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Title : Development of Skeletal Kinetic Mechanism of Methane Oxidation for High Pressures and Temperatures

Theme :

Attached documents :

Abstract_Zhukov_Rome(2016).pdf

Resume :

There is an increasing interest on methane as rocket propellant in recent years. The origin on the interest is a demand for the further development of liquid rocket technologies where methane can provide an attractive compromise between performance (Isp) and costs. Methane is currently considered as a propellant for low stages, upper stages, and for interplanetary missions, especially to Mars.
Oxidation kinetics of methane is relatively well-known. However, practically all reduced methane mechanisms are developed for gas-turbine conditions, while detailed methane mechanisms consists of around 200 reactions within around 40 species and are too heavy for two-dimensional and three-dimensional simulations. The conditions in rocket combustion chambers are very specific: in rocket engines, fuel burns in mixture with pure oxygen at very high pressures and temperatures. Thus, there is a need for reduced methane mechanism developed especially for rocket application.
The detailed mechanism of alkane oxidation by Zhukov [1] was taken as a basis in the current study. This mechanism has been validated at pressures up to 500 atm and contains the kinetics of alkanes up to heptane, which distinguishes this mechanism from others. The reduction of the detailed mechanism has been performed in three stages. On the first stage, the reaction path analysis has been done. Species, which are formed in a negligible quantity and do not participate in the formation of final products, have been cut off from the mechanism. On the next stage, sensitivity analysis has been carried out. It showed reactions that do not influence on flame temperature and ignition delay time, and therefore can be excluded from the mechanism. The reaction path and sensitivity analyses allowed reducing of the mechanism down to 26 species and 82 reactions. The further application of the try-and-method to all remain species and reactions reduced the size of the kinetic mechanism to 23 species and 49 reactions. After the reduction, the obtained mechanism has been successfully validated against high-pressure ignition delay data and verified against the original detailed mechanism. The comparison with other mechanisms shows the reduction of computational time and the better accuracy in comparison with other reduced methane mechanisms.
[1] Zhukov, V. P. "Kinetic Model of Alkane Oxidation at High Pressure from Methane to n-Heptane." Combustion Theory and Modelling 13.3 (2009): 427-42.

Development of Skeletal Kinetic Mechanism of Methane Oxidation for High Pressures and Temperatures

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Methane as rocket fuel

- $I_{spC11H22} < I_{spCH4} < I_{spH2}$
- $\rho_{C11H22} > \rho_{CH4} > \rho_{H2}$
- $T_{C11H22} > T_{CH4} \approx T_{O2} > T_{H2}$

- LM10-MIRA: AVIO(Italy) + CADB(Russia) =
  10 tonn expander cycle

Generic methane rocket operating conditions

- Propellants: pure CH_4 and O_2
- Injection temperature = 300K
- $\varphi \approx 1$
- Pressure ≈ 60 bar

Motivation

- Q.: Do we need a special methane kinetic mechanism for rocket conditions when we have already GRI 3.0?
  - A.: At least in mixtures with air, methane needs specific kinetic models for high pressures.

- Q.: Do we need kinetic mechanisms for CFD modelling of methane combustion in rocket combustion chambers?
  - A.: At least in some areas of rocket combustion chambers, the kinetics is a limiting factor.

Chemical kinetic model and CFD

- Major goals of CFD simulations:

1) Thermal loads on walls
2) Performance of rocket engine

- Contribution of flame temperature to uncertainty:
  - 50% for thermal loads
  - 50% for performance (I_{sp})

- Requirements for combustion model:

a) Predict the flame temperature with an accuracy of 2% (~1% for I_{sp})
b) Be small as possible (i.e. have the smallest set of species)

Model with 35-50 species -> simulated volume as big as match box

Methane kinetic mechanisms

- Detailed mechanisms:
  - Zhukov's MECH – C1-C4, 207 specie, 1260 reaction [1]
    - Validated $p \leq 530$ bar, $T = 850K–1700$ K
  - RAMEC – C1-C2 (Stanford), 38s and 190r
    - Validated $p = 40–260$ bar, $T = 1040–1500$ K
  - GRI MECH 3.0 (used as standard benchmark, not accurate at high pressures)
- Reduced mechanisms: REDRAM (Stanford) 22s and 34r
  - Jones&Lindstedt 4 reactions

- High pressures -> peroxy species (XO_2)
- High pressures -> faster recombination -> ¿C2 -> C3 -> C4 kinetics?

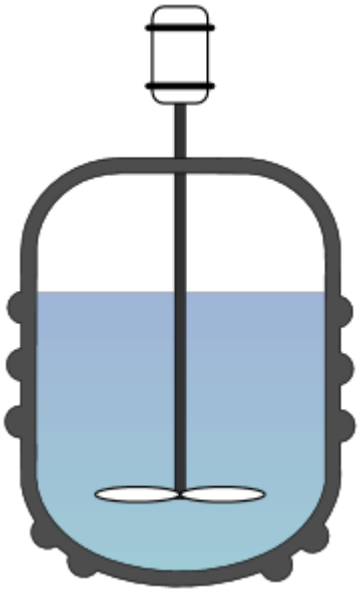
[1] V.P. Zhukov, V.A. Sechenov, A.Yu. Starikovskii, "Autoignition of a lean propane–air mixture at high pressures", *Kinetics and Catalysis*, Vol. 46, No. 3, 2005, pp. 319–327.

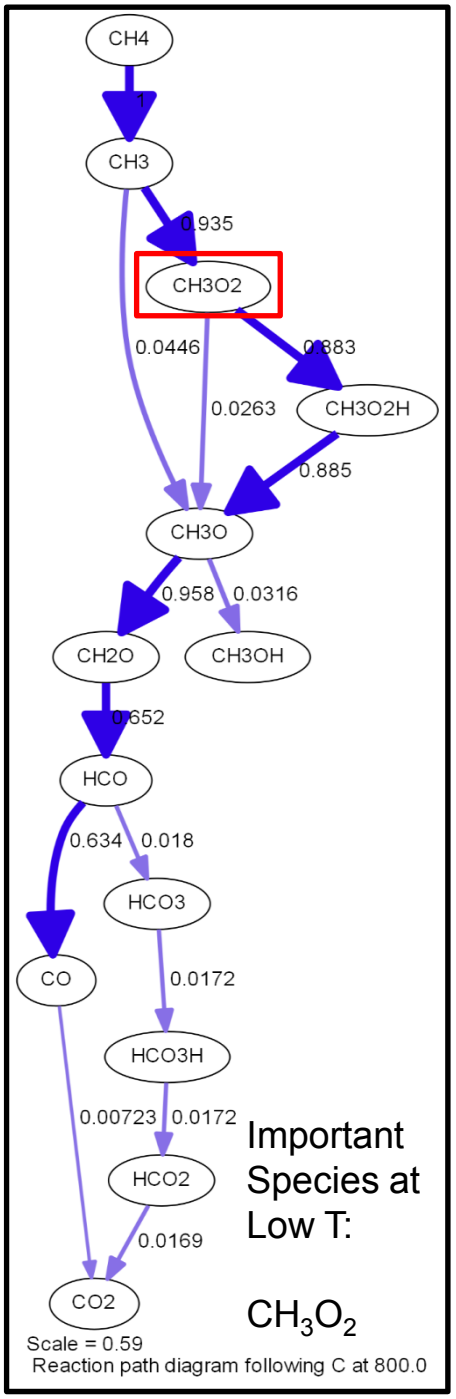
Reduction technique

- Skeletal mechanism:=∑important elementary reactions
- Two types of simulations:
  - 0D homogenous batch reactor
  - 1D counterflow diffusion flame
- Mechanism Analyses:
  - Reaction Path diagram, 0D/1D
  - Sensitivity Analysis, 0D/1D
- Verification&Validation:
  - Validation against ignition delay times (Petersen and Zhukov)
  - Verification with full mechanism
- Software: Cantera by Prof. Dave Goodwin from Caltech (Open sour.)

Reaction path analysis, batch reactor

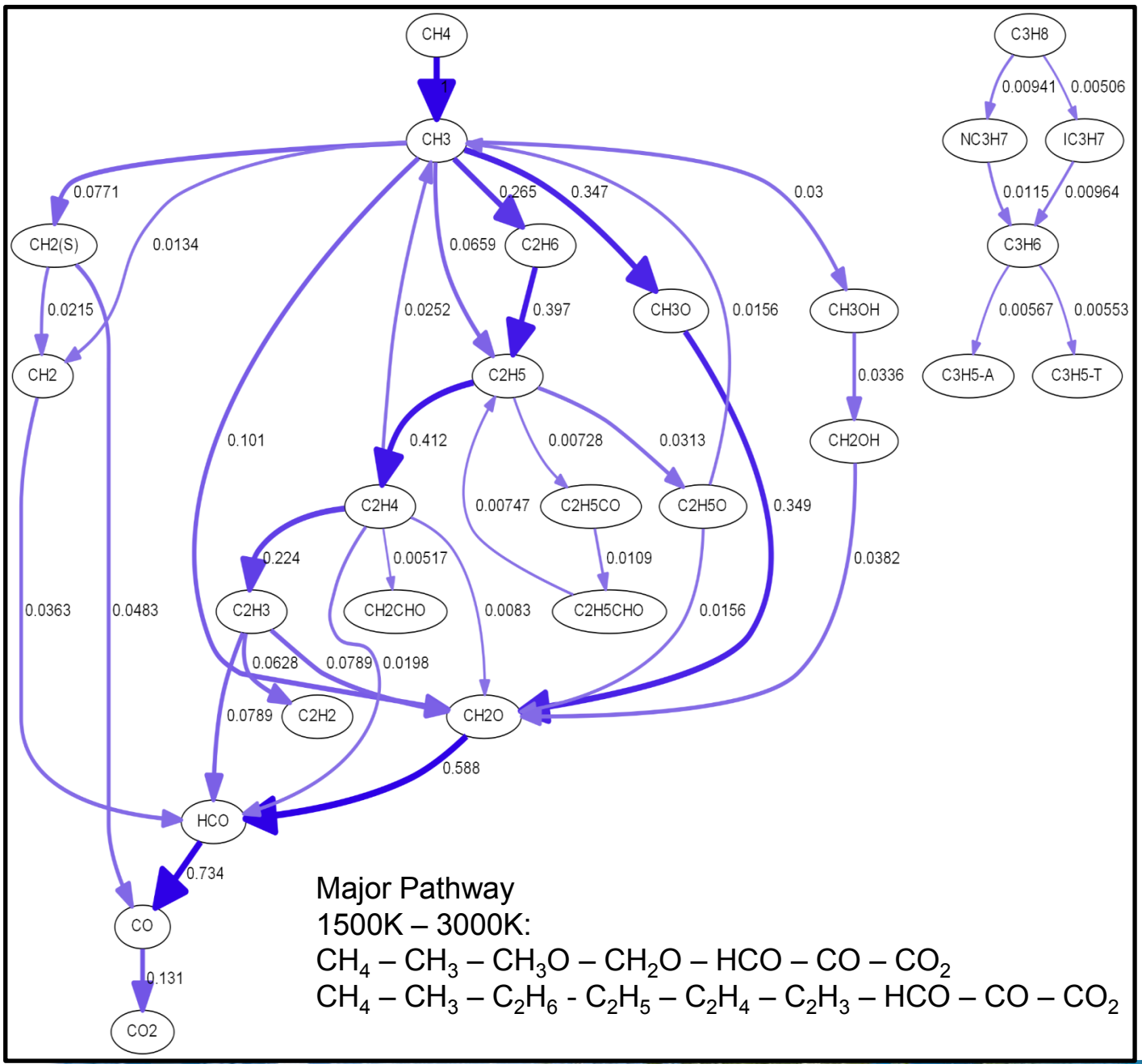
- **0D:** Homogeneous, premixed, Constant HP:
  - Non Transport Model (no diffusion, convection)
  - Pressure 60 bar
  - φ = 1, CH_4:O_2=1:2
  - Reaction path diagram at 100 K interval from T_i to T_{eq}





Important Species at Low T:

CH_3O_2



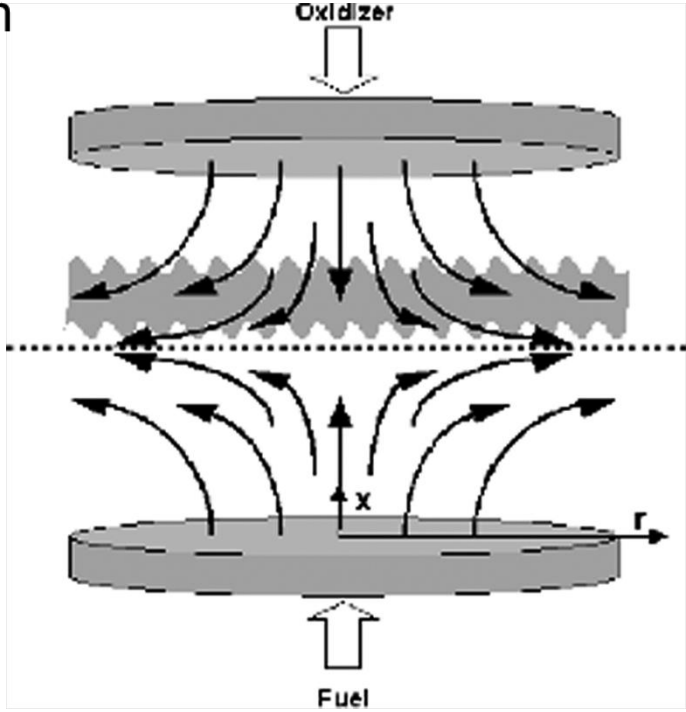
Major Pathway
1500K – 3000K:

$CH_4 – CH_3 – CH_3O – CH_2O – HCO – CO – CO_2$

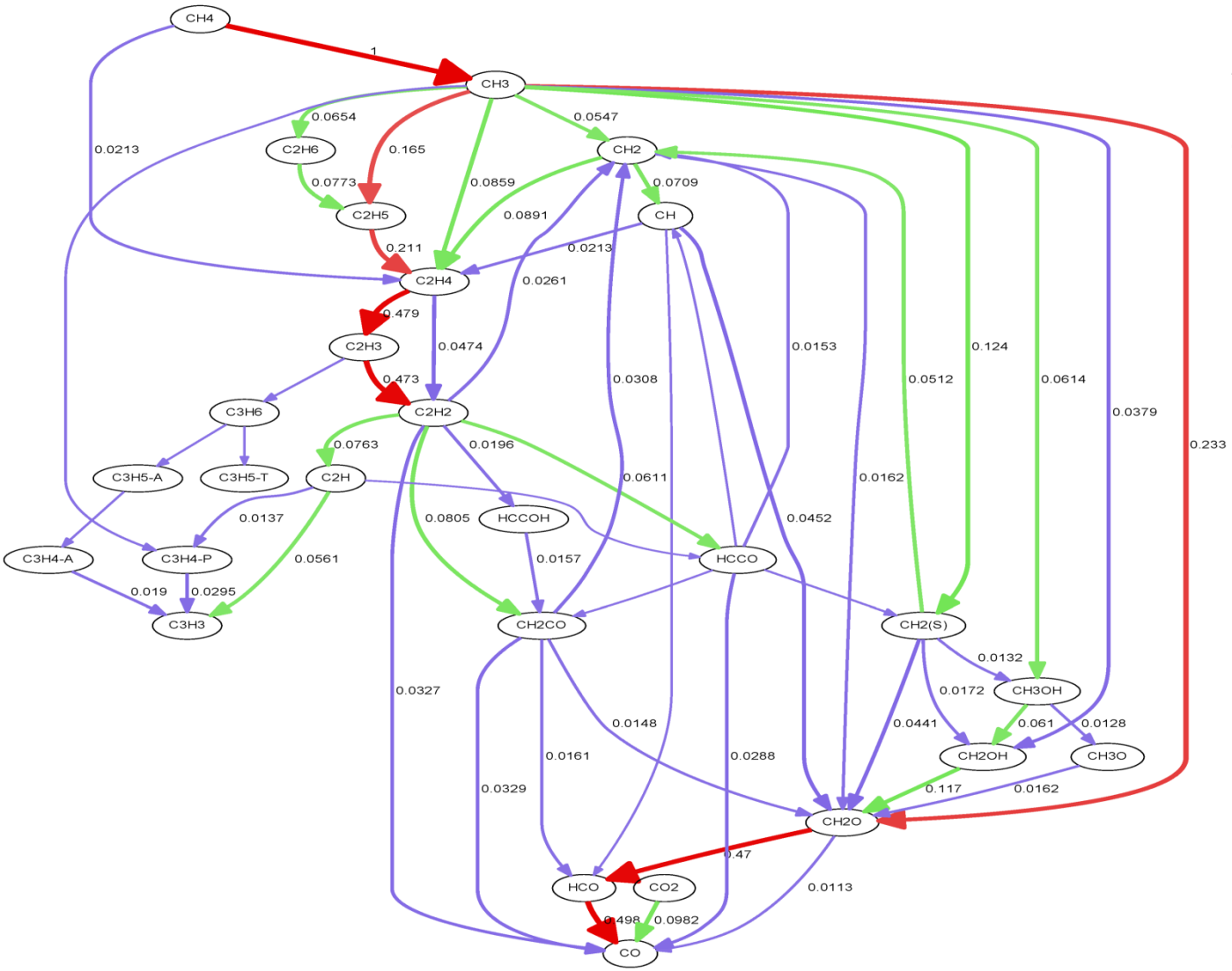
$CH_4 – CH_3 – C_2H_6 - C_2H_5 – C_2H_4 – C_2H_3 – HCO – CO – CO_2$

Reaction path analysis, counterflow diffusion flame

- **1D**
  - Include mixture average diffusion
  - Counterflow laminar non-premixed flame
  - Steady State Solution
  - T_{fuel} and $T_{oxidizer}$ = 300 K at inlet, p = 60 atm
  - CH_4:O_2=1:2 moles (Does not affect chemistry much)
  - Strain Rate = 10000 (1/s)
  - $\dot{m}_f$= 24 kg/s, $\dot{m}_o$= 82 kg/s, ROF = 3.4
  - Reaction path diagram at each grid point



Reaction path diagram, counterflow flame (max $\frac{dT}{dz}$, CH_4 side)



p = 60 atm, CH_4:O_2=1:2

Point of max change in T

T ≈ 2800 K

Major pathways:

- $CH_4 \rightarrow CH_3 \rightarrow C_2H_5 \rightarrow C_2H_4 \rightarrow C_2H_3 \rightarrow C_2H_2$
- $CH_4 \rightarrow CH_3 \rightarrow CH_2O \rightarrow HCO \rightarrow CO$

- Oxidizer side

$CO \rightarrow CO_2$

Results of reaction path analysis

- C4 and C3 species can be removed
- HCCO, C_2H, C, HCCOH, CH_2CHO, CH_2CO appears in very low flux and at narrow range of high T (2500K – 3000K), can be eliminate
- HCO_2, HCO_3, HCO_3H can also be eliminate
- Intermediate reduced mechanism - *ReduceRXN* : 26 species, 165 reactions

Sensitivity Analysis

- Sensitivity analyses for batch reactor and counterflow diffusion flame
- Identify important reactions at different conditions
- Determine how a change in the reaction rate will affect the simulation results
- Batch reactor :
  - Using Sensitivity module from CANTERA, solve for $S_i = \frac{r_i}{T}\frac{\partial T}{\partial r_i}$, where r_i is reactions rates
  - Temperature selected: 800 K, 2500 K
- Counterflow diffusion flame:
  - Perturbate each reaction rates, r_i for each reaction and determine the sensitivity coefficients $S_i = \frac{r_i}{C}\frac{\partial C}{\partial r_i}$ using finite difference for some criteria C
  - C selected: T_{max}, Q_{max}, max$\frac{\partial T}{\partial z}$($CH_4$ side), and max$\frac{\partial T}{\partial z}$($O_2$ side).

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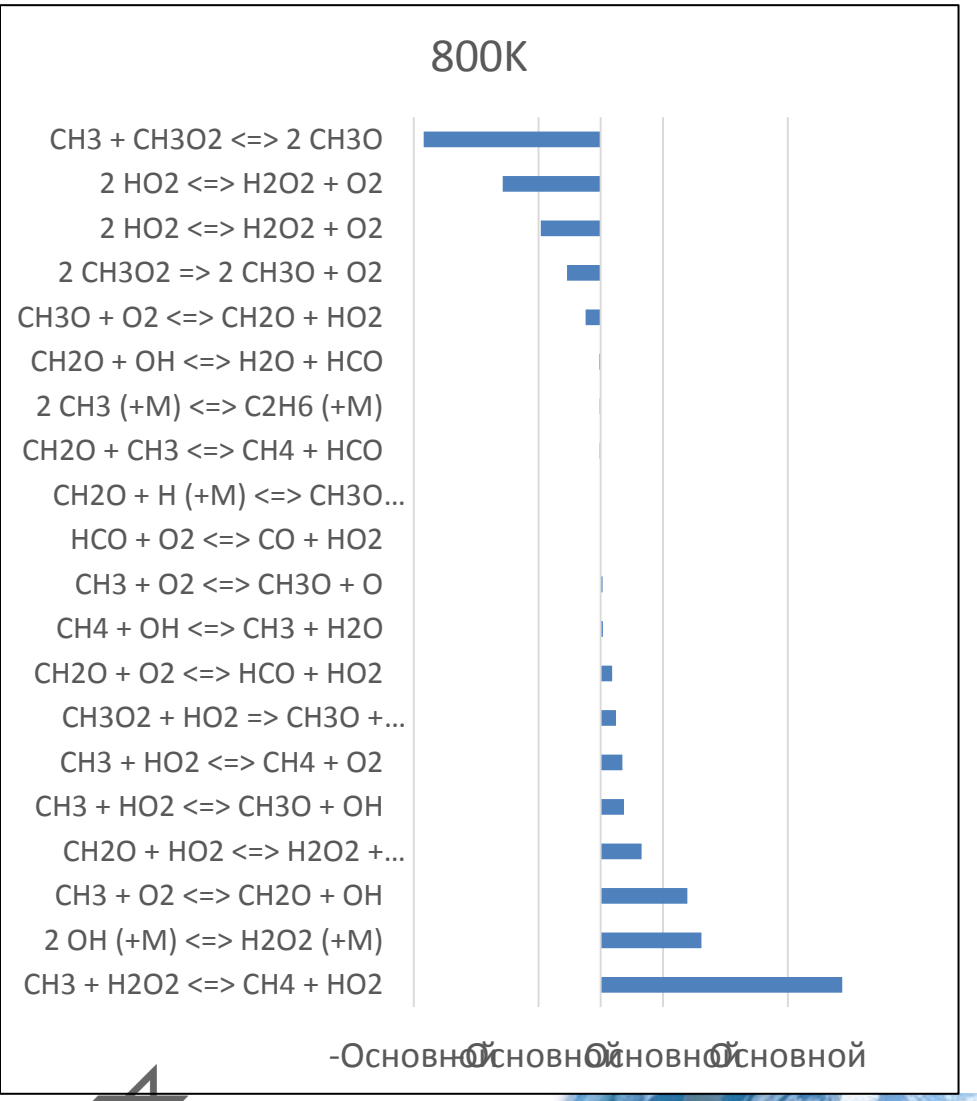
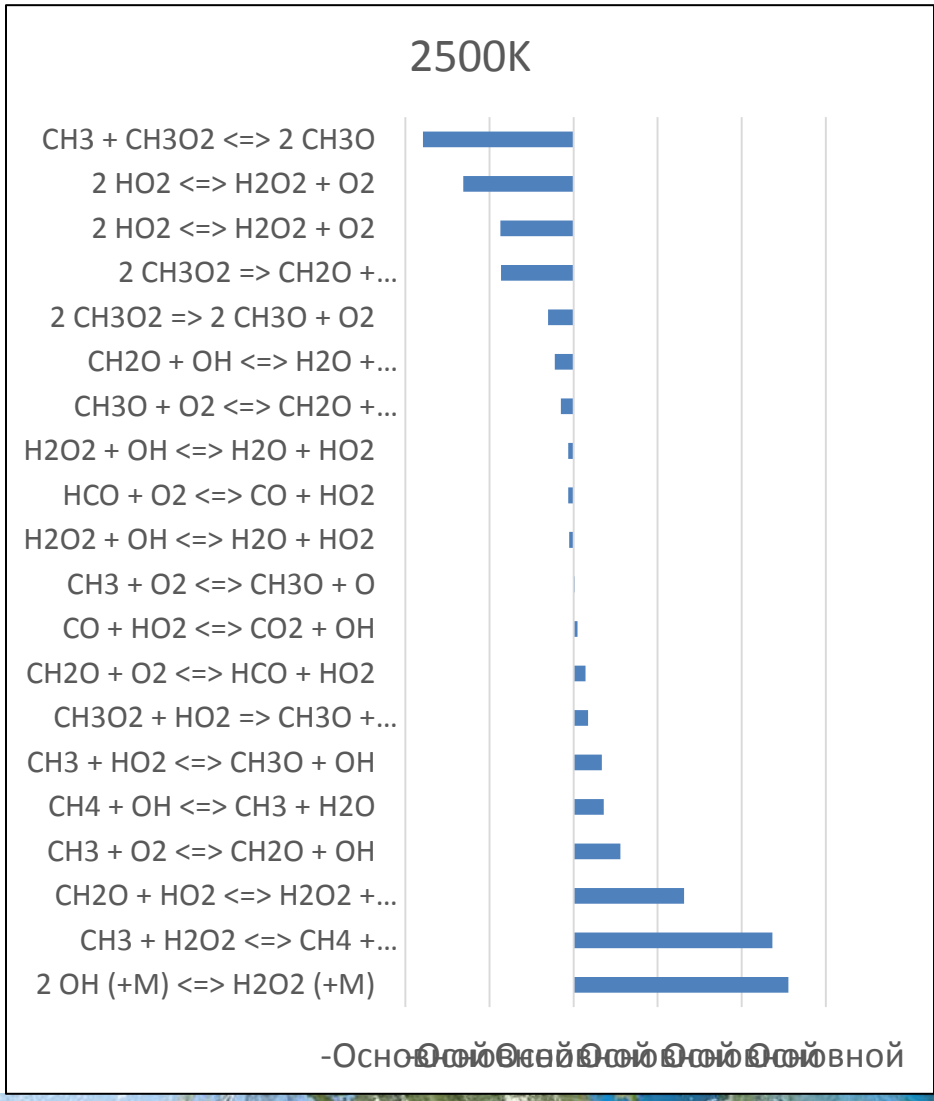
Sensitivity analysis, ignition in batch reactor





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Knowledge for Tomorrow

Summary of reduction method

- Reaction Path Analysis, Round 1
    - Remove C4, C3 chemistry and species that do not appear in any of the reaction path diagrams generated
    - Remove Species that have element net flux is <1% of max net flux in the diagram. Threshold for flux arrow generated is set at 0.5% of max flux for each diagram
    - Species remove C, C_2H, HCCO, CH_2CHO, CH_2CO, C_2H_5O, CH_3O_2H, CH_2OH and CH_3OH produces low net element flux (~0.7%)-> Remove
  - Resulting mechanism, *ReduceRXN*, after reaction path analysis is **26 species, 165 reactions**
- Sensitivity Analysis, Round 2
    - Sensitivity analyses for batch reactor and counterflow flame
    - C_2H_2, CH_2(s) and CH are in reactions with low sensitivity coefficients
    - Remove 3 species and 33 reactions with them
- Cut-and-try method, Round 3
    - Cut reactions with low sensitivity
    - Resulting mechanism, *ReduceSens*, **23 species, 49 reactions**

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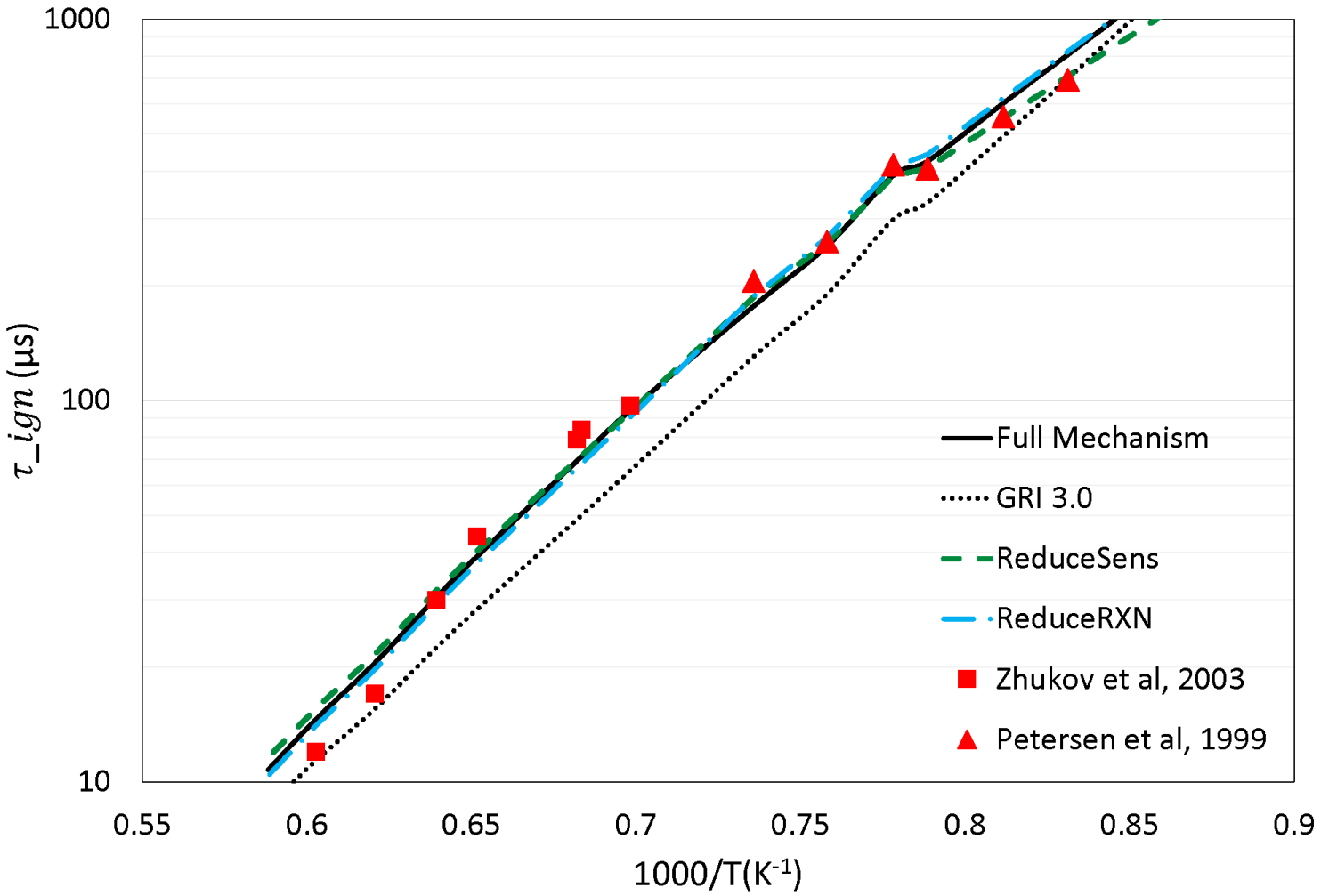
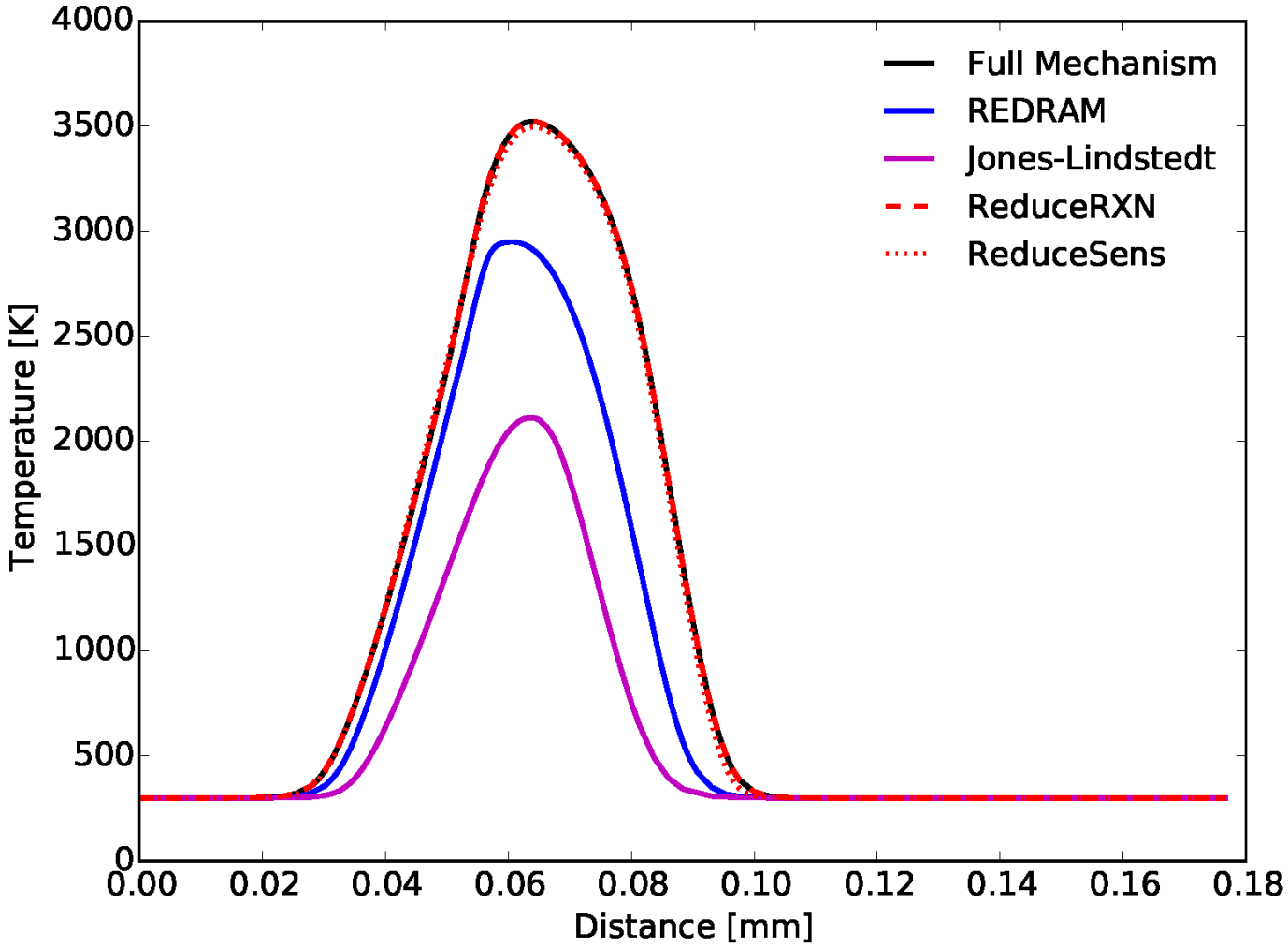
Validation, ignition delay time

CH_4/air, φ = 0.5, p = 50 atm



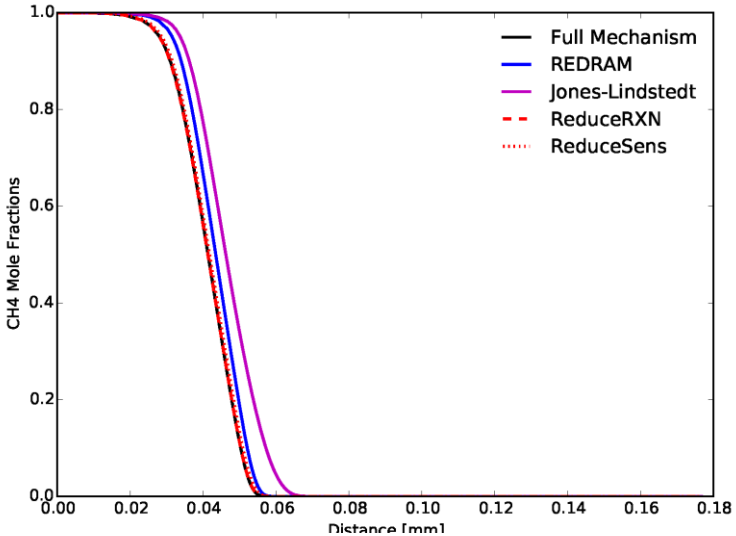
Verification, counterflow diffusion flame



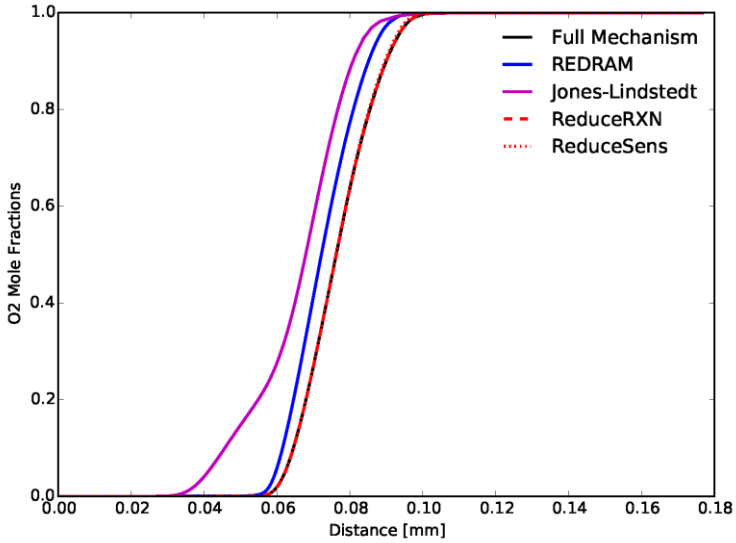
CH_4/O_2,
$\varphi = 0.1$,
$p = 60$ atm

Verification, mole fractions of products and reactants

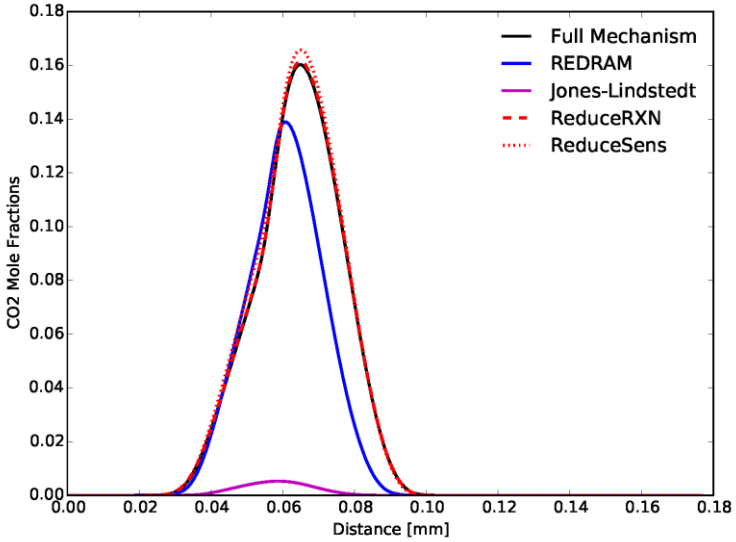
CH_4



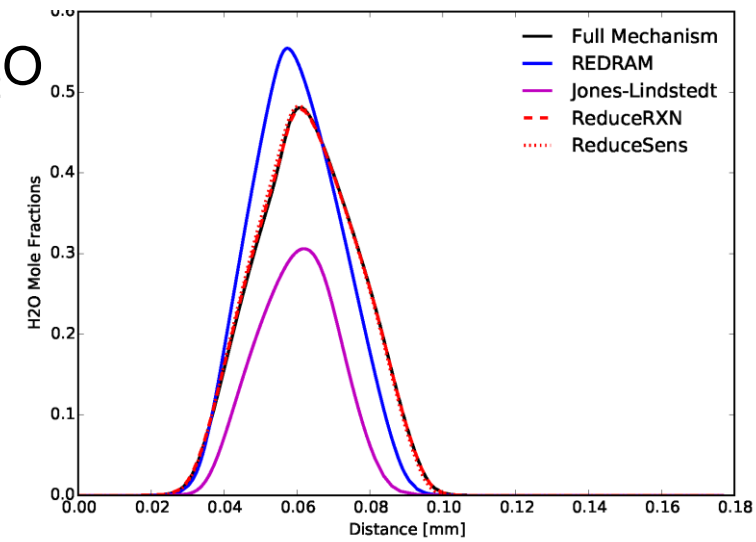
O_2



CO_2



H_2O



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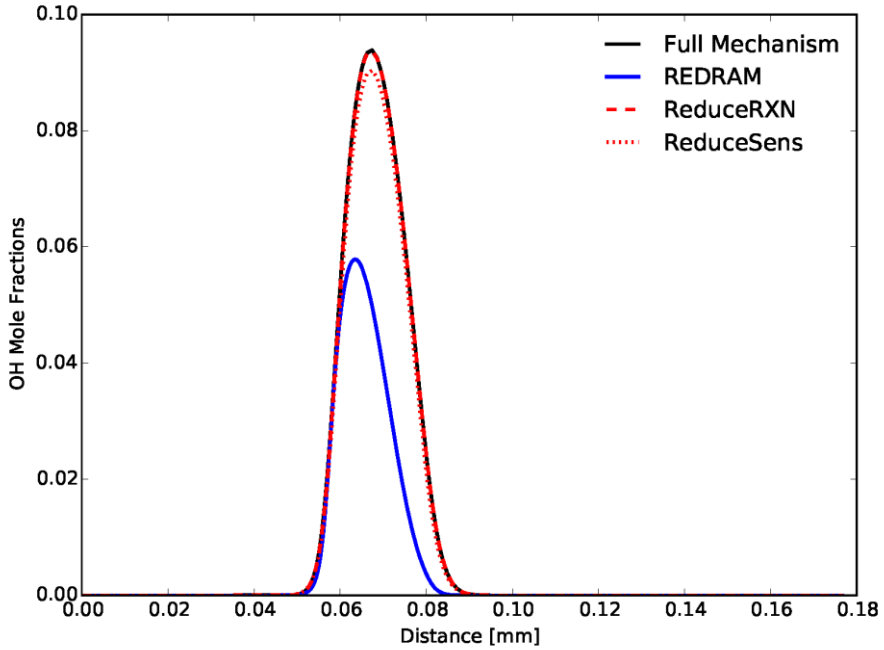
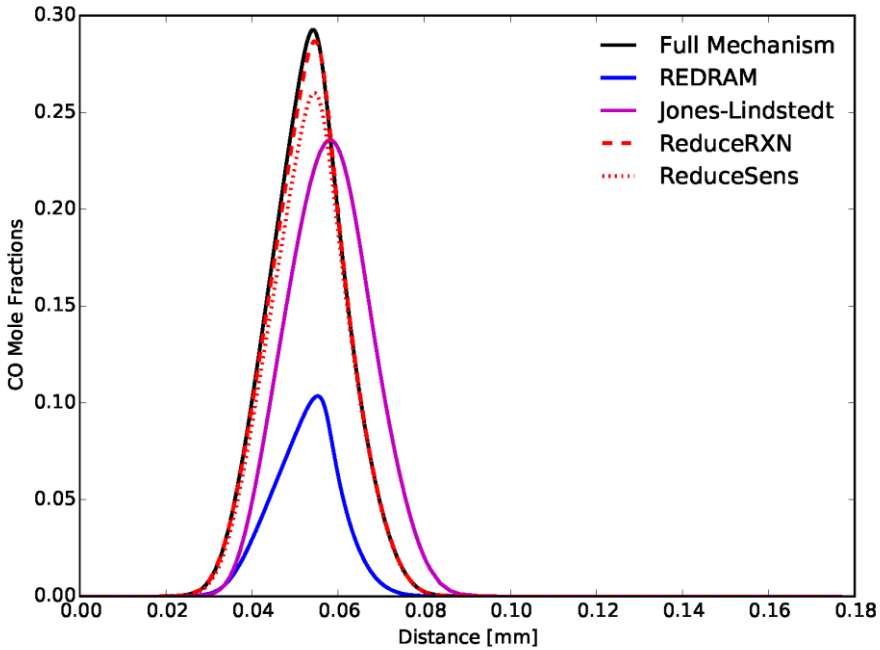
Verification, radicals OH and CO



OH

CO



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Conclusions and outlook

1. Skeletal methane mechanism has been developed for rocket engine applications.
2. The reduction technique based on reaction path and sensitivity analyses.
3. The mechanism consists of 23 species and 49 reactions.
4. The skeletal mechanism is 10–100 times faster
5. The working version is available by request at victor.zhukov@dlr.de
6. The further validation and testing will be performed.