Simplified Structure Models for Premixed n-Alkane Cool Flames

Vedha Nayagam, Forman A. Williams, and Mar Battistella

Supplementary Material

This supplement outlines the details of the asymptotic analysis presented in the paper.

Steady state approximations

The seven step mechanism used in the analysis is shown in Table 1 of the main paper. We assume steady state for the species R and OH. As described in Section 2 of the main text, this allows us to eliminate ω_1, and ω_2 from consideration. The conservation equations along with their source terms are shown below.

Conservation equations

The conservation equations in terms of ξ are:

$$\rho_u u = \rho_u S_L = \rho_f S_f = m \text{ (constant)}$$

$$\frac{\mathrm{d}Y_F}{\mathrm{d}\xi} = \frac{1}{L}\frac{\mathrm{d}^2 Y_F}{\mathrm{d}\xi^2} - \frac{\rho D}{m^2} W_F \omega_4,$$

$$\frac{\mathrm{d}Y_O}{\mathrm{d}\xi} = \frac{\mathrm{d}^2 Y_O}{\mathrm{d}\xi^2} - \frac{\rho D}{m^2} W_O \omega_4,$$

$$\frac{\mathrm{d}Y_I}{\mathrm{d}\xi} = \frac{1}{L}\frac{\mathrm{d}^2 Y_I}{\mathrm{d}\xi^2} + \frac{\rho D}{m^2} W_I (\omega_4 - \omega_5 - \omega_6 - \omega_7),$$

$$\frac{\mathrm{d}Y_K}{\mathrm{d}\xi} = \frac{1}{L}\frac{\mathrm{d}^2 Y_K}{\mathrm{d}\xi^2} + \frac{\rho D}{m^2} W_K (\omega_3 - \omega_4),$$

$$\frac{\mathrm{d}T}{\mathrm{d}\xi} = \frac{\mathrm{d}^2 T}{\mathrm{d}\xi^2} + \frac{\rho D}{m^2} W_K T_Q \omega_4.$$

where

$$\xi = \int \frac{m}{\rho D}\, dx$$

Outer zone

In this zone reactions are frozen and convection-diffusion balance occurs for all the species and temperature, except for I which is zero in this zone. The Lewis number is L, and it is the same for F, K, and I. Oxygen Lewis number is unity. The solution for the species and temperature are

$$Y_F = Y_{Fu} + (Y_{Ff} - Y_{Fu}) e^{L\xi}$$

$$Y_O = Y_{Ou} + (Y_{Of} - Y_{Ou}) e^{\xi}$$

$$Y_K = Y_{Kp} e^{L\xi}$$

$$Y_I = 0$$

$$T = T_u + (T_f - T_u) e^{\xi} = T_u + \Delta T e^{\xi}$$

The slopes of these solutions are to be matched with the inner equations as $\xi \to 0$.

Inner zones

Inner heat release zone:

This is the thinnest zone with the highest activation energy corresponding to T_4. In this zone fuel and oxygen are consumed, I is produced, K is consumed, and heat is released all at the rate of step 4. The independent variable ξ is stretched as

$$\eta = \frac{\xi}{\epsilon} \quad \text{with} \ \ \epsilon = \frac{T_f^2}{T_4(T_f - T_u)}.$$

The energy conservation equation becomes in the limit $\epsilon \to 0$,

$$\frac{d^2T}{d\eta^2} = -\frac{\rho D}{m^2}\epsilon^2 W_K T_Q (\rho Y_K / W_K) A_4 e^{-T_4/T},$$

where we have written $[K] = \rho Y_K / W_K$, and expanded T and K as

$$Y_K = 0 + \epsilon\frac{L}{T_Q}\Delta T z; \quad T = T_f - \epsilon \Delta T z$$

with $\Delta T = T_f - T_u$. The inner equation in terms of "z" then becomes,

$$\frac{d^2 z}{d\eta^2} = \Lambda z e^{-z}$$

with

$$\Lambda = \left(\frac{\rho_f^2 D_f L}{m^2}\right)\left(\frac{T_f^4}{T_4^2 \Delta T^2}\right) A_4 e^{-T_4/T_f},$$

where we have used

$$e^{-T_4/T} = e^{-T_4/T_f}\ e^{-z}$$

The differential equation for z is solved subject to the boundary obtained by matching the slopes to the downstream zone and to the upstream preheat zone, namely

$$\eta \to \infty, \ \ z \to 0 \ \ (\text{since } T \to T_f),$$

$$\eta \to -\infty, \ \ dz/d\eta \to -1.$$

The solution for z is now obtained by setting $dz/d\eta = p$, which leads to

$$\frac{dp^2}{dz} = 2\Lambda z e^{-z}$$

Integrating between ∞ and $-\infty$:

$$p^2|_{-\infty}^{\infty} = -2\Lambda(1+z)e^{-z}|_{-\infty}^{\infty}$$

$$0 - 1 = -2\Lambda; \ \ \text{giving} \ \ \Lambda = 1/2.$$

Note that jump conditions across this zone for the variables Y_O, Y_I, and Y_K can be obtained since coupling function between T and these variables exist.

Flame spread formula

Using the definition of Λ, and setting it equal to 1/2, we obtained,

$$\frac{T_f^4}{T_4^2 \Delta T^2}\left(\frac{\rho_f^2 D_f}{m^2}\right) L A_4 e^{-T_4/T_f} = \frac{1}{2}.$$

Substituting $m = \rho_u S_L$, we get:

$$S_L = \frac{T_f^2(\rho_f/\rho_u)}{T_4(T_f - T_u)}\sqrt{2LD_f A_4 e^{-T_4/T_f}}$$

or

$$S_f = \frac{T_f^2}{T_4 \Delta T}\sqrt{2LD_f A_4 e^{-T_4/T_f}}$$

The flame temperature T_f is still unknown and it is obtained from the solutions of the species equations.

Y_O solutions

From the outer solution, the slope of Y_O as $\xi \to 0$ is

$$\frac{dY_O}{d\xi} \to (Y_{Of} - Y_{Ou})$$

The jump condition from the inner zone is

$$\left.\frac{dY_K}{d\xi}\right|_{0-} = -\frac{W_O}{W_K T_Q}\Delta T$$

The oxygen mass fraction at the flame becomes

$$Y_{Of} = Y_{Ou} - \frac{W_O}{W_K T_Q}\Delta T$$

Y_I solutions

Downstream I-consumption zone:

In this zone consumption of I occurs through step-5 (and step-6), and the flame temperature remains constant at T_f. The conservation equation for I becomes,

$$\frac{\mathrm{d}^2 Y_I}{\mathrm{d}\xi^2} - L\frac{\mathrm{d}Y_I}{\mathrm{d}\xi} - \frac{\rho D}{m^2} L \rho Y_I A_5 (1 + \omega_6/\omega_5) e^{-T_5/T_f} = 0.$$

The solution to this equation subject to the boundary conditions $Y_I(0) = Y_{If}$, and $Y_I(\infty) = 0$ is

$$Y_I(\xi) = Y_{If} e^{-\frac{1}{2}\xi\left(\sqrt{4b^2 + L^2} - L\right)},$$

where

$$b^2 = \frac{\rho_f^2 D_f L A_5}{m^2}(1 + \omega_6/\omega_5) e^{-T_5/T_f}$$

with

$$\omega_6/\omega_5 = A_3 e^{-T_3/T_f} A_6 e^{-T_6/T_f} / [A_2 A_5 e^{-T_5/T_f}].$$

The matching condition to the inner zone is

$$\left.\frac{Y_I}{d\xi}\right|_{0+} = -\frac{1}{2} Y_{If} \left(\sqrt{4b^2 + L^2} - L\right),$$

Upstream I-consumption zone:

Again I consumption occurs through step-5 (and step-6) in this zone. However the temperature here is not a constant, and therefore stretching is necessary. Let,

$$\zeta = -\xi/\delta$$

and

$$T = T_f - \Delta T \delta \zeta; \quad Y_I = Y_{If} - \delta y$$

Then

$$\frac{d^2 y}{d\zeta^2} = -\frac{\rho_f^2 D_f}{m^2} L Y_{If} \delta A_5 (1 + \omega_6/\omega_5) e^{-T_5/T_f} Y_{If} e^{-\zeta}$$

or,

$$\frac{d^2 y}{d\zeta^2} = -c Y_{If} e^{-\zeta}$$

where

$$c = \frac{\rho_f^2 D_f}{m^2} L \frac{T_f^2}{T_5 \Delta T} A_5 e^{-T_5/T_f}$$

which can be simplified to

$$c = \frac{1}{2} \left(\frac{A_5 (1 + \omega_6/\omega_5) e^{-T_5/T_f}}{A_4 e^{-T_4/T_f}} \right) \frac{T_4^2}{T_5} \frac{\Delta T}{T_f^2}.$$

Integrating from 0 to ∞:

$$\left.\frac{dy}{d\zeta}\right|_0^\infty = +c Y_{If} e^{-\zeta} \Big|_0^\infty$$

Change in slope across this zone is

$$\Delta \left(\frac{dy}{d\zeta} \right) = c Y_{If}$$

The change in slope in terms of ξ is

$$\Delta \left(\frac{dY_I}{d\xi} \right) = \frac{1}{2} \left(\frac{A_5 e^{-T_5/T_f}}{A_4 e^{-T_4/T_f}} \right) (1 + \omega_6/\omega_5) \frac{T_4^2}{T_5} \frac{\Delta T}{T_f^2} Y_{If},$$

since

$$\frac{dY_I}{d\xi} = -\frac{\delta}{-\delta} \frac{dy}{d\zeta} = \frac{dy}{d\zeta}.$$

Upstream I-destruction zone (through ω_7):

In this zone I is completely consumed. The conservation equation is

$$\frac{\mathrm{d}Y_I}{\mathrm{d}\xi} = \frac{1}{L}\frac{\mathrm{d}^2Y_I}{\mathrm{d}\xi^2} - \frac{\rho D}{m^2}W_I\omega_7$$

$$\omega_7 = [I][O_2]\frac{A_3A_7}{A_2}e^{-(T_3+T_7)/T}$$

Now T_3=-8,360 K and T_7 = 1,760 K and let $T_r = T_3 + T_7$ =-6,600 K. The activation energy for K production via ω_3 is -8,360 K. So we pick an intermediate value of T_s=-7,500 K to stretch this common zone for both K production and I destruction. Define a small positive parameter υ:

$$\upsilon = \frac{T_f}{(-T_s)} \quad T = T_f - \upsilon T_f x = T_f(1-\upsilon x)$$

The conservation equation for Y_I becomes

$$\frac{\mathrm{d}Y_I}{\mathrm{d}\xi} = \frac{1}{L}\frac{\mathrm{d}^2Y_I}{\mathrm{d}\xi^2} - \frac{\rho^2 D}{m^2}\left(\frac{\rho Y_{Of}}{W_O}\right)\left(\frac{A_3A_7}{A_2}e^{-T_r/T_f}\right)Y_Ie^x$$

where we have assumed $T_r/T_s \approx 1$. Both Y_I and T in the form of x appears in the equation. So, we write the equation in terms of x rather than a stretched independent variable. Note that:

$$\frac{\mathrm{d}Y_I}{\mathrm{d}\xi} = \Delta T\frac{\mathrm{d}Y_I}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}x} = -\left(\frac{\Delta T}{\upsilon T_f}\right)\frac{\mathrm{d}Y_I}{\mathrm{d}x}$$

$$\frac{\mathrm{d}^2Y_I}{\mathrm{d}\xi^2} = \left(\frac{\Delta T}{\upsilon T_f}\right)^2\frac{\mathrm{d}^2Y_I}{\mathrm{d}x^2}$$

The conservation equation becomes:

$$\frac{\mathrm{d}^2Y_I}{\mathrm{d}x^2} = AY_Ie^x,$$

where

$$A = \left(\frac{T_f^2}{T_s\Delta T}\right)^2\frac{DL}{S_f^2}\left(\frac{\rho Y_{Of}}{W_O}\right)\left(\frac{A_3A_7}{A_2}e^{-T_r/T_f}\right)$$

Substituting for S_f:

$$A = \frac{1}{2}\left(\frac{T_4}{T_s}\right)^2\left(\frac{\rho_f Y_{Of}}{W_O}\right)\left(\frac{A_3A_7}{A_2A_4}\right)e^{(T_4-T_r)/T_f}$$

This differential equation can be solved, requiring Y_I remains finite and $Y_I(0) = Y_{If}$, to obtain

$$Y_I(x) = c_1K_0(2\sqrt{Ae^x})$$

where,

$$c_1 = \frac{Y_{If}}{K_0(2\sqrt{A})}$$

Slope at $x = 0$ becomes:

$$\frac{\mathrm{d}Y_I}{\mathrm{d}x} = -\frac{2\sqrt{A}K_1(2\sqrt{A})}{K_0(2\sqrt{A})}Y_{If}$$

In terms of ξ:

$$\frac{\mathrm{d}Y_I}{\mathrm{d}\xi} = \left(\frac{\Delta T(-T_s)}{T_f^2}\right)\frac{2\sqrt{A}K_1(2\sqrt{A})}{K_0(2\sqrt{A})}Y_{If}$$

Putting all the slopes together and rearranging we get the following expression for Y_{If}

$$Y_{If} = \frac{2W_I\Delta T}{W_K T_Q}\left(\frac{4(-T_s)\Delta T\sqrt{A}K_1(2\sqrt{A})}{LT_f^2K_0(2\sqrt{A})} + \frac{\Delta T T_4^2 R}{LT_f^2T_5} + \sqrt{1+\frac{2T_4^2\Delta T^2 R}{L^2T_f^4}} - 1\right)^{-1}, \quad (1)$$

which is shown as equation (1) in the main text.

Y_K solutions

Y_K is consumed in the inner heat release zone (by ω_4). It is produced in the lower temperature region through ω_3 (a zone in common with ω_7 where Y_I is destroyed completely). In the preheat zone convection-diffusion balance occurs for Y_K.

Preheat zone for Y_K:

$$\frac{\mathrm{d}^2Y_K}{\mathrm{d}\xi^2} - L\frac{\mathrm{d}Y_K}{\mathrm{d}\xi} = 0$$

The solution,

$$Y_K(\xi) = Y_{Kp}e^{L\xi}$$

with Y_{Kp}, the maximum in the Y_K production zone, to be determined. Since $T(\xi) = T_u + \Delta T e^{\xi}$, in the preheat zone, Y_K can also be expressed as a function of T as

$$Y_K(T) = Y_{Kp}\left(\frac{T-T_u}{\Delta T}\right)^L$$

The slope as $T \to T_f$ (or $\xi \to 0$) is

$$\frac{\mathrm{d}Y_K}{\mathrm{d}T} = \frac{LY_{Kp}}{\Delta T},$$

which is needed for matching with the Y_K production zone, considered below.

Y_K production zone:

$$\frac{\mathrm{d}Y_K}{\mathrm{d}\xi} = \frac{1}{L}\frac{\mathrm{d}^2Y_K}{\mathrm{d}\xi^2} + \frac{\rho D}{m^2}W_K\omega_3,$$

$$\omega_3 = [I][O_2]A_3e^{-T_3/T}$$

$$\frac{\mathrm{d}Y_K}{\mathrm{d}\xi} = \frac{1}{L}\frac{\mathrm{d}^2Y_K}{\mathrm{d}\xi^2} + \frac{\rho^2 D}{m^2}W_K\left(\frac{\rho_f Y_{Of}}{W_O}\right)\left(\frac{Y_I}{W_I}\right)A_3e^{-T_3/T}$$

As in the Y_I destruction zone, we set

$$\upsilon = \frac{T_f}{(-T_s)}, \quad T = T_f(1-\upsilon x)$$

and write the conservation equation in terms of x in the limit $\upsilon \to 0$, namely

$$\frac{\mathrm{d}^2Y_K}{\mathrm{d}x^2} = -\left(\frac{T_f^2}{T_s\Delta T}\right)^2\frac{\rho^2 DL}{m^2}\left(\frac{\rho_f Y_{Of}}{W_O}\right)\left(\frac{Y_I}{W_I}\right)W_KA_3e^{-T_3/T_f}e^{bx}$$

or, with $m = \rho_f S_f$ we have

$$\frac{\mathrm{d}^2 Y_K}{\mathrm{d}x^2} = -\left(\frac{T_f^2}{T_s \Delta T}\right)^2 \frac{DL}{S_f^2}\left(\frac{\rho_f Y_{Of}}{W_O}\right)\left(\frac{Y_I}{W_I}\right) W_K A_3 e^{-T_3/T_f} e^{bx}$$

or

$$\frac{\mathrm{d}^2 Y_K}{\mathrm{d}x^2} = -B Y_I e^{bx}$$

where B is given by (after substituting for S_f)

$$B = \frac{1}{2}\left(\frac{T_4}{T_s}\right)^2 \left(\frac{\rho_f Y_{Of}}{W_O}\right)\left(\frac{W_K}{W_I}\right) \frac{A_3 e^{-T_3/T_f}}{A_4 e^{-T_4/T_f}}$$

Since Y_I is known in terms of x, the ODE can be integrated once. Let $p = dY_K/dx$, and $t = 2\sqrt{Ae^x} \Rightarrow e^x = t^2/(4A)$ and $dt/dx = t/2$:

$$\frac{\mathrm{d}p}{\mathrm{d}x} = \frac{dp}{dt}\frac{dt}{dx} = \frac{dp}{dt}\frac{t}{2} = -c_1 B K_0(t)(t^2/4A)$$

Integrate from $x = 0$ to $x \to \infty$ or $t = 2\sqrt{A}$ to $t \to \infty$ to get

$$\int_{2\sqrt{A}}^{\infty} \frac{dp}{dt} dt = -\int_{2\sqrt{A}}^{\infty} \left(\frac{c_1 B}{2A}\right) K_0(t) t dt$$

$$p(t) = \left(\frac{c_1 B}{2A}\right) t K_1(t) + const$$

$$\left.\frac{dY_K}{dx}\right|_0^{\infty} = \left.p\right|_{2\sqrt{A}}^{\infty} = 0 - \left(\frac{c_1 B}{\sqrt{A}}\right) K_1(2\sqrt{A})$$

This is the change in slope of Y_K across this zone. Matching with the inner zone and the preheat zone we get

$$-(\upsilon T_f)\frac{L Y_{Kp}}{\Delta T} - \frac{\upsilon T_f L}{T_Q} = -\left(\frac{c_1 B}{\sqrt{A}}\right) K_1(2\sqrt{A}),$$

which in turn yields,

$$Y_{Kp} = \frac{Y_{If} W_K (-T_s)(T_f - T_u) A_2 \sqrt{A} K_1(2\sqrt{A})}{W_I L T_f^2 A_7 e^{-T_7/T_f} K_0(2\sqrt{A})} - \frac{T_f - T_u}{T_Q},$$

which is shown as equation (2) in the main text. Setting Y_{Kp} to be small, we get

$$Y_{If} = \frac{T_f^2}{(-T_s)} \frac{L}{T_Q} \left(\frac{\sqrt{A}}{B} \frac{K_0(2\sqrt{A})}{K_1(2\sqrt{A})}\right) \tag{2}$$

with

$$\frac{A}{B} = \frac{W_I}{W_K} \frac{A_7}{A_2} e^{-T_7/T_f}.$$

We now have two expressions for Y_{If}, equation (1) and (2), and they can be iteratively solved to get T_f for a given condition. A simplified version of that equation is shown as equation (3) in the main text. This completes the problem formulation.