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AN EXISTING GLOBAL HEPTANE MECHANISM AUGMENTED WITH DIFFUSIVE TRANSPORT

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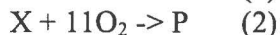
ABSTRACT

The couplings between diffusive transport and the temperature and species concentration distributions associated with low and intermediate temperature heptane oxidation are explored using an existing four-step heptane mechanism, tuned for elevated pressures. The energy and species concentration equations are augmented with diffusive fluxes for heat and species and solved numerically in a one-dimensional domain. The ignition delay times are also tabulated and compared with the zero-dimensional data reported in the literature.

INTRODUCTION

With reduced and global kinetic models, the interactions between fluid transport and chemistry can be explored. Recent work has considered the effect of diffusive fluxes on: (1) the Sal'nikov two-step mechanism for thermal ignition [1], (2) the Gray-Yang model for low temperature oxidation and cool flames [2] and (3) a newly-developed reduced propane oxidation mechanism valid for low and intermediate temperatures [3]. In this study, the spatio-temporal temperature and species concentration distributions associated with low and intermediate temperature heptane kinetics is considered using the four-step, reduced mechanism, developed by Müller et al. [4], augmented with diffusive fluxes of heat and species. This mechanism was originally reduced from a 1011 elementary reactions with 171 species, tuned with shock tube data at 40 atm, and validated for temperatures in the range of 600 to 1200 K.

The mechanism has two high temperature reactions (endothermic fuel decomposition and exothermic oxidation of the smaller hydrocarbons into final products) and two degenerate chain branching steps (steps 3 and 4).



F represents the parent fuel (n-C₇H₁₆), and X and I represent the grouped intermediates: X=3C₂H₄ + CH₃ + H (radicals resulting from the breakup of n-heptyl radicals) and I=HO₂R"O + H₂O. P represents the products 7CO₂ + 8 H₂O and R represents the n-heptyl radical (C₇H₁₅) and R" represents C₇H₁₃ -- an n-heptyl radical that has undergone two internal H-abstractions. Step 3 is the only reversible step with an activation energy of the reverse reaction greater than that of the forward reaction.

The associated energy and species concentration equations are:

$$\text{Energy Equation: } \frac{\partial T}{\partial t} = \alpha \nabla^2 T + T_1 k_1 X_F + T_2 k_2 X_X X_O + T_3 (k_{3f} X_F X_O - k_{3b} X_I) + T_4 k_4 X_I X_O$$

$$\text{Diffusion of F: } \frac{\partial X_F}{\partial t} = \nabla \cdot (D_F \nabla X_F) - k_1 X_F - k_{3f} X_F X_O + k_{3b} X_I$$

$$\text{Diffusion of X: } \frac{\partial X_X}{\partial t} = \nabla \cdot (D_X \nabla X_X) + k_1 X_F - k_2 X_X X_O$$

$$\text{Diffusion of I: } \frac{\partial X_I}{\partial t} = \nabla \cdot (D_I \nabla X_I) + k_{3f} X_F X_O - k_{3b} X_I - k_4 X_I X_O$$

$$\text{Diffusion of O}_2: \frac{\partial X_{O_2}}{\partial t} = \nabla \cdot (D_{O_2} \nabla X_{O_2}) + 11 \frac{\partial X_F}{\partial t} + 11 \frac{\partial X_X}{\partial t} + 9 \frac{\partial X_I}{\partial t}$$

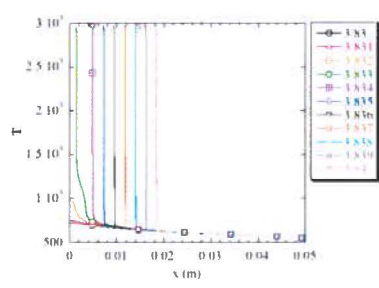
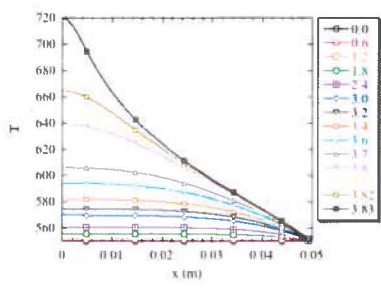
where $\alpha \equiv k/\rho c_p$ (cm²/s), X_i is the i species concentrations (mol/cm³), D_i is the mass diffusivity of the species i (cm²/s), k_i is the reaction rate of steps 1-4, noting that step 3 is reversible. The temperatures in the energy equation taken from Müller et al. [4] are $T_1=20400\text{K}$, $T_2=149800\text{K}$, $T_3=1550\text{K}$, and $T_4=127850\text{K}$. The Arrhenius reaction rates:

$$k_1 = A_1 \exp\left(\frac{-E_1}{RT}\right), \quad k_2 = \frac{p}{RT} A_2 \exp\left(\frac{-E_2}{RT}\right), \quad k_{3f} = \frac{p}{RT} A_{3f} \exp\left(\frac{-E_{3f}}{RT}\right),$$

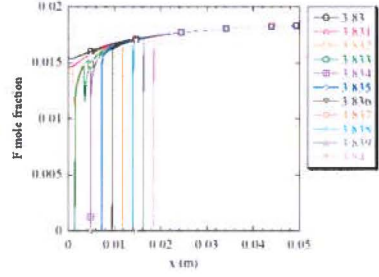
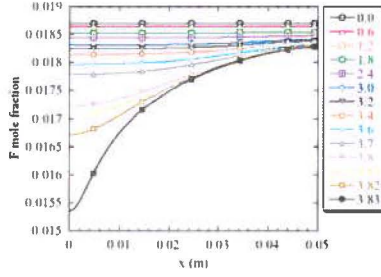
$$k_{3b} = A_{3b} \exp\left(\frac{-E_{3b}}{RT}\right), \quad k_4 = \frac{p}{RT} A_4 \exp\left(\frac{-E_4}{RT}\right)$$

where $A_1 = 1\text{E}10 \text{ s}^{-1}$, $A_2 = 2\text{E}12 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $A_{3f} = 3\text{E}18 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $A_{3b} = 4\text{E}22 \text{ s}^{-1}$, $A_4 = 5\text{E}13 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $E_1/R = 21650 \text{ K}$, $E_2/R = 7217 \text{ K}$, $E_{3f}/R = 21650 \text{ K}$, $E_{3b}/R = 37285 \text{ K}$, $E_4/R = 13230 \text{ K}$.

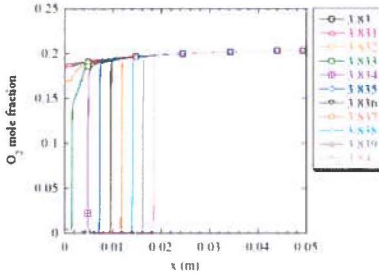
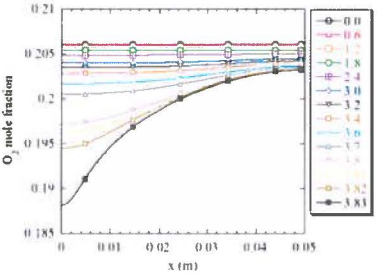
The energy and species equations are solved using the coupled PDE solver, UMFPAK, in a one-dimensional domain meshed non-uniformly with 2344 segments that vary in length from 0.0001m to 0.00001m (refined in the vicinity of $x=0.05\text{m}$). At $x=0\text{m}$, no flux boundary conditions are applied for the temperature and species concentration gradients ($\nabla T = \nabla X_i = 0$). At $x=5\text{cm}$, $\nabla X_i = 0$ for all species and the temperature at the boundary ($x=0.05\text{m}$) is fixed. The time-step is variable. The absolute tolerances on the temperature and species mole fractions X , O_2 , F , I are set to 10^{-4} , 10^{-12} , 10^{-6} , 10^{-6} , 10^{-6} , respectively. The maximum backwards differentiation order is five. The initial heptane-air mixture is taken to be stoichiometric and the initial mole fractions are: $X_{F0} = 0.0187$, $X_{O_20} = 0.2061$, $X_{X0} = 0$, $X_{I0} = 0$. The pressure is taken to be $40 \times 10^5 \text{ Pa}$, since the mechanism was validated with experiments at 40atm [4]. The temperature and species mole fraction distributions are shown in Figs. 1a-e for an initial gas and boundary temperature equal to 550K. The mixture thermal diffusivity and mass diffusivities for all species are constant and equal to $5 \times 10^{-5} \text{ m}^2/\text{s}$. For each variable, plots for $t \leq 3.83\text{s}$ capture the slow reaction process prior to ignition, which is followed by a plot for $3.831\text{s} < t < 3.837\text{s}$ showing the transition to ignition and subsequent propagation of the wave from left to right.



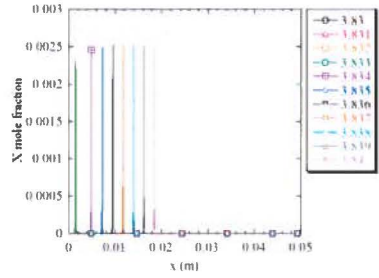
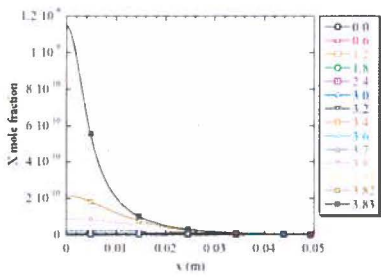
(a)



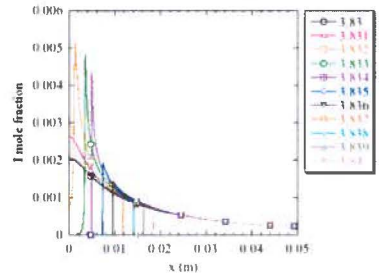
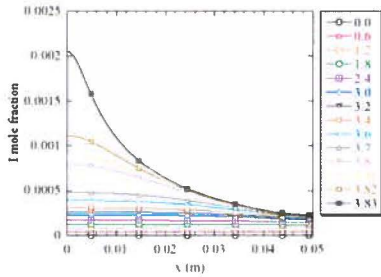
(b)



(c)



(d)



(e)

Fig.1: The (a) temperature, (b) parent fuel: F, (c) O₂, (d) X and (e) I species mole fraction distributions. $T(x=0.05m, \forall t)=550K$, $D_i=\alpha=5 \times 10^{-5} m^2/s$.

For $t < 3.831s$, the temperature increases slowly with a local maximum at $x=0$. As expected, a corresponding decrease in the fuel and oxidizer concentrations and an increase in the intermediates, X and I, are computed. Prior to hot ignition at $t=3.833s$, the temperature at $x=0$ increases $255^{\circ}C$ from 724 K to 979 K during the interval from 3.831s and 3.832s; the corresponding fuel fraction doesn't change at $x=0$, decreases to a minimum of 0.011215 at $x=0.0013m$ and then decreases to a lesser extent for $0.0013m < x < 0.05m$. This is characteristic of its Negative Temperature Coefficient. O_2 consumption shows a weaker nonlinear spatial variation at 3.832s. As for X, a narrow region of high concentration develops coincident with the high temperature gradient, while I peaks ahead of the front in the lower temperature region. At $t=3.833s$, ignition occurs and the temperature rises to 2970K. This value is close to the calculated adiabatic flame temperature for a stoichiometric, heptane-air mixture at an initial temperature of 550K and 40atm of 2883 K, computed with the GASEQ chemical equilibrium code [5]. The front then propagates from left to right at nearly constant speed. Also, at low temperatures, diffusion times become competitive with chemical times. Table 1 lists the 0-D and 1-D ignition times, respectively, for 530-600K and an increase in ignition time is observed due to thermal losses and species redistributions.

T (K)	Ignition Time (s): 0-D	Ignition Time (s): 1-D	Δ
530	12.420	13.923	1.503
540	6.796	6.984	0.188
550	3.692	3.833	0.141
560	2.198	2.199	0.001
570	1.211	1.297	0.086
580	0.779	0.780	0.001
590	0.478	0.479	0.001
600	0.298	0.299	0.001

Discussion

A global heptane mechanism has been extended to include diffusive fluxes of heat and species. The model clearly shows the spatio-temporal evolution of the temperature, fuel, oxidizer, and intermediate species. Additional analyses of the temperature and species profiles will be conducted at higher temperatures and experiments in reduced-gravity drop facilities will be considered for model validation.

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