COMPUTATIONALLY EFFICIENT MODELING OF HYDROCARBON OXIDATION CHEMISTRY AND FLAMES USING CONSTITUENTS AND SPECIES

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Outline

- Background

- Concept description for chemical kinetics in a constant-volume perfectly stirred reactor

- Fuel pyrolysis in the presence of nitrogen (non-premixed flames)

- Flame model
  - Premixed
  - Non-premixed

- Results

- Summary and conclusions

- Future work

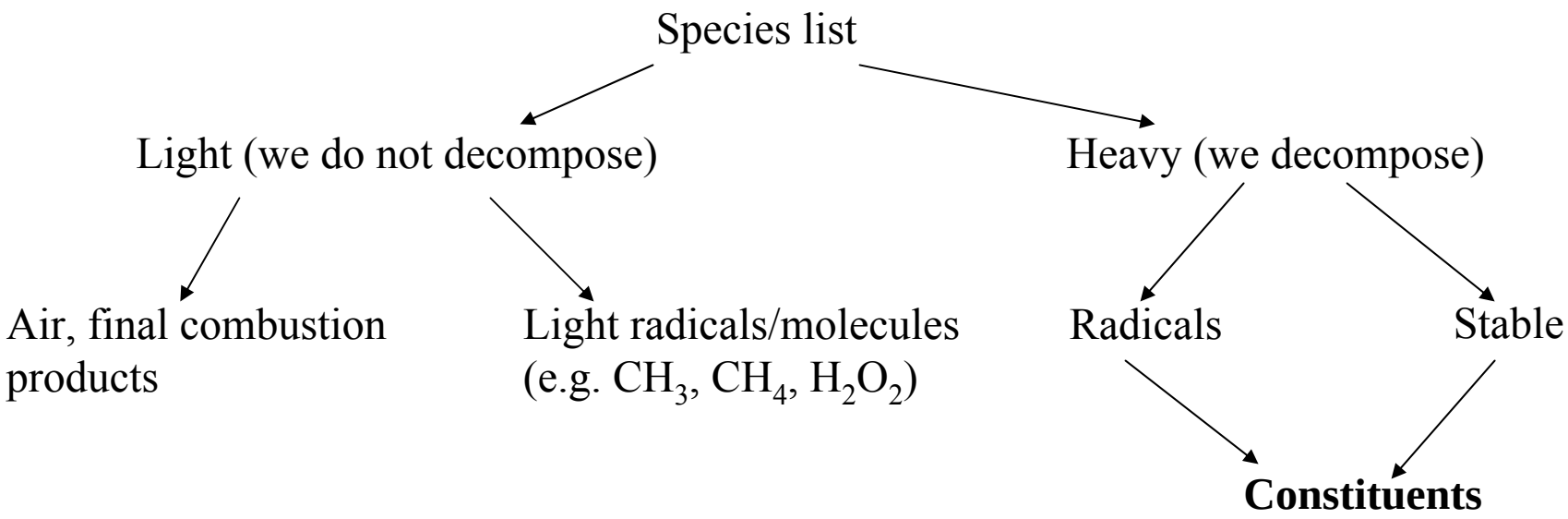
Background

- Necessity to reduce the computational cost of chemistry in simulations of turbulent combustion

- None of the existing chemistry reduction schemes is considered the ultimate solution to the problem of chemical kinetic reduction

- Novel methods of reduction are still sought

Chemical kinetics: The concept of a base



For general alkane or alkene with air:

The base = Light species + Constituents
(26) (13)

Remove NOx, C, C2, and N at this preliminary stage, and then,

The base = Light species + Constituents + N_2
(20) (13) (null rates)

Kinetic model summary, 1 of 2

- *n*-heptane: 13 constituents, CH2, CH3, CH, C2H3, C2H2, C2, HC2, CO (keto), HCO, HO, HO2, OO, O

$$N_c \equiv \sum_{k=1}^{13} N_k$$

- iso-octane, PRF fuels, mixtures of iso-octane and *n*-pentane or iso-hexane: 14 constituents (C atom added)

$$N_c \equiv \sum_{k=1}^{14} N_k$$

- other aspects of the model

$$N^* \equiv \frac{N_{n2}}{N_{ref}}$$

$$\theta \equiv \frac{T - T_0}{T_r(\phi, N^*)}$$

$$T_r \equiv 2065 (N^*)^{0.06} w(\phi)$$

$$w(\phi) = \phi \frac{1.5 + 1.31\phi}{1 + 0.71\phi + 1.1\phi^2}$$

Kinetic model summary, 2 of 2

$$\mathcal{R}_i \equiv \left(\frac{dN_i}{dt}\right)_{reac} = \left.\frac{dN_i}{dt}\right|_{heavies} + \left.\frac{dN_i}{dt}\right|_{lights}$$

$$\left.\frac{dN_i}{dt}\right|_{heavies} = N_c(KG_i - X_i KL_i)$$

$$\left(N_c C_{p,h} + \sum_{i \in lights} C_{p,i} N_i\right)\frac{dT}{dt} = -\sum_{i \in lights} h_i \mathcal{R}_i + N_c(R_u T_{ref})K_h$$

$$C_{p,h} \equiv \frac{\left(\sum_{l \in heavies} C_{p,l} N_l\right)}{N_c}$$

$$K_h \equiv -\left(\sum_{l \in heavies} h_l \mathcal{R}_l\right)\frac{1}{R_u T_{ref} N_c}$$

Findings from the kinetic model

1. N_c exhibits a self-similarity with respect to θ, modulo T_0 (600-1200 K), for a wide range of p_0 (5-50 bar) and ϕ (1/4 to 4)

2. In the cold ignition regime (600-900 K), the self-similarity is independent of T_0

3. The molar densities of O2 and H2O exhibit a quasi-linear behavior versus θ

4. Eleven species progress variables: the unsteady light species

5. The capability of the model was assessed from the viewpoints of predicting species, the temperature evolution and the ignition time.

- The species prediction was excellent in all cases, with the exception of the multivalued regions occurring for very rich situations.
- The temperature values were excellently to very well predicted, except for the temperature decrease from the maximum observed for rich mixtures.
- The ignition times were reproduced within percentages of those computed with the full mechanism.

6. The above evaluation was valid for all single fuels and mixtures considered.

Fuel pyrolysis in counterflow diffusion flames

Non-premixed model

- air jet counterflow to fuel/nitrogen jet
- need estimate of fuel pyrolysis before mixing with air occurs
- calculations performed using LLNL rates with Chemkin II

Results

- rates minimal for $T \leq 900$ K (≤ 1 s^{-1})
- only 3 light species (H2, CH4, C2H4) are produced having mole fractions as large as $O(10^{-2})$; all other mole fractions are much smaller
- a single rate form describes the rates of these species

$$\dot{N}_i = N_c \times K_i, \quad K_i = a_i \times 10^{12} (\phi')^{0.37} \times \exp(-T_p/T)$$

- $T_p = 2.9 \times 10^4$ K is the characteristic pyrolysis temperature
- ϕ' is an effective equivalence ratio (air replaced by N2)
- $a_{H2,CH4} \doteq 0.35 + 4.25\, w_{oct} - 2.7\, (w_{oct})^2 \quad 0 \leq w_{oct} \leq 1$ is the octane fraction in the PRF
- $a_{C2H4} \doteq 0.78 + 3.9\, w_{oct} - 4.6\, (w_{oct})^2$

Interpolation procedure for the rate functions

The reduced rate functions have the general form

$$K = f(\theta, \phi_m, T_m), \quad \theta = (T - T_m)/T_r, \quad T_r = T_r(\phi_m, N_{N2})$$

where T_m and ϕ_m are the temperature and ϕ at the initial fuel/air mixing; K is in s^{-1}.

-Tables are generated numerically at fixed ϕ_m and T_m.
-The K rates are found by numerical interpolation. Detailed comparisons with the LLNL rates shows that this local interpolation is accurate using

$$K = K_f(\theta) \times \phi_m^s \times \exp(-T_*/T)$$

where s and T_* are interpolation parameters.
e.g.: $s = (\ln K_2 - \ln K_1)/(\ln \phi_{m2} - \ln \phi_{m1})$

Flame model, 1 of 3

continuity $$\rho v = r\frac{\dot{M}}{\pi R^3}\frac{dR}{dx}$$

momentum A. $$\xi \doteq 1-(1-\xi_L)\left[\int_0^x \left(\frac{\rho}{\rho_0}\right)_{x\neq x_a} dx\right] \Big/ \left[\int_0^L \left(\frac{\rho}{\rho_0}\right)_{x\neq x_a} dx\right] \qquad \xi(x) \equiv R_0/R(x)$$

B. $$\xi^2 = 1 - k\int_0^x \zeta(x')\frac{\rho(x')}{\rho_0}x'dx'$$

k determined by BCs; ζ=1 outside the flame; ζ is a cst, model parameter inside the flame chosen to minimize the residue to the momentum eqn.

species $$J_i = J_{i,light} + J_{i,heavy}$$

$$J_{i,light} = -n\left(X_i D_{T,i}\frac{d\ln T}{dx} + \sum_j \mathcal{D}_{ij}\frac{dX_j}{dx}\right)$$ i, j ∈ ensemble L

$$J_{i,heavy} = -n\sum_l \mathcal{D}_{il}\frac{dX_l}{dx} \equiv J_{H,i}$$ l ∈ ensemble H

$$J_{H,i} \doteq -n\mathcal{D}_{H,i}\frac{d\ln C_{ave}}{dx}$$

$$\mathcal{D}_{H,i} \equiv \frac{1}{n}\sum_l \mathcal{D}_{il}N_l = \sum_l \mathcal{D}_{il}X_l = X_H\mathcal{D}_{iH}$$

$$C_{ave} \equiv \frac{N_c}{n} = \sum_{k,l} C_{kl}X_l$$ k ∈ ensemble C

Flame model, 2 of 3

species

$$J_i = -n\left[\sum_j \mathcal{D}_{ij}\frac{dX_j}{dx} + X_H\mathcal{D}_{iH}\frac{d\ln C_{ave}}{dx} + X_i D_{T,i}\frac{d\ln T}{dx}\right]$$

i and j to the unsteady light species and q to the quasi-steady light species

$$X_u = 1 - X_H - \sum_q X_q \qquad m = \frac{X_u}{\sum_i \frac{Y_i}{m_i}}$$

$$\mathcal{D}_i^a \equiv \frac{1}{X_u}\sum_j \mathcal{D}_{ij}X_j.$$

$$J_i = -n\left[\sum_j (\mathcal{D}_{ij} - \mathcal{D}_i^a)\frac{m}{m_j}\frac{dY_j}{dx} + B_{T,i}^e\frac{dT}{dx}\right]$$

$$B_{T,i}^e \equiv X_i\frac{D_{T,i}}{T} + \sum_q (\mathcal{D}_{iq} - \mathcal{D}_i^a)\frac{\delta X_q}{\delta T} + X_H\mathcal{D}_{iH}\frac{\delta\ln C_{ave}}{\delta T} - \mathcal{D}_i^a\frac{\delta X_H}{\delta T}$$

$$\frac{dY_i}{dx} = \frac{A}{\dot{M}}m_i\mathcal{R}_i - \frac{d}{dx}\left(\frac{A}{\dot{M}}m_i J_i\right)$$

$$\mathcal{R}_i = \mathcal{R}_i|_{lights} + \mathcal{R}_i|_{heavies} \qquad \mathcal{R}_i|_{heavies} = N_c K_{net,i}$$

Flame model, 3 of 3

energy

$$q \doteq -\lambda \frac{dT}{dx} - \sum_i \left(\frac{m_i}{m_H} h_H - h_i\right) J_i \qquad h_H = (1/X_H) \sum_l X_l h_l$$

$$\frac{C_p}{m}\frac{dT}{dx} = \frac{d}{dx}\left(\frac{A}{\dot{M}}\lambda\frac{dT}{dx}\right) - \frac{A}{\dot{M}}\left\{\frac{dT}{dx}\left[\sum_i\left(\frac{C_{p,i}}{m_i} - \frac{C_{p,H}}{m_H}\right)(m_i J_i)\right] + \sum_i h_i \mathcal{R}_i - R_u T_{ref} N_c K_H\right\}$$

equation of state

$$p = \frac{R_u T}{(v_{PR} - b_{mix})} - \frac{a_{mix}}{(v_{PR}^2 + 2b_{mix} v_{PR} - b_{mix}^2)}$$

$$a_{mix} = \sum_p \sum_n X_p X_n a_{pn}(T) \qquad b_{mix} = \sum_p X_p b_p$$

$$a_{pn} = (1 - k')\sqrt{\alpha_{pp}\alpha_{nn}} \qquad b_p = 0.077796 \frac{R_u T_{C,p}}{p_{C,p}}$$

$$\alpha_{pp}(T) \equiv 0.457236 (R_u T_{C,p})^2 \left[1 + c_p\left(1 - \sqrt{T_{red,p}}\right)\right]^2 / p_{C,p}$$

$$c_p = 0.37464 + 1.54226\Omega_p - 0.26992\Omega_p^2$$

Computation of T_m and ϕ_m for non-premixed flames

• The original reduced rate model is based on premixed flow situations where the initial temperature and ϕ correspond to the fuel/air being completely mixed.

• For non-premixed situations, mixing occurs continuously through diffusion along fluid paths: the temperature and at ϕ which mixing occurs vary according to location.

• An assumption is made that mixing occurs continuously (no 'puffs') along the fluid path. This is valid for many, if not most, situations.

• Based on this view, the local mean 'mixing temperature and ϕ' are estimated through

$$T_m = (T + T_0)/2 \qquad Lean: \ \phi_m = \phi/2; \quad Rich: \ \phi_m = 2\phi$$

where T_0 is the temperature at the first location where either there is non-negligible fuel in the air or non negligible air in the fuel. T_0 is a constant for either side of the flow.

• At the location having temperature T the rates correspond to those computed from the tables using the local values of ϕ_m, θ computed using T_m and ϕ_m, and T_m.

Transport coefficients

- Mass diffusion
  - need the full matrix of pairwise diffusion coefficients
  - base the pairwise diffusion coefficients on binary diffusion coefficient models (Harstad & Bellan 2004a) and all-pressure mixing rules (Harstad & Bellan 2004b)
- Thermal conductivity for the mixture
  - model from Reid et al.
- Thermal diffusion ratios
  - based on the all-pressure model of Harstad & Bellan 2004b
- Inviscid fluid:
  - in principle the viscosity is not needed
  - in fact it is needed for the modeling of the thermal conductivity

Premixed and diffusion flames

- Premixed flames
  - Version A of momentum equation, large Pé (valid outside but not throughout the flame); study the influence of diffusion for constant area flow
  - Version B of momentum equation, general Pé values (needed to compute through the flame peak)

- Counterflow diffusion flame
  - Version B of momentum equation, general Pé values

Premixed flames, large Pé

- Defined two parameters

$$\varepsilon_i \equiv -m_i J_i/(\rho u)_0$$

$$\varepsilon_i' \equiv -\varepsilon_i/Y_i = \rho u_{D,i}/(\rho u)_0$$

- Based on a large Péclet number approach, i.e. convection dominates diffusion

$$|\varepsilon_i'| \ll 1$$

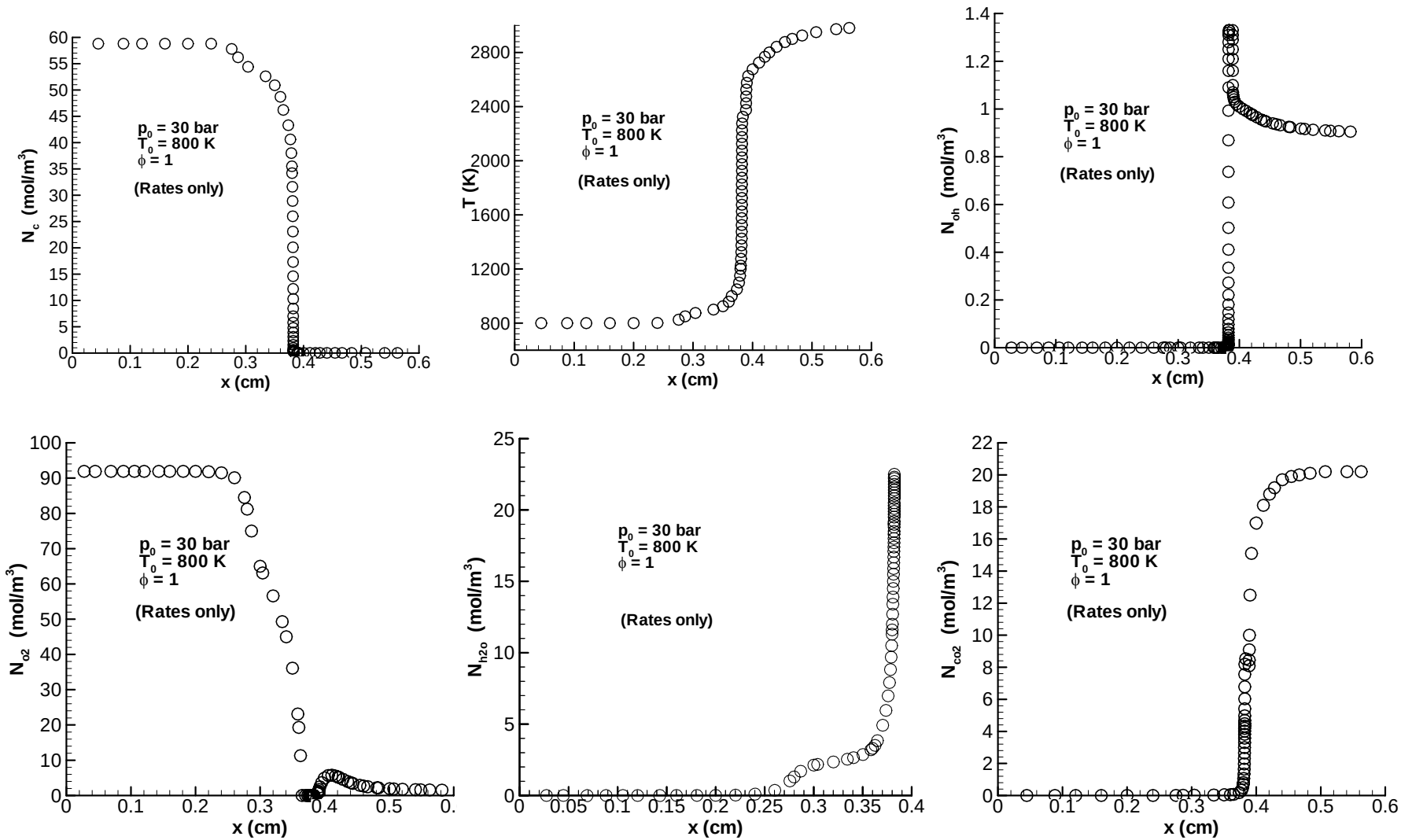
- The equations are solved using a stiff integrator

Initial conditions

- 90% iso-octane and 10% n-heptane
- 50% iso-octane and 50% n-heptane
- $\phi = 1$
- $(\rho u)_0$=0.8 g/(cm^2 s)
- T_0 prescribed
- p_0 prescribed
- Constant area situation

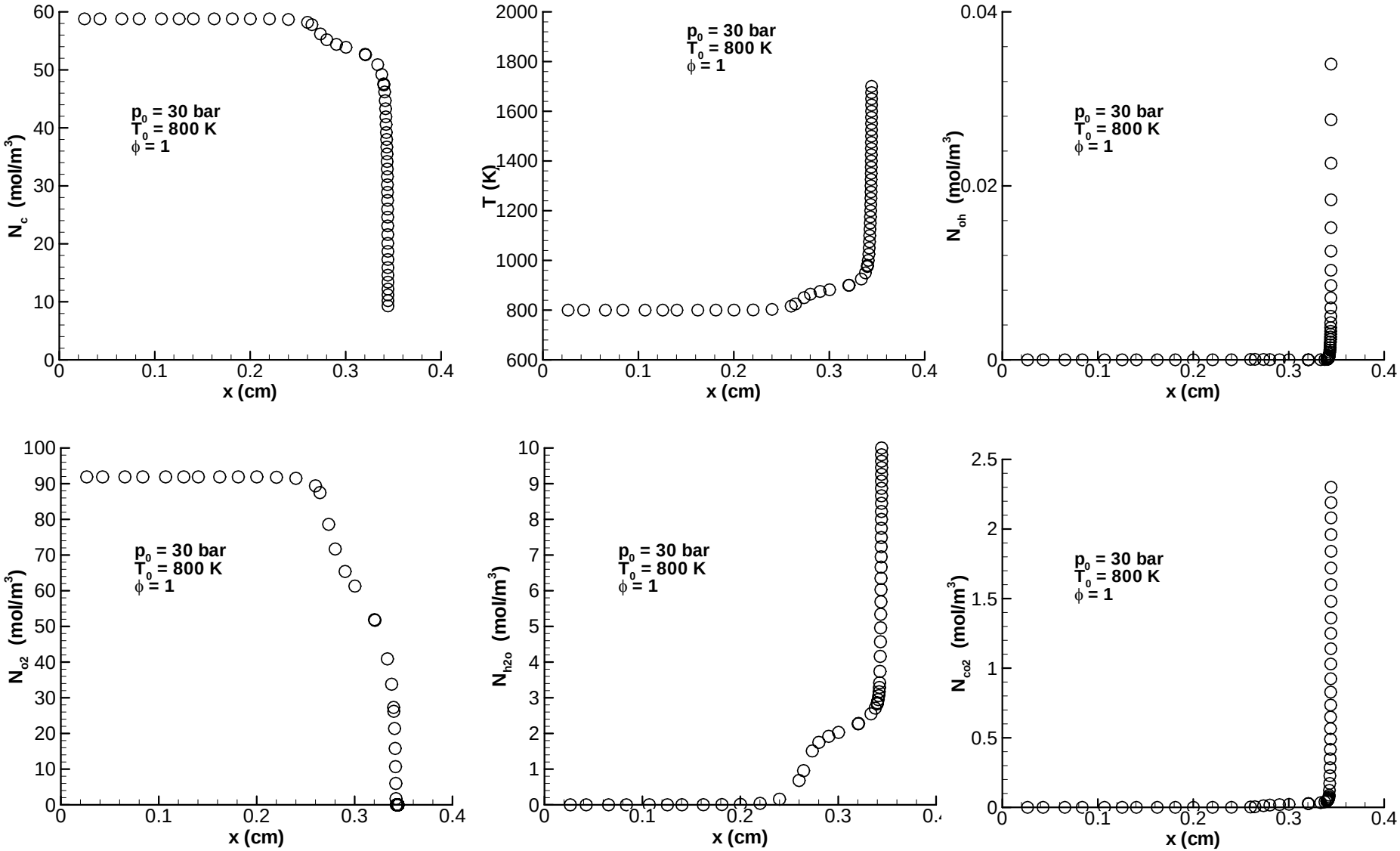
Premixed flame, large Pé; 1 of 5

90/10; p_0 = 30 bar, T_0 = 800 K; no diffusion



Premixed flame, large Pé; 2 of 5

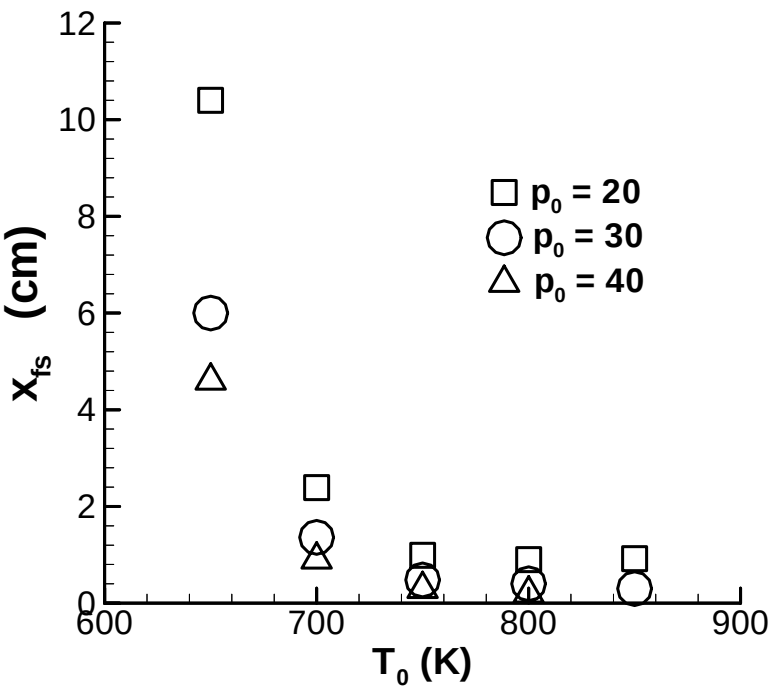
90/10; p_0 = 30 bar, T_0 = 800 K; with diffusion

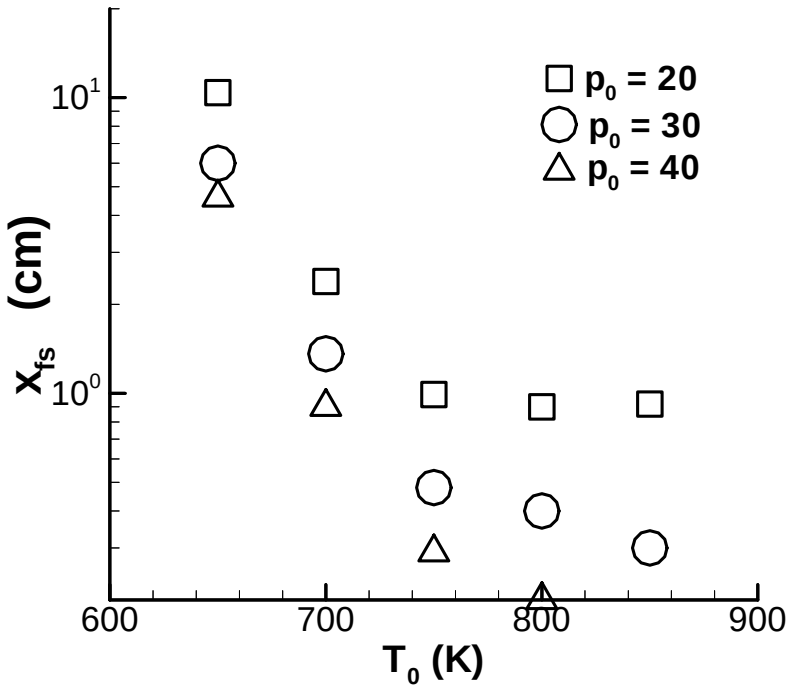


Premixed flame, large Pé; 3 of 5

90/10

x_{fs} is that at T_0+900K



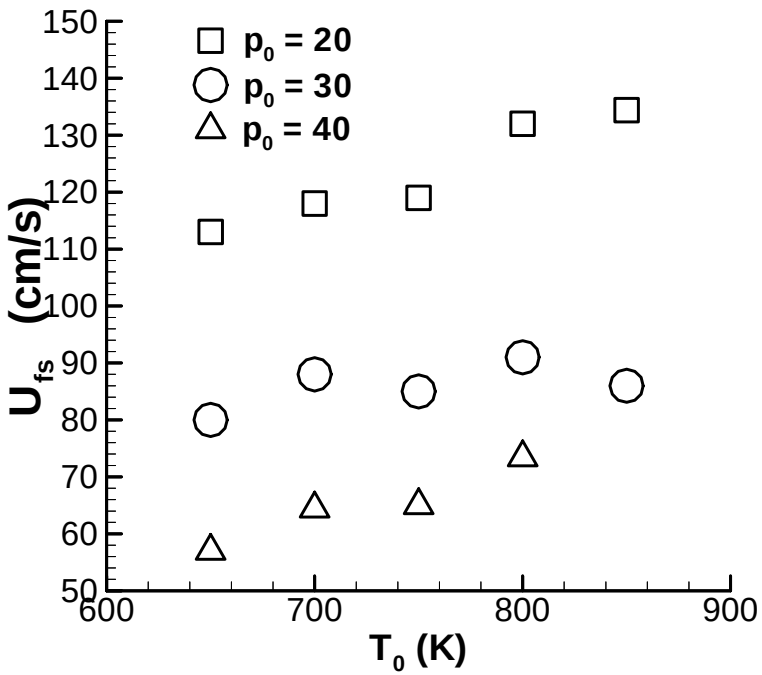


p_0 in bar, T_0 in K

Premixed flame, large Pé; 4 of 5

90/10

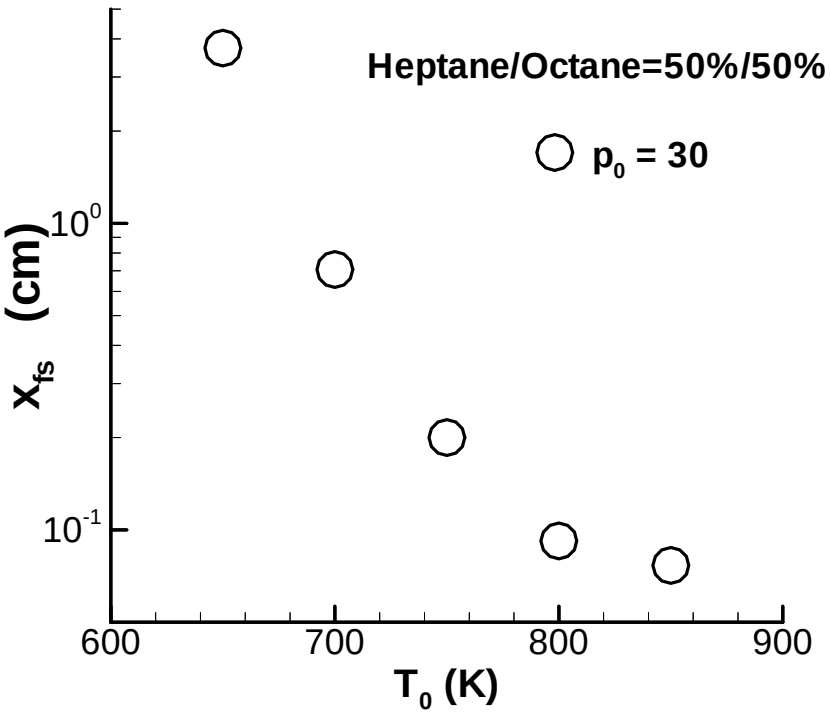
ϕ=1

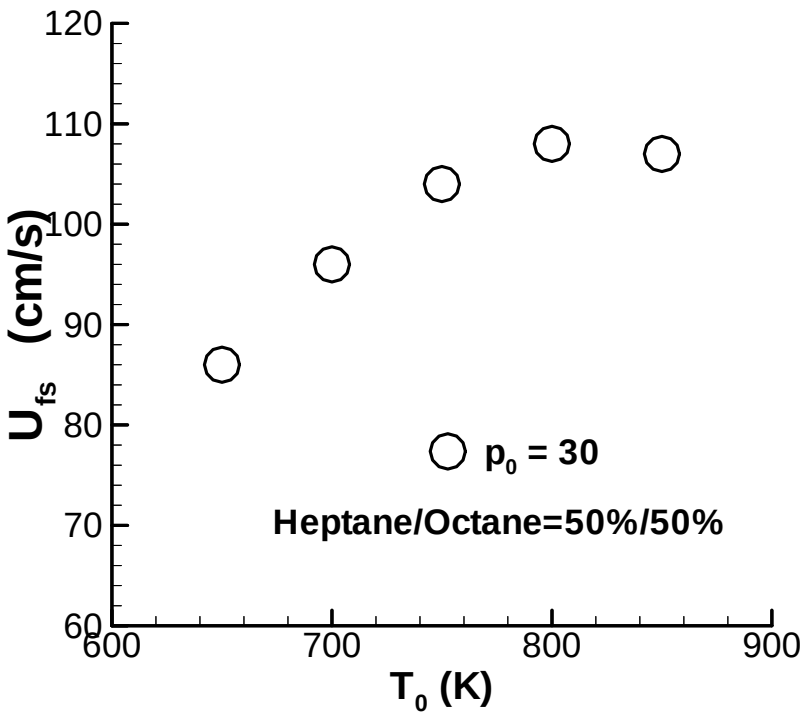


Premixed flame, large Pé; 5 of 5

50/50

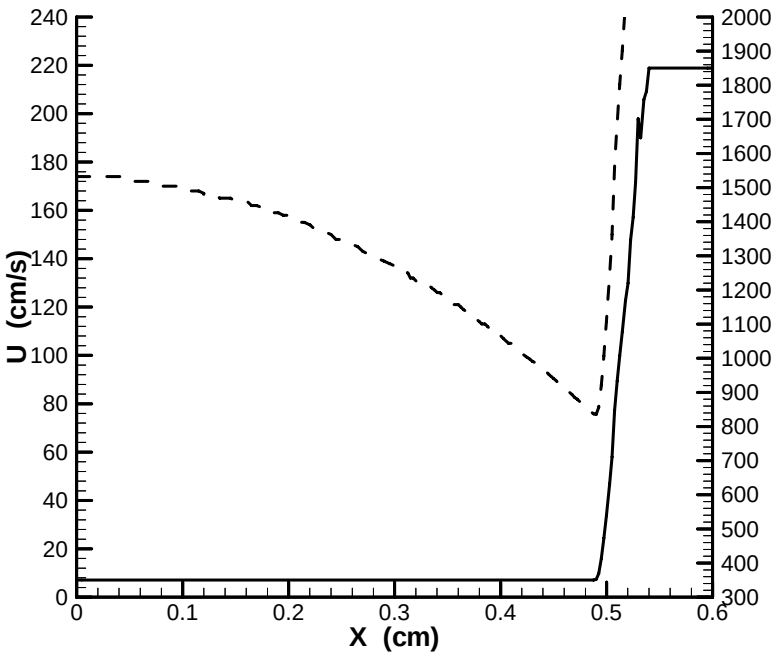
ϕ=1

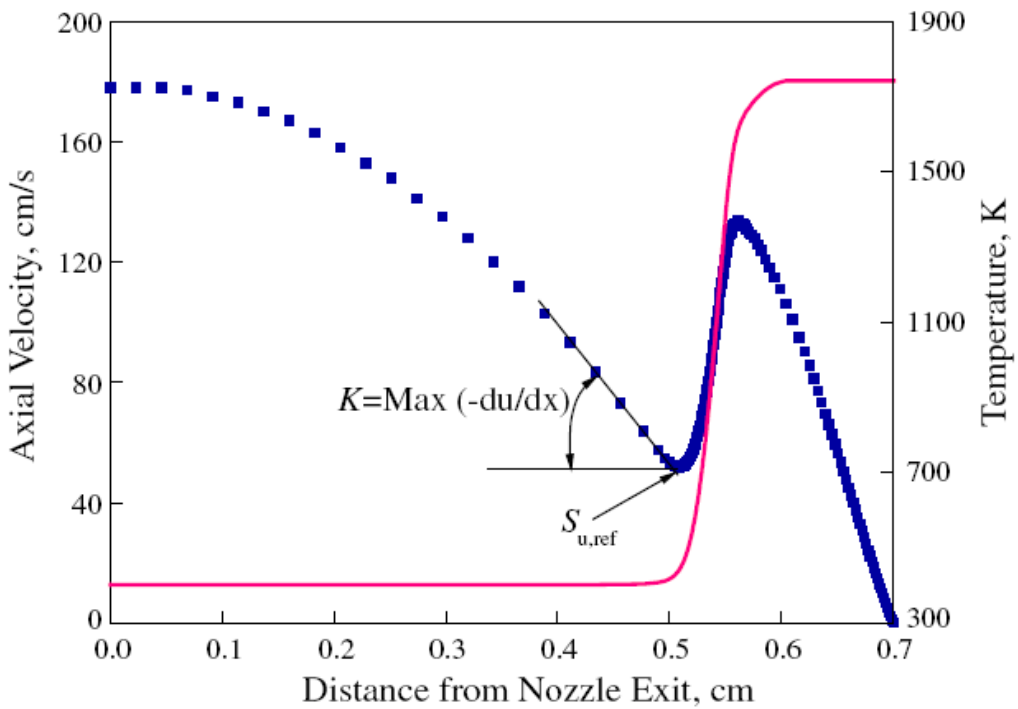




Premixed flame; general Pé

Ji. C. et al., "Propagation and extinction of premixed C5-C12 *n*-alkane flames", *Combust. Flame*, 157, 277-287, 2010.



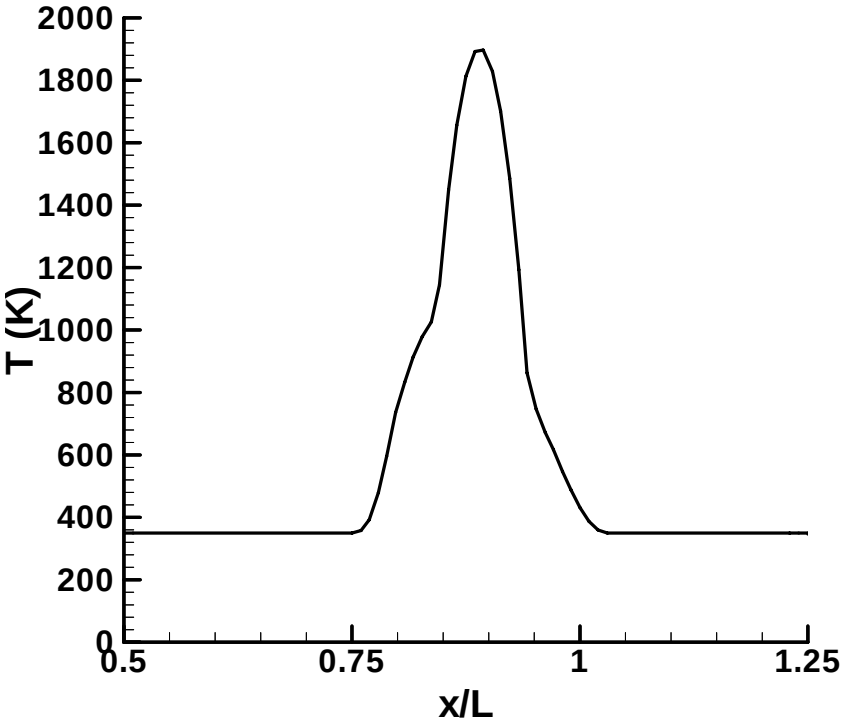


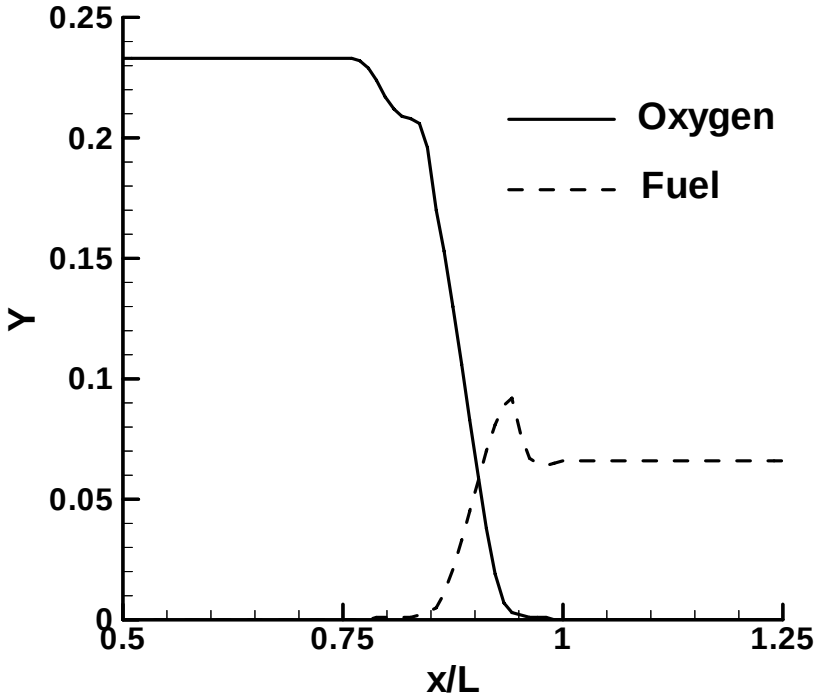
The experimental profiles were stated to be for C5-C8 *n*-alkanes (unburned temperature: 353K), and *n*-heptane was used .

Counterflow flame: computation feasibility

$p = 1$ bar, $T_{jet} = 350$ K, $(\rho u)_{air\text{-}jet} = 4.8 \times 10^{-2}$ g/cm^2, $(\rho u)_{fuel\text{-}jet} = 4.85 \times 10^{-2}$ g/cm^2, $L = 2$ cm

$(\rho u Y_F)_{fuel\text{-}jet} / (\rho u Y_{O2})_{air\text{-}jet} = \phi_s$





u (@max R) = 56 cm/s

Summary and conclusions, 1 of 2

- Developed a model of steady quasi-1D flame with variable area, including
  - Full mass-diffusion coefficient matrix
  - Thermal diffusion factors
  - Mixture thermal conductivity
  - Real-gas EOS
- Preliminary results obtained for premixed flames and constant area flow show that the predictions are qualitatively correct
  - U_{fs} varies with the inverse of a power of pressure
  - The position of the flame initiation depends on T_0
  - The position of the flame initiation depends of the initial pressure over the entire T_0 regime
  - Increasing the % heptane in the PRF results in larger U_{fs}

Summary and conclusions, 2 of 2

- Limited results were obtained for premixed flow with variable area
  - Results compare well with experimental data
- The model has been extended to non-premixed flow
  - Preliminary results are qualitatively correct.
  - The numerics must be improved as stability problems are still preventing routine computations and comparisons with experiments.

Future work

- Solidify the numerical method to enable routine computations

- Investigate whether the same constituents-and-species concept holds for higher alkanes and cycloalkanes