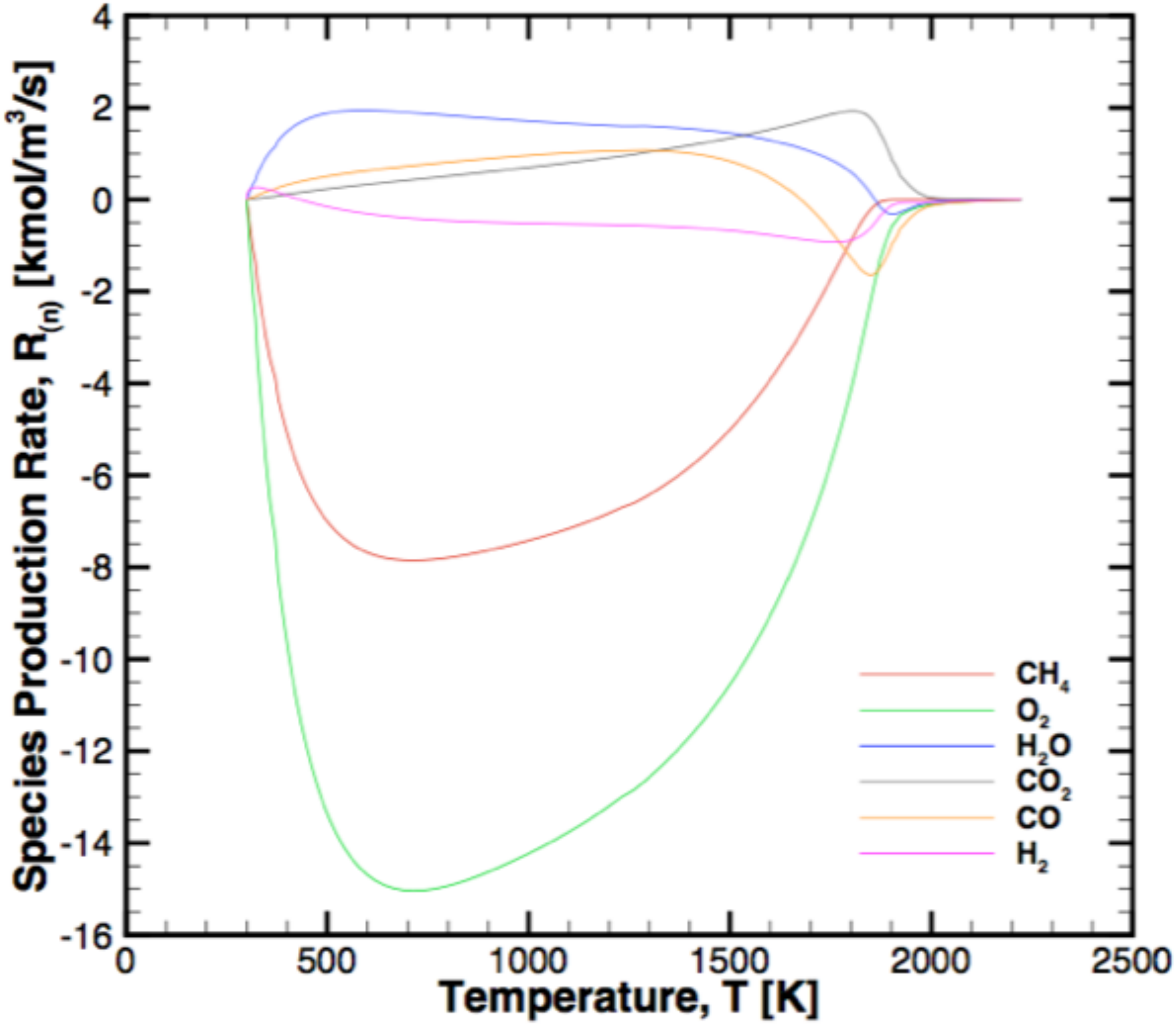
RESULTS

PREMIXED LAMINAR FLOW





RESULTS (2)


Species Production Rate, $R_{(n)}$ [kmol/m^3/s]
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
0
500
1000
1500
2000
2500
Temperature, T [K]
CH_4
O_2
H_2O
CO_2
CO
H_2

RESULTS (3)

Optimized Two-Step Mechanism Arrhenius Parameters[1]

Reaction	Equation	A	β	E
1	$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$	3.1623×10^{14}	0.8308	2.3855×10^{4}
2_f	$CO + 0.5O_2 \rightarrow CO_2$	4.2094×10^{6}	0.1251	7.3969×10^{3}
2_b	$CO_2 \rightarrow CO + 0.5O_2$	1.4286×10^{9}	0.2851	1.7072×10^{5}

Units are cm, mol, cal, s, and K.

Optimized Three-Step Mechanism Arrhenius Parameters[2]

Reaction	Equation	A	β	E
1	$CH_4 + O_2 \rightarrow CO + H_2 + H_2O$	4.8801×10^{12}	0.4452	2.3849×10^{4}
2_f	$CO + H_2O \rightarrow CO_2 + H_2$	2.3037×10^{11}	-1.0206	2.3901×10^{3}
2_b	$CO_2 + H_2 \rightarrow CO + H_2O$	1.4286×10^{12}	0.2851	1.7072×10^{5}
3	$O_2 + 2H_2 \rightarrow 2H_2O$	1.0000×10^{9}	2.5903	1.1360×10^{2}

Units are cm, mol, cal, s, and K.

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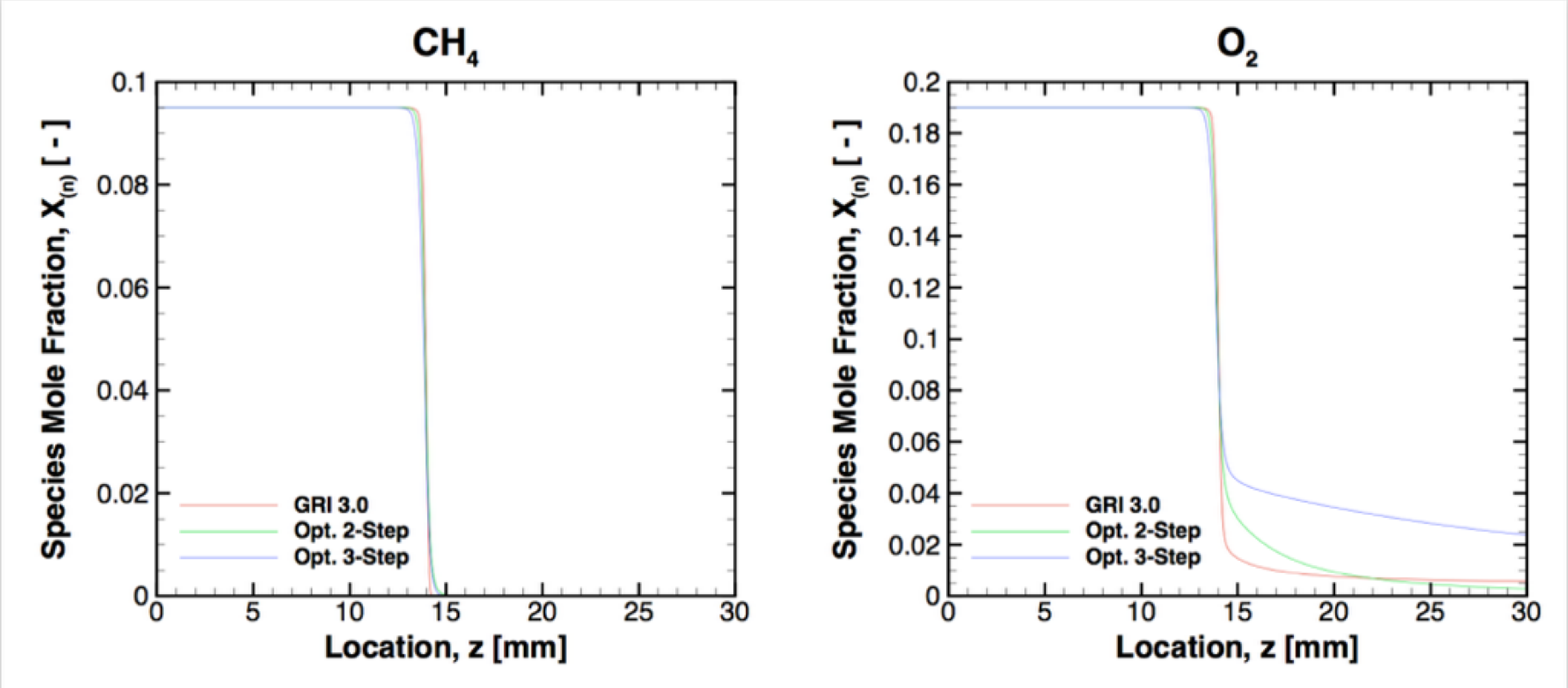
[1] modified from Westbrook and Dryer, Simplified Reaction Mechanisms for the Oxideation of Hydrocarbon Fuels in Flames. Combustion Science and Technology, 27:31–43, 1981.

[2] modified from Peters and Williams, The Asymptotic Structure of Stoichiometric Methane-Air Flames. Combustion and Flame, 68:185–207, 1987.

RESULTS (4)


CH$_4$
O$_2$
Species Mole Fraction, $X_{(n)}$ [-]
Location, z [mm]
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
5
10
15
20
25
30
GRI 3.0
Opt. 2-Step
Opt. 3-Step

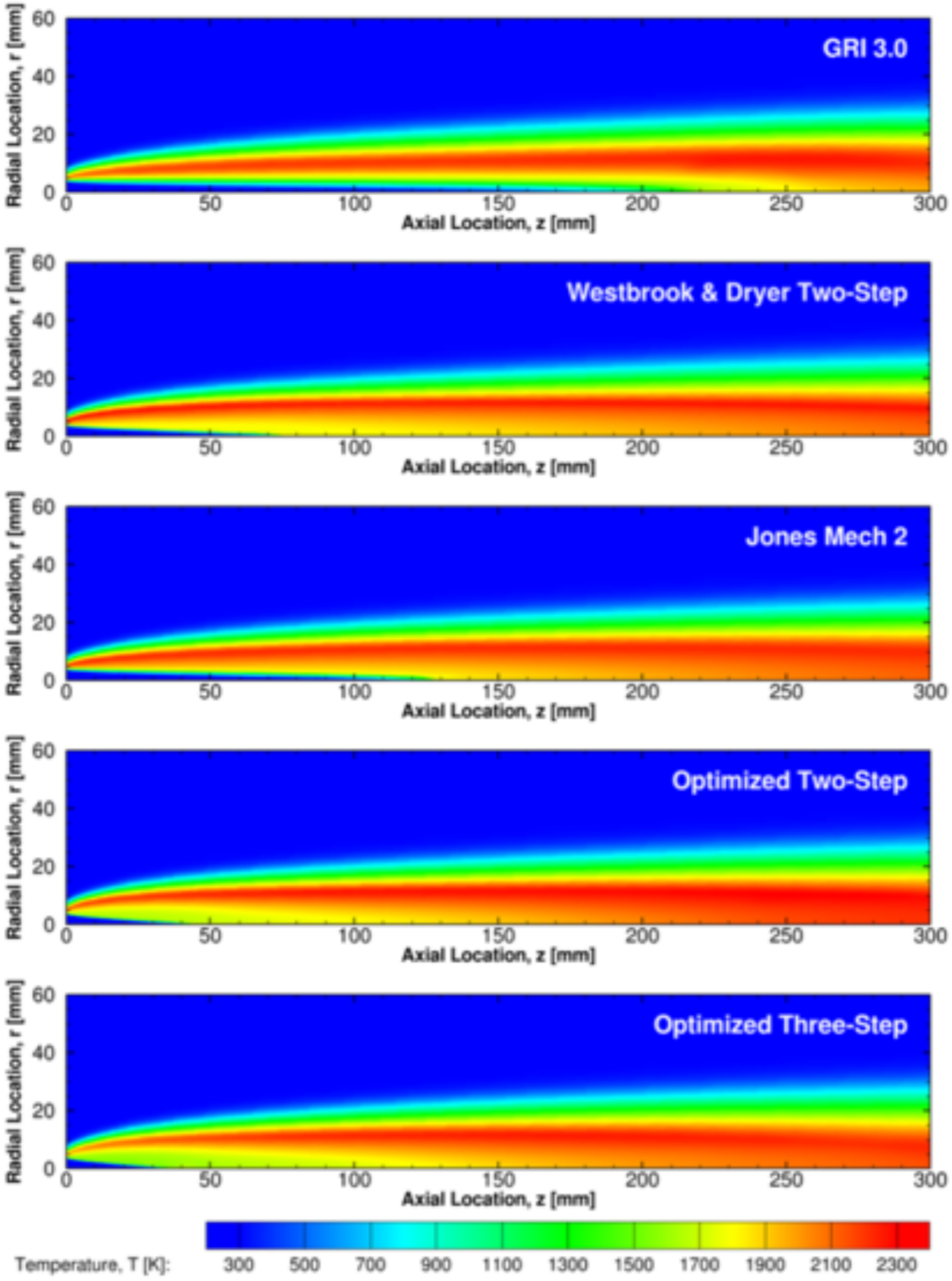
FLAME SPEED COMPARISON OF VARIOUS MECHANISMS

Mechanism	Flame Speed [cm/s]	Error [%]
GRI 3.0	38.05	-
Optimized 2-step	28.43	25.28
Optimized 3-step	22.57	40.28
Jones Mech 2	10.35	72.80

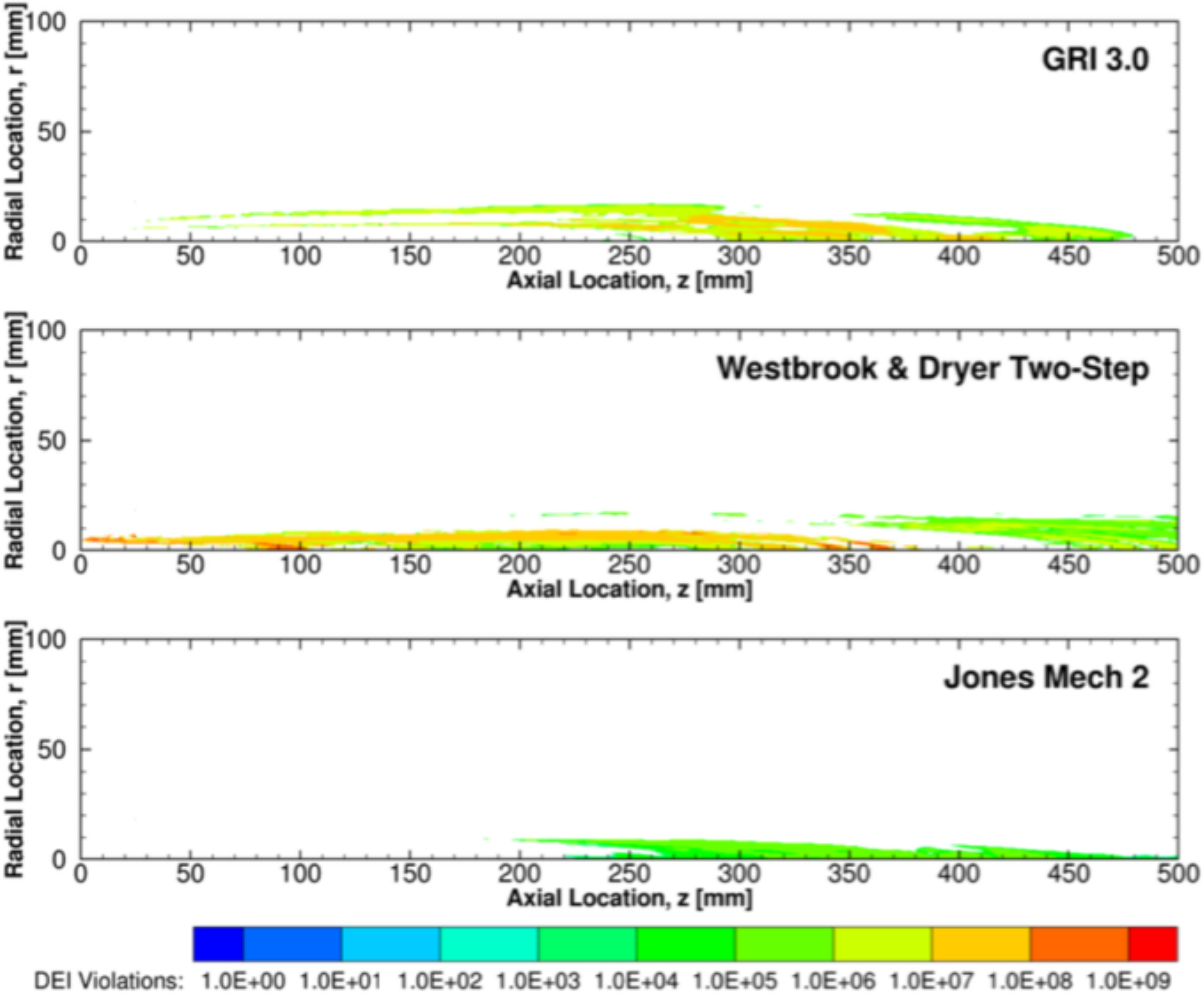
VIOLATIONS OF THE DEI FOR VARIOUS MECHANISMS

Mechanism	Number of Cells	Volume Fraction [%]	Maximum Value
GRI 3.0	3513	3.98×10^{-3}	5.72×10^{7}
Westbrook & Dryer	20653	3.62×10^{-2}	1.40×10^{9}
Jones Mech 2	2075	1.15×10^{-3}	1.71×10^{6}
Optimized 2-step	0	0	-
Optimized 3-step	0	0	-

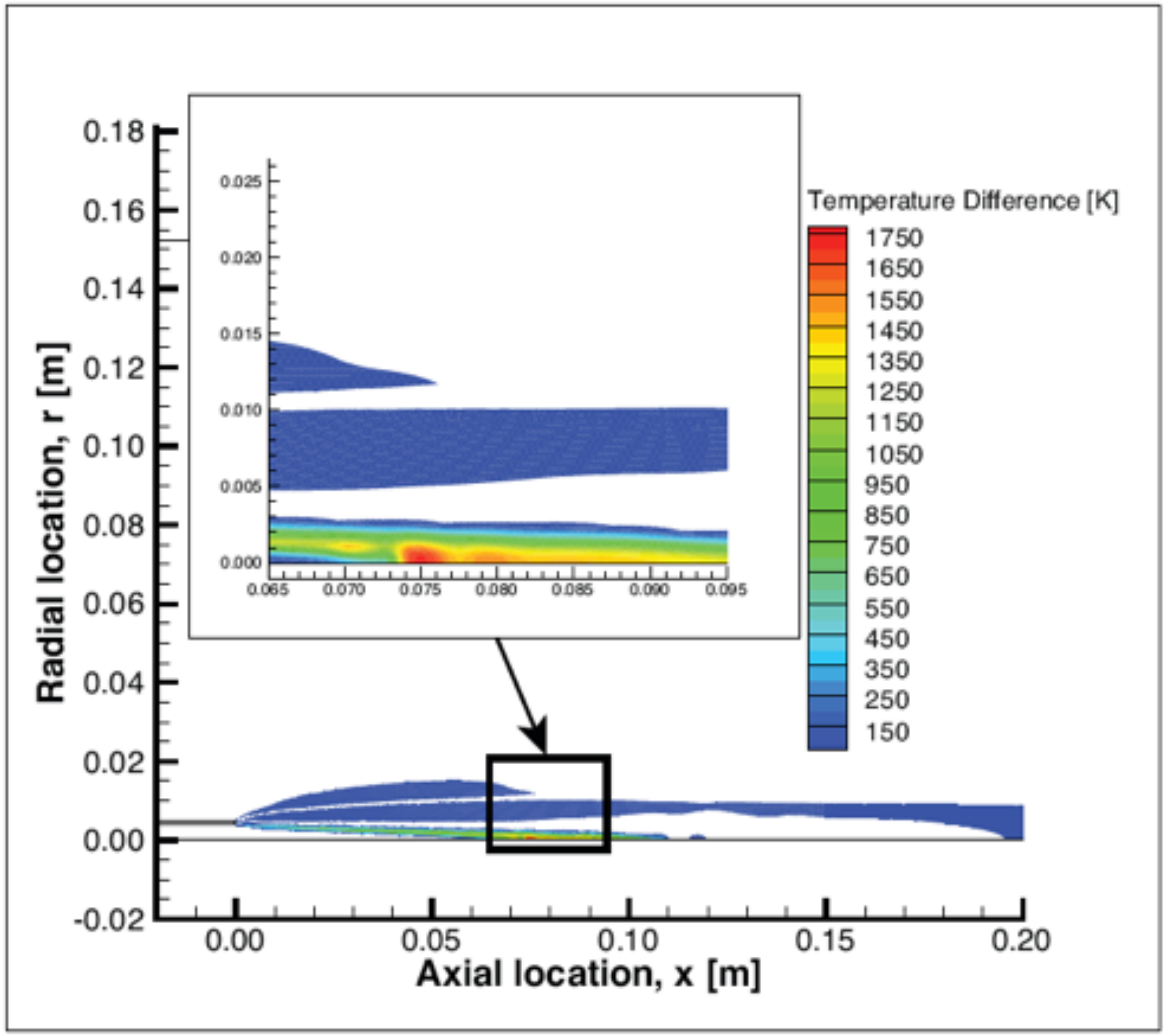
SANDIA FLAME A



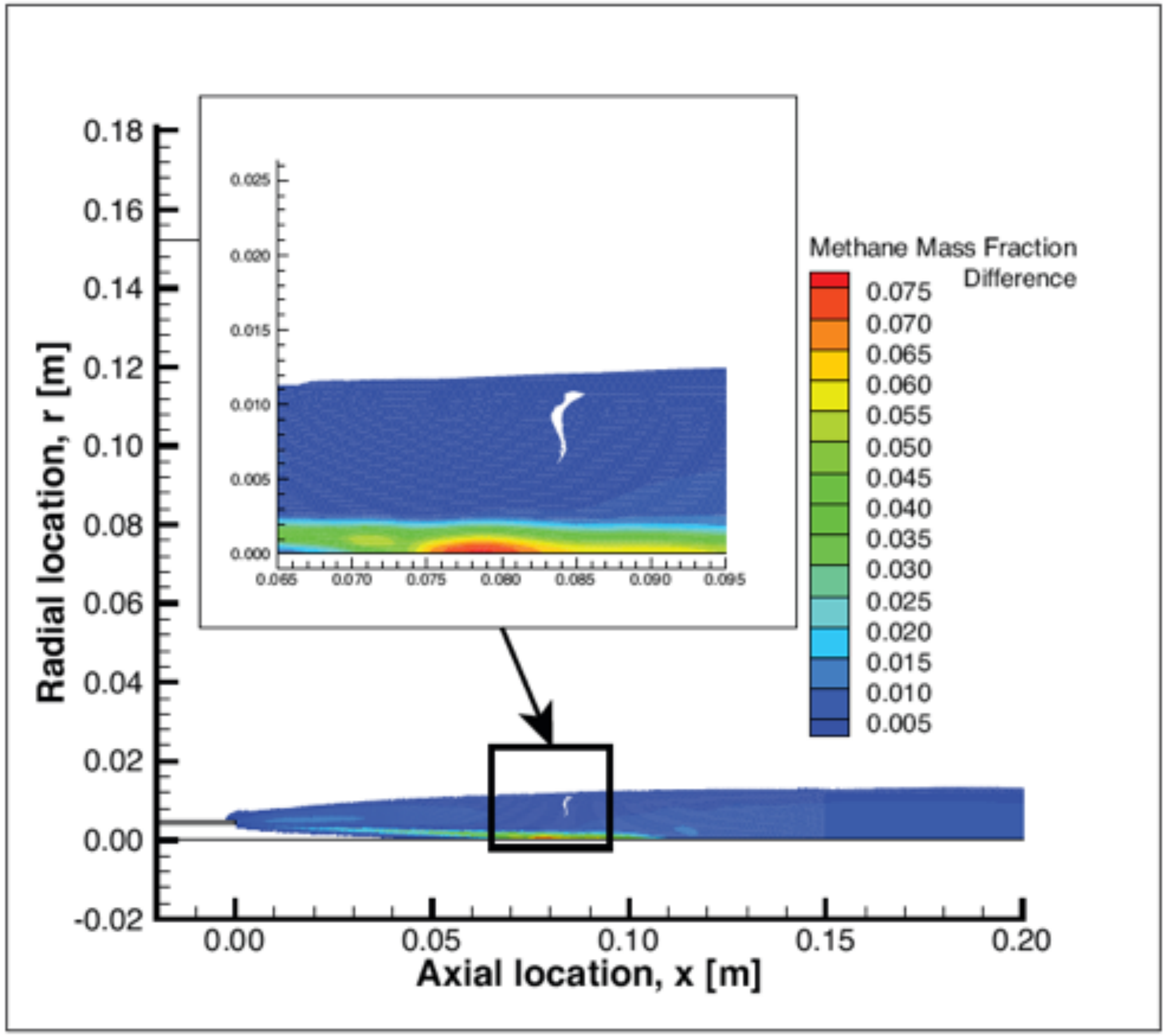
VIOLATIONS OF THE DEI FOR VARIOUS MECHANISMS



TEMPERATURE AND METHANE MASS FRACTION DIFFERENCES



(a)



(b)

CONCLUSIONS

- Existing reduced kinetics models that do not satisfy differential entropy inequality can be easily modified to satisfy it
- Numerical results obtained using new reduced kinetics model that satisfies DEI were closer to experimental data than results obtained using a reduced kinetics model that did not satisfy DEI
- DEI, the local form of second law of thermodynamics, should be enforced the same way mass, momentum and energy conservation are

Thank You!