Burning Velocities and a High Temperature Skeletal Kinetic Model for n-Decane

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Motivation

- Robust kinetic models are needed to predict the combustion process in engines

- Laminar Flame Speed

    - fundamental information on diffusivity, reactivity, and exothermicity

    - used for partial validation of kinetic models

- *n*-Decane:

    - chemical characteristic species for distillate-type fuels

    - good simple candidate for investigating fuel chemistry relevant to engine fuels

- Mechanistic complexity versus predictive robustness:

    - partially reduced skeletal mechanism (Zeppieri et. al 2000)

- The mechanism has been shown to successfully predict experimental data:

    - burner-stabilized flame, jet-stirred reactor, shock tube, atmospheric flow reactor data

n-Decane Laminar Flame Speeds
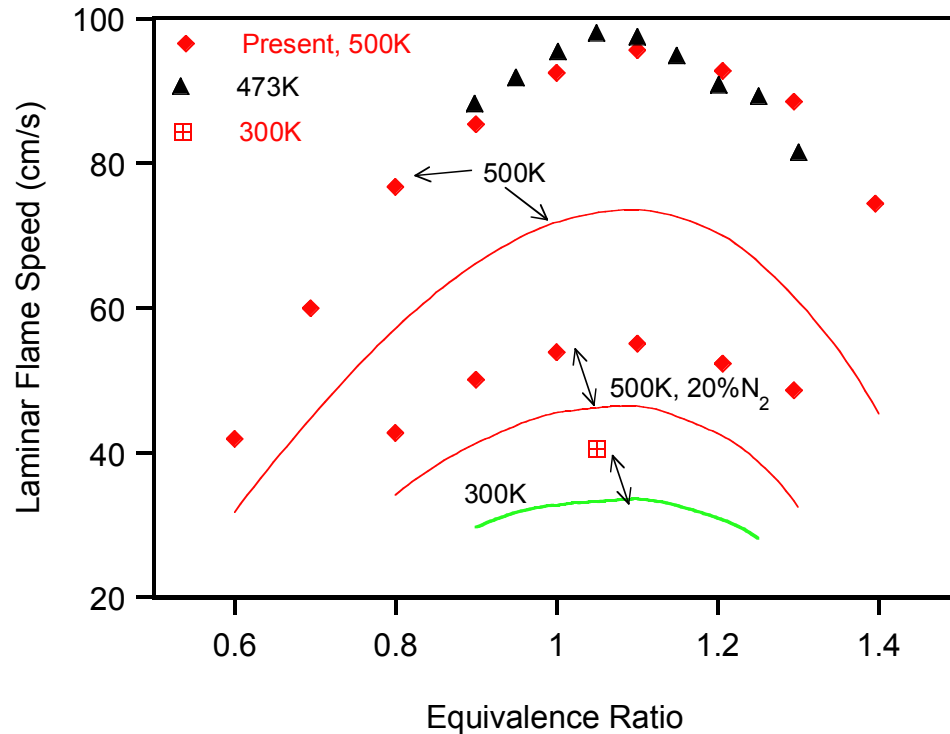
line: model prediction of Zeppieri et al. (2000)

473K: Skjøth-Rasmussen et al. (2003)

300K: Wagner & Dugger(1955)

- Laminar flame speed was experimentally determined by using PIV (Particle Image Velocimetry) on stagnation flame and linear extrapolation

- Present experimental data are consistent with the data of Wagner & Dugger (1955), by using their temperature correlation. The present data essentially overlap the data of Skjøth-Rasmussen et al. (2003) obtained at a lower initial temperature of 473 K

- Zeppieri et al. model significantly underpredicts experimental data

n-Decane Skeletal Reduced Kinetic Model

Since the development of the original Zeppieri et al. model, significant advances in fundamentals (mechanistic issues, thermochemical and kinetic parameters) have occurred particularly for H_2/O_2 and C_1-C_3 kinetics. As a result, we investigated and updated the small molecule and radical kinetics and thermochemistry utilized in the Zeppieri et al. model to evaluate recent updates on the predicted laminar flame speeds

- Primary route for fuel consumption is H-atom abstraction

- N-alkyl (C5-C10) radicals are in partial equilibrium, and react through H-abstraction, decomposition, and C-C bond β-scission (Zeppieri et al. 2000)

- C1-C3, from Qin et al. (2000)

  - $aC_3H_5 + HO_2 \rightarrow OH + C_2H_3 + CH_2O$ replaced by

    - $aC_3H_5 + HO_2 = OH + C_3H_5O$ (R$_1$)

    - $C_3H_5O = C_2H_3CHO + H$ (R$_3$)

    - $C_3H_5O = C_2H_3 + CH_2O$ (R$_2$)

  - $CH_3 + X$ reactions by Scire et al. (2001)

- H_2/O_2 submechnism from Li et al. (2004)

- ❖ The complete mechanism used in this study may be obtained electronically by contacting the corresponding author

n-Decane Laminar Flame Speeds
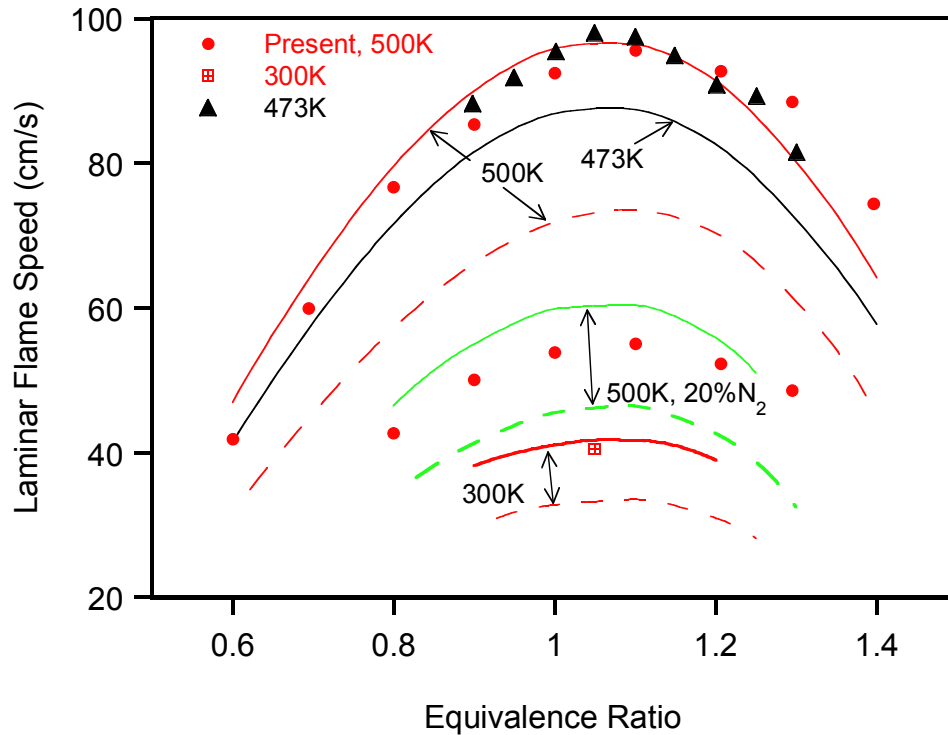
line: model predictions (dashed line-Zeppieri et al. (2000), solid line - present *n*-decane model)
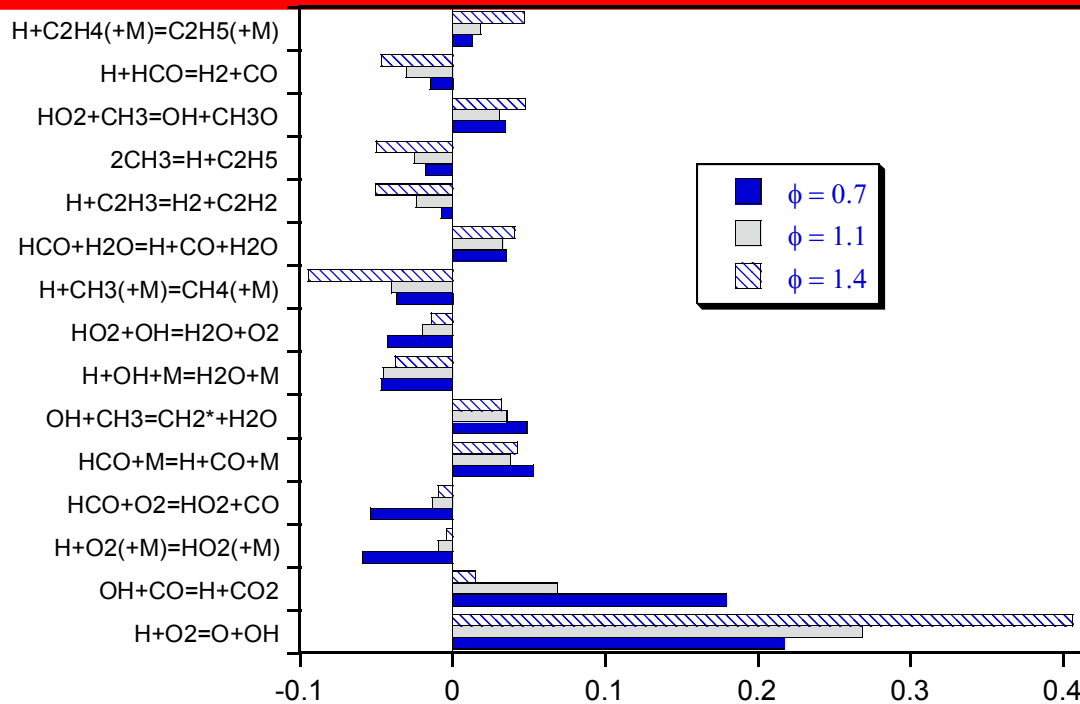
473K: Skjøth-Rasmussen et al. (2003)

300K: Wagner & Dugger(1955)

- Present model well predicts the laminar flame speed at 500 K and 300 K against the present data and the data of Wagner & Dugger(1955)
- Skjøth-Rasmussen et al. data are significantly higher than the present model predictions

# Sensitivity of n-C₁₀H₂₂ Flame Speeds

— Normalized sensitivity coefficients of *n*-decane flame speeds at 500 K for the present kinetic model

• Exhibits features typically observed previously and well documented for flames of small (e.g., see Qin et al., 2000; Smith, et al., 1999) as well as larger molecular weight (e.g., see Held et al., 1997) alkanes

• The sensitivity spectrum is dominated by
  — Main chain branching reaction, $H + O_2 = OH + O$,
  — CO oxidation, $CO + OH = CO_2 + H$,
  — Reactions of formyl radical, particularly $HCO + M = CO + H + M$ and $HCO + O_2 = CO + HO_2$
  — Several C_2 and C_3 reactions
• No significant contribution from reactions involving the fuel itself or species larger than C_4
• Lack of utility of using flame speed values to validate large molecule (and high molecular weight fragments) kinetic chemistry
• Inadequacy in predicting flame speeds of large carbon number fuels is related to the inadequacies of the small species kinetics
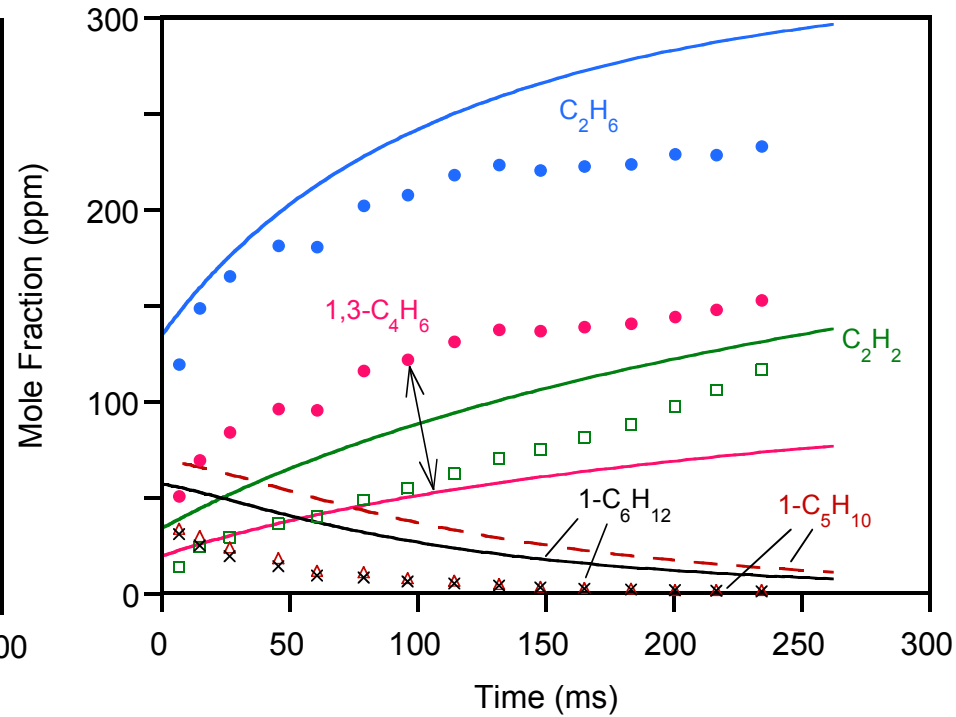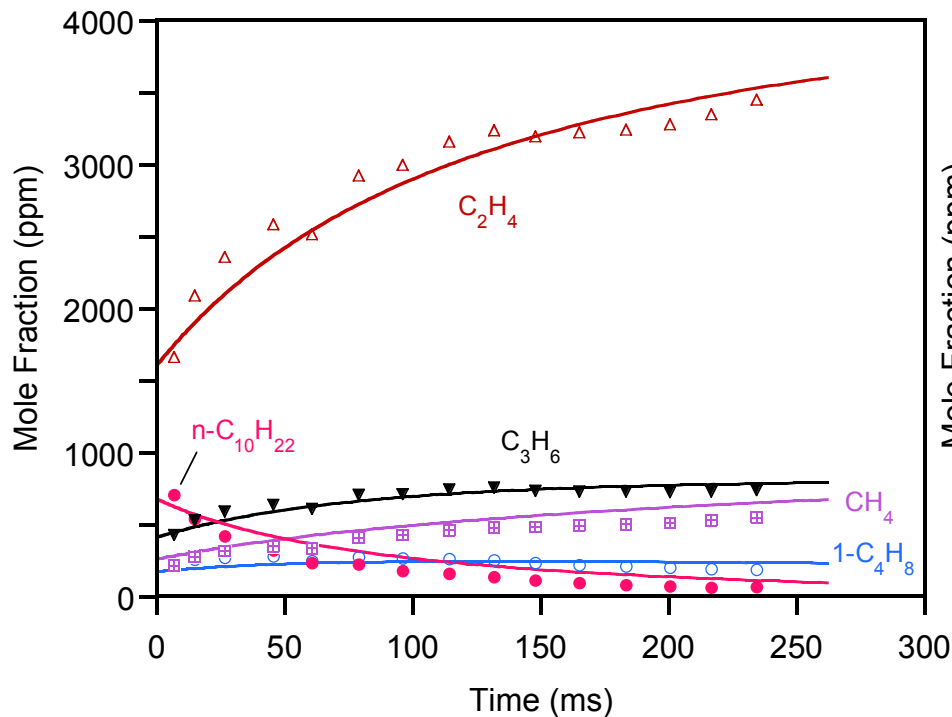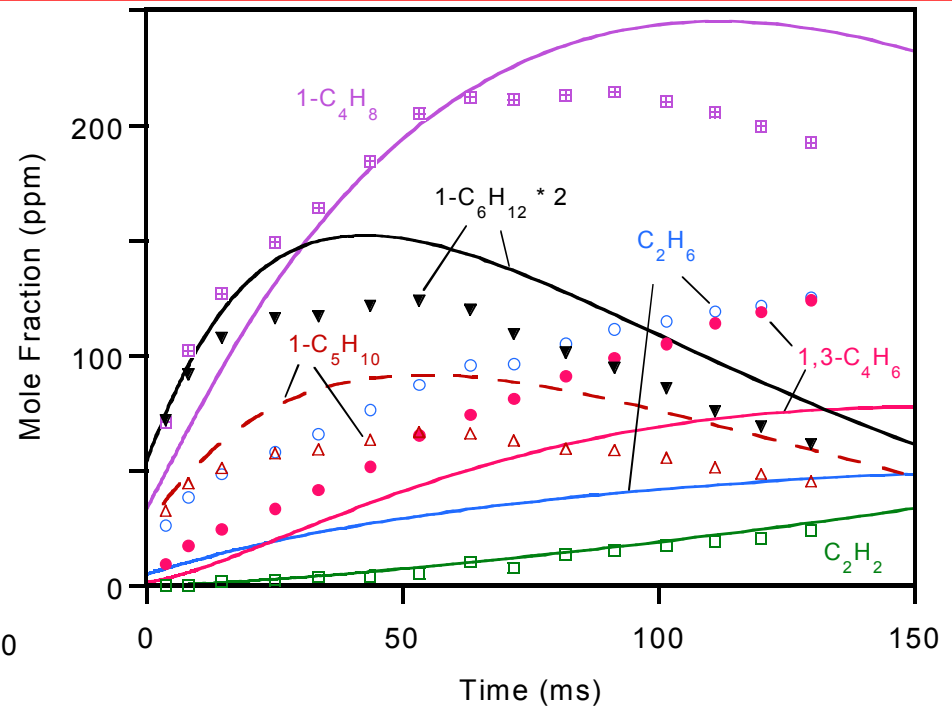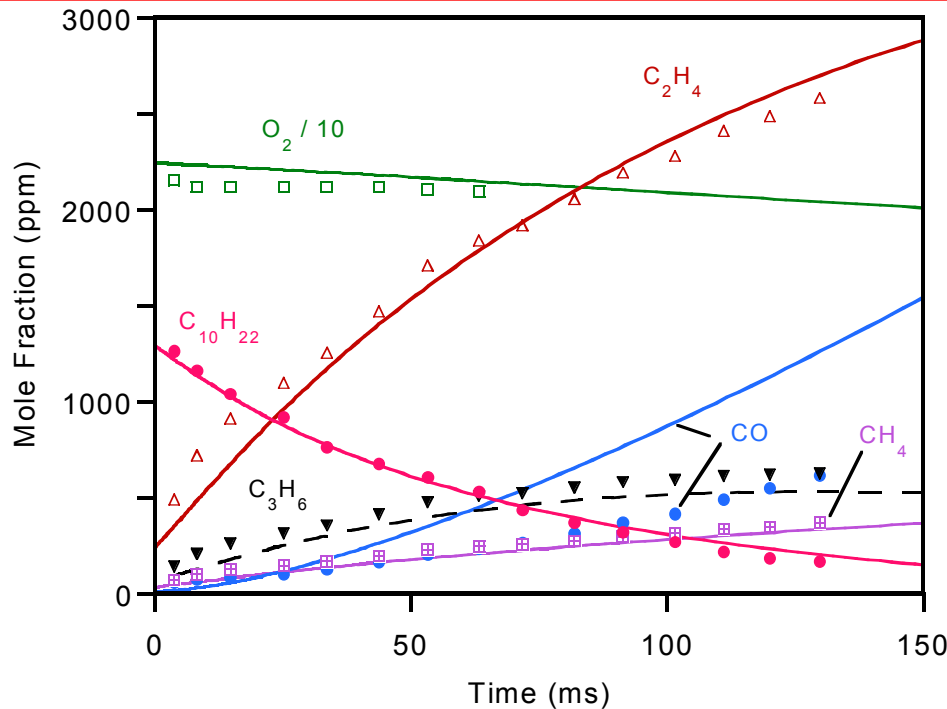
- *n*-decane pyrolysis, P = 1 atm, T_i = 1060 K, initial *n*-decane concentration 1456 ppm in N_2
  - Symbols: experimental (Zeppieri et al., 2000)
    Lines: Model predictions (shifted by 46 ms)
- The agreement is essentially of similar quality as that achieved with the Zeppieri et al. model for major species and intermediates (e.g., n-decane, ethane, ethene, methane, and propene)
- Trace intermediates (e.g., 1,3-butadiene, pentene) remains less satisfactory

- n-decane oxidation, P = 1 atm, T_i = 1019 K, $\phi \approx 1.0$, initial n-decane concentration 1452 ppm in N_2
  - Symbols: experimental (Zeppieri et al., 2000)
    Lines: Model prediction (shifted by 11.6 ms)
- Good agreement similarly as of the Zeppieri et al. model
- Disparities still remaining for CO and 1,3-butadiene
- The sensitivity analysis suggest the need for further model refinement for reactions involving both pentene and 1,3-butadiene, such as $C_5H_{10} + OH = H_2O + C_4H_6 + CH_3$, as well as in the sub-mechanism at the C_3 level
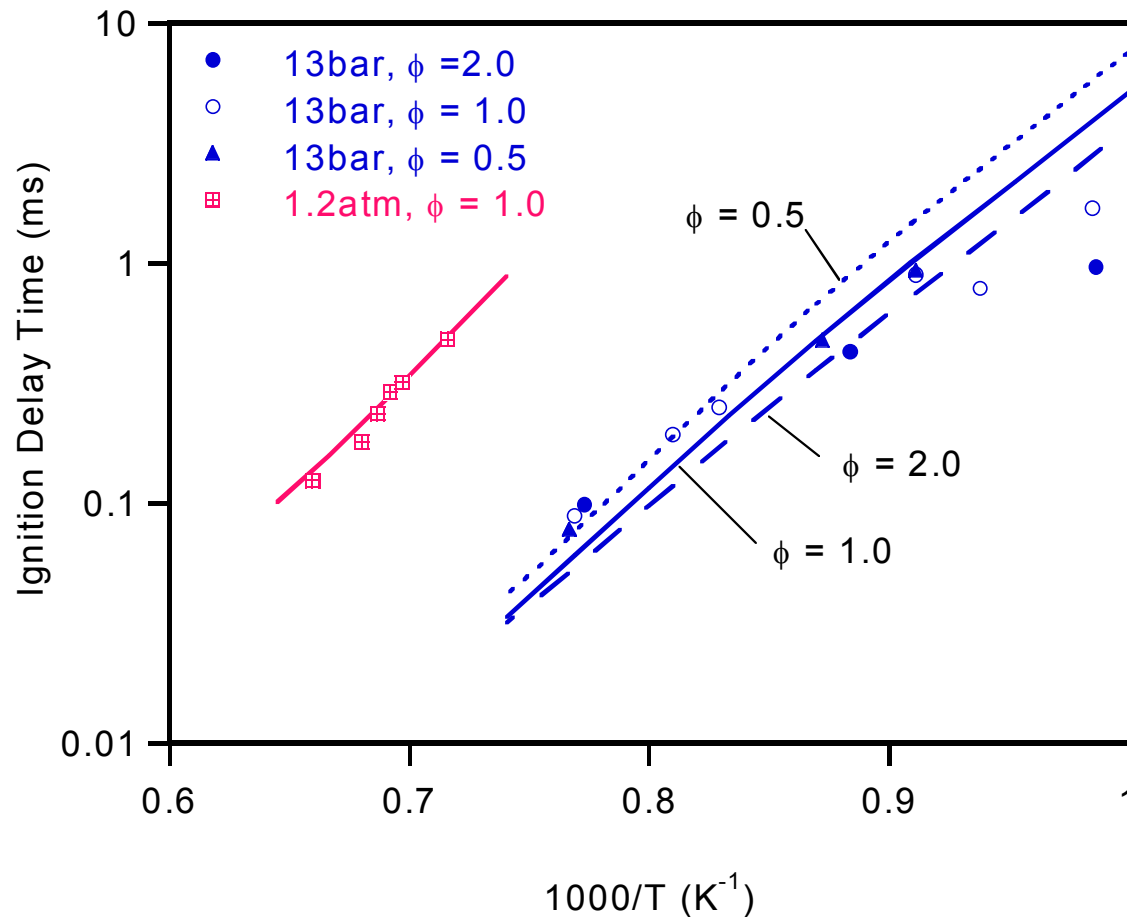
Burner Stabilized Flame
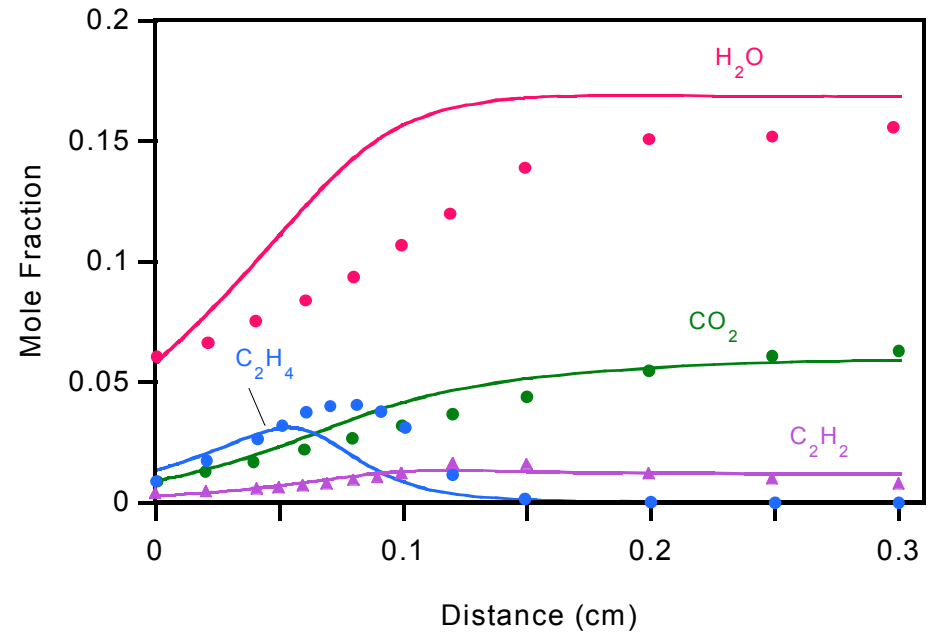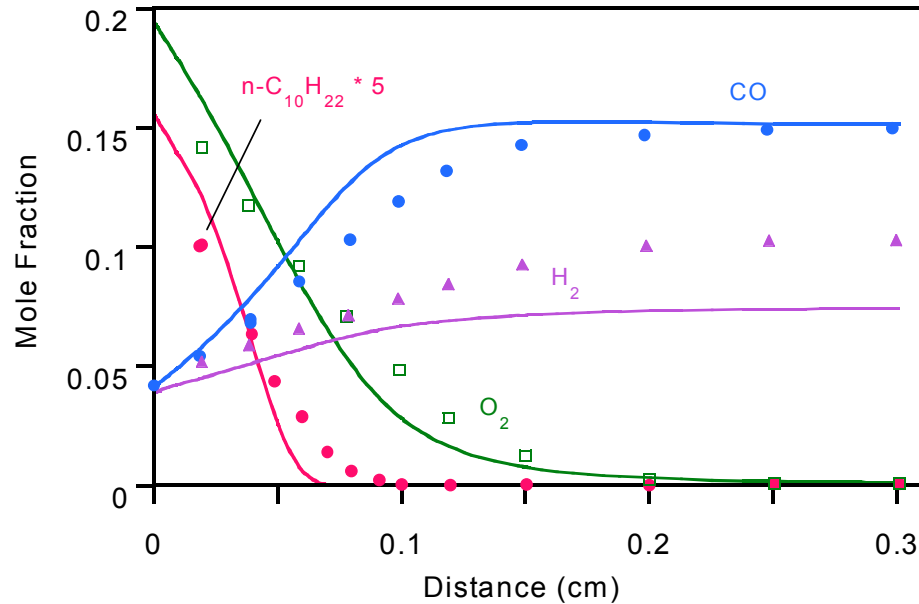
- *n*-decane-O_2-N_2 at P = 1 atm, ϕ = 1.7
  - — Symbols: experimental (Doute et al. 1995)
  - — Lines: model predictions
- The model reproduces very well the observed fuel/O_2 decay and the major species evolution (e.g., H_2O, CO_2, C_3H_6)
- Some slight discrepancies for minor species such as CO and 1,3-butadiene

Comparison with Ignition Delay Time Data

- The predicted ignition delays are in excellent agreement with 1.2 atm, high temperature cases (Horning et al., 2002)
- Comparisons with the high pressure ignition delay data (Pfahl et al., 1996) are also very good at high temperatures, but discrepancies become substantial below 1100 K.
- This disagreement is expected since the high temperature mechanism utilized here does not include radical-oxygen addition reactions characteristic of low and intermediate temperature oxidation of large carbon number species

— Symbols: experimental data, 0.2% *n*-decane-O_2-Ar (Horning et al. 2002) and *n*-decane/air (Pfahl et al. 1996)
— Lines: model prediction

Comparison with Jet-Stirred Reactor Data
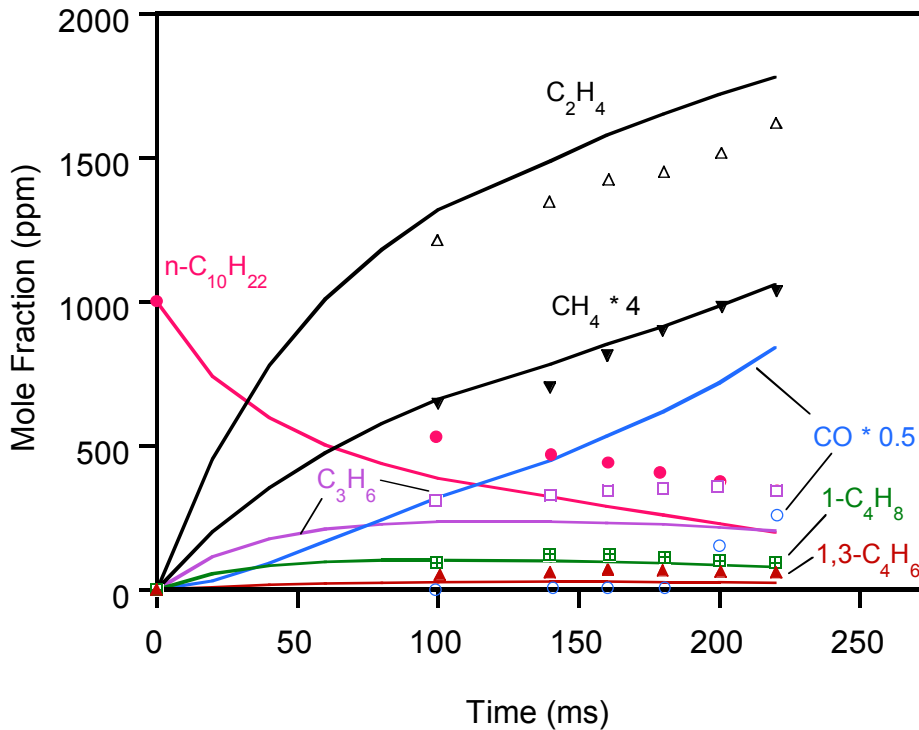
- The comparison of model prediction against the published jet-stirred reactor data (Bales-Gueret et al. 1992) performed over temperature range of 920-1030 K, at a fixed pressure of 1 atm
- Similar level of agreement as that of Zeppieri et al. and an automatically generated decane mechanism (Battin-Leclerc et al., 2000) with much more species and reactions

— Symbols: experimental data (Bales-Gueret et al., 1992), $P = 1$ atm, $T = 1030$ K, $\Phi = 1.0$, n-decane = 1000 ppm.
— Lines: model prediction

Conclusion

- Laminar flame speeds for n-decane/air mixtures at atmospheric pressure and initial temperature of 500 K were determined on a stagnation flame burner using PIV

- Predictions of the experimental data with the partially reduced skeletal mechanism for n-decane pyrolysis and oxidation of Zeppieri et al. (2000a) were found to be in poor agreement. The analyses of these results further support that laminar flame speed data for large carbon number alkanes primarily constrains the kinetic sub-mechanisms for hydrogen/carbon monoxide oxidation and small carbon containing species with carbon number generally less than 3

- Revision of the Zeppieri et al. model by updating the hydrogen/oxygen and small carbon number C_1-C_3 sub mechanisms results in acceptable prediction of the experimental results

- Predictions using the revised model were found to reproduce data used in validating the original model in (Zeppieri et al., 2000a) including high temperature, atmospheric pressure flow reactor pyrolysis and oxidation, high pressure shock tube ignition delay, and stirred reactor species measurements. The revised model predictions also agrees well with atmospheric pressure, burner stabilized flame data and recently published shock tube ignition delay measurements at both low and high pressure

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