

Asymptotic Analysis of Quasi-Steady Heptane Droplet Combustion Supported by Cool-Flame Chemistry

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A skeletal chemical-kinetic mechanism for heptane cool flames is simplified to the maximum extent possible by introduction of steady-state approximations for intermediaries, following procedures employed previously. A pair of ordinary differential equations in mixture-fraction space is thereby obtained, describing the quasi-steady structures of the temperature and heptylketohydroperoxide (KET) fields. Application of activation-energy asymptotics for the partial-burning regime to this pair of equations is shown to provide convenient expressions for flame structures and extinction. With the mixture-fraction co-ordinate related to radius, these results are used to address droplet-combustion experiments that have been performed in the International Space Station (ISS). Droplet diameters at extinction are predicted as a function of the oxygen concentration in the atmosphere, and compared with measurements. While the results are encouraging, there are noticeable differences that point to deficiencies in the analysis resulting from oversimplifications. Further investigation therefore is recommended.

2 Introduction

Premixed combustion processes of normal alkanes (except methane and ethane) are known to exhibit unique characteristics that depend on the initial temperature and pressure of the combustible mixture [1]. Autoignition of these alkanes involves a different chemical-kinetic mechanisms at high and low temperatures, and there is a temperature range in between, the negative-temperature-coefficient (NTC) range, over which ignition occurs in two stages and the total ignition delay time tends to decrease with increasing temperature [1]. In homogeneous mixtures, transient cool-flame phenomena also are observed over this intermediate temperature range, leading to the chemical mechanism being characterized as cool-flame chemistry. Until recently, such phenomena have not been associated with diffusion flames, although cool-flame chemistry had been found to be of significance in autoignition of alkane droplets in heated atmospheres [2]. Experiments performed at the International Space Station (ISS), however, revealed instances of two-stage alkane droplet combustion in which a hot-flame stage, after extinguishing through a radiant-heat-loss mechanism, was followed by a quasi-steady stage of combustion sustained by cool-flame chemistry [3]. The present contribution is an analytical investigation addressing the objective of advancing understanding of quasi-steady cool diffusion flames, which occur in this NTC region [4]. Previous work has shown how asymptotic analyses can be applied to a short *n*-heptane mechanism to

explain the NTC behavior [5]. The chemical-kinetic developments employed in this previous study are applied here to describe quasi-steady droplet burning and extinction. Use will be made of our previous formulation [4] and of results obtained in that study. In particular, based on the chemistry and stoichiometry obtained there, the partial-burning regime of the classical investigation of Liñán [6] will be adopted here, as the closest approximation of the four regimes identified in that classical paper.

3 The Chemistry

The starting point for describing the chemistry is the most recent skeletal mechanism [4]. The heptyl radical, one of many intermediate species that obeys well a steady-state approximation, can decompose, unimolecularly in a reasonable first approximation, as it does during the high-temperature chemistry, or it can undergo the bimolecular addition of an oxygen molecule, which initiates the path to the low-temperature chemistry. The fraction of the radical consumed by the second of these processes determines the fraction of the chemistry that proceeds by the low-temperature path. If the total unimolecular rate constant for heptyl consumption is denoted by A and the total bimolecular rate constant is denoted by B , then the fraction following the low-temperature path is $\alpha = B[O_2]/(A + B[O_2])$, where $[O_2]$ denotes the oxygen concentration.

The NTC region is the only region in which the cool diffusion flame is stable [4], and this occurs in a close vicinity of $\alpha = 1/2$, which is satisfied at a temperature T equal to T^* , defined as the temperature at which $A = B[O_2]$. Since A increases rapidly with T , while B depends only weakly on temperature, α increases strongly as T decreases, as it must, to describe properly the transition from high-temperature to low-temperature chemistry. An expansion of α about $T = T^*$ [5] is central to an analytical description of the NTC chemistry. In an Arrhenius approximation for the ratio A/B with an activation temperature for this ratio of $T_a = 14,400$ K, this expansion is $\alpha = 1/2 - (T - T^*) T_a / (4T^{*2})$.

Heptylketohydroperoxide, denoted as KET in [5] and simply as K hereafter is the key intermediate species in the NTC region. It is the unimolecular decomposition of K that ultimately leads to the chain branching which carries the chemistry of the low-temperature path, in contrast to the hydroperoxyl production associated with heptyl decomposition, which carries the chemistry in the high-temperature autoignition path [1]. The NTC chemistry transpires to produce an autocatalytic net rate of production of K for $\alpha < 1/2$ and a net rate of consumption of K for $\alpha > 1/2$. The dominant chemistry in the center of the NTC region can then be expressed in terms of a net molar rate of production of K given by $(2\alpha - 1)w$, with $w = [K]C \exp(-T_K/T)/(1 - \alpha)$, where C is a constant unimolecular prefactor, and T_K is the associated activation temperature. These rate parameters are, in fact, the rate parameters for the unimolecular decomposition of K , so that [5], $C = 8.4 \times 10^{14} \text{ s}^{-1}$ and $T_K = 21,650$ K.

The energetics associated with this autocatalytic rate-controlling step lead to an expression for the rate of increase of temperature, correspondingly obtained from Eq. (44) of [5], given by $(Q/c_p)(\alpha - 0.2)w$, where c_p is the specific heat at constant pressure (to be assumed constant), and Q is a constant determining the ultimate net heat release associated with the decomposition reaction of K .

4 Formulation

Following our previous work [4], the problem is formulated employing as the independent variable the mixture fraction Z , having the value 0 in the ambient gas, where conditions are identified by the subscript 0 and unity in the interior of the liquid, where conditions are identified by the subscript 1. The strain rate $\chi = 2D(dZ/dr)^2$ then appears in the conservation equations, where D denoted the thermal

diffusivity and r the radial co-ordinate. In terms of the mass fraction of species K , $Y = [K]W_K/\rho$ and the non-dimensional temperature $\theta = c_p T W_K / Q$, where W_K denotes the molecular weight of K and ρ the density, the equations for conservation of K and of energy become, respectively,

$$(1 - \alpha) \frac{\chi}{2} \frac{d^2 Y}{dZ^2} = - (2\alpha - 1) Y C \exp(-T_K/T) \quad (1)$$

and

$$(1 - \alpha) \frac{\chi}{2} \frac{d^2 \theta}{dZ^2} = - (\alpha - 0.2) Y C \exp(-T_K/T), \quad (2)$$

with the boundary conditions $Y = 0$ at $Z = 0$ and also at $Z = 1$, $\theta = \theta_0$ at $Z = 0$, and $\theta = \theta_1$ at $Z = 1$. Here $\theta_0 = c_p T_0 W_K / Q$ and $\theta_1 = c_p T_1 W_K / Q$, where T_0 is the temperature of the oxidizing atmosphere, and $T_1 = 189 \text{ K}$ is the effective temperature of the fuel droplet, as modified by properly taking into account the heat of vaporization in the energy conservation [4]. In view of other anticipated inaccuracies, the Lewis number of K has been set equal to unity here for simplicity. These equations apply only for $Z < Z_L$, its value at the liquid surface, the boundary condition at $Z = 1$ having been obtained by employing the interface energy conservation condition. The source term strictly vanishes over the small range $Z_L < Z < 1$, and in the asymptotic analysis it is negligibly small everywhere except near the flame, located at $Z = Z_b$, a value that turns out to be slightly less than $1/2$ and therefore is consistent with these approximations.

5 Outer Solutions

In the partial-burning regime [6], the chemistry is negligibly slow except in the vicinity of the reaction zone of the flame, located at $Z = Z_b$ in this outer variable, where the temperature in the first approximation is $T = T_b$, the highest temperature anywhere in the flow field. Activation-energy asymptotics (AEA) are applied with the small parameter

$$\epsilon = T_b^2 Z_b / [T_K (T_b - T_0)] \quad (3)$$

In addition to (1) and (2), equations for the conservation of fuel and oxygen are also needed, but for the partial-burning regime, in which both of these reactants leak through the flame, they do not appear in the flame-structure analysis [6]. For this regime, they impose the conditions that, for the outer structure, at $Z = Z_b$ the magnitudes of the temperature gradients must be the same on both sides of the flame, that is, $|dT/dZ|$ is the same, but beyond that they do not enter into the analysis. This equality of slopes is dictated by the form taken by the reaction-rate function in the inner region.

In the outer zones, where the chemistry is negligible, the solutions to (1) and (2) are linear, so that

$$Y = Y_b (Z/Z_b), \quad T = T_0 + (T_b - T_0) (Z/Z_b), \quad \text{for } Z < Z_b \quad (4)$$

and

$$Y = Y_b [(1 - Z) / (1 - Z_b)], \quad T = T_1 + (T_b - T_1) [(1 - Z) / (1 - Z_b)], \quad \text{for } Z > Z_b, \quad (5)$$

where Y_b is the first approximation to Y at $Z = Z_b$. The condition of equal magnitudes of slopes of the temperature on the two sides of the reaction zone provides a relationship between T_b and Z_b , namely,

$$T_b = T_0 + (T_0 - T_1) Z_b / (1 - 2Z_b). \quad (6)$$

In the present application, since $T_0 - T_1$ is positive, the requirement that $T_b > T^0$ implies that $Z_b < 1/2$.

6 Inner Equations

The independent variable in the reaction region is the stretched mixture fraction

$$\xi = (Z - Z_b) / \epsilon \quad (7)$$

The dependent variables Y and θ are correspondingly expanded about their outer-zone values at $Z = Z_b$ as

$$Y = Y_b (1 - \epsilon y), \quad \theta = \theta_b - \epsilon \varphi (\theta_b - \theta_0) / Z_b, \quad (8)$$

the negative signs having been selected so that the functions $y(\xi)$ and $\varphi(\xi)$ will be positive, reflecting the fact that Y and T will be less than Y_b and T_b , respectively, in the reaction zone. Equation (8) represents the first term in the expansion of the solution in powers of ϵ in the reaction zone. The boundary conditions that are to be applied for ξ approaching ∞ or $-\infty$ are that the slopes of the inner solutions must match the slopes of the outer solutions. The expansions of (1) and (2) in the inner zone to leading order in ϵ result in the differential equations

$$d^2 y / d\xi^2 = (2\alpha - 1) \Lambda (\theta_b - \theta_0) \exp(-\varphi) / (0.3 Y_b Z_b) \quad (9)$$

and

$$d^2 \varphi / d\xi^2 = \Lambda \exp(-\varphi), \quad (10)$$

where

$$\Lambda = (1.2 / \chi_b) \epsilon [Z_b / (\theta_b - \theta_0)] Y_b C \exp(-T_K / T_b), \quad (11)$$

and α has been set equal to $1/2$ in the first approximation. The difference from the classical Arrhenius problem is that the eigenvalue Λ in (10) depends on Y_b , as seen in (11), thereby necessitating consideration of (9), with an expansion of α about $\alpha = 1/2$, to finally determine the value of Y_b . The profile of species K in the reaction zone thus must be addressed, using the matching conditions

$$\begin{aligned} d\varphi/d\xi &\rightarrow \pm 1 \text{ as } \xi \rightarrow \pm \infty \\ dy/d\xi &\rightarrow 1/Z_b \text{ as } \xi \rightarrow \infty, \quad dy/d\xi \rightarrow -1/(1 - Z_b) \text{ as } \xi \rightarrow -\infty, \end{aligned} \quad (12)$$

the last of which approaches the symmetric condition $|dy/d\xi| = 2$ only as Z_b approaches $1/2$.

In the stretched inner variables, the expansion of α about $\alpha = 1/2$ gives, to leading order in ϵ ,

$$2\alpha - 1 = \frac{T_a}{2T_K} \left[\varphi - \frac{(T_b - T^*) T_K}{T^{*2}} \right], \quad (13)$$

where it has been assumed that T_a and T_K are of the same order of magnitude and that $(T_b - T^*) / T^*$ is of order ϵ . Introducing the parameters

$$a = \frac{T_a c_p W_K (T^* - T_0)}{0.6 Y_b T_K Q Z_b}, \quad b = \frac{(T_b - T^*) T_K}{T^{*2}}, \quad (14)$$

both being taken to be of order unity, then converts (9) to

$$d^2 y / d\xi^2 = a \Lambda (\varphi - b) \exp(-\varphi), \quad (15)$$

so that (10) and (15), with the conditions (12), provide, at leading order, the inner problem that must be solved.

7 Inner Solutions

Equation (10) and its associated matching conditions can be addressed first, independently of (15), since y does not appear there. The resulting problem, which is identical to that of the partial-burning regime [6], results in a symmetric function $\varphi(\xi)$, having a minimum value $\varphi_m = \ln 4$, with the eigenvalue $\Lambda = 2$, the use of which in (11) serves to relate Y_b to Z_b through (6). Equation (15) and its associated matching conditions then finally will serve to determine the value of Z_b for a given strain rate χ_b .

The formulation for T is more accurate than that for Y in that, while the expansion of T in (8) is reasonably well satisfied, that of Y is not, since the value of Y varies over a factor of 4 in the reaction zone [4]. This variation clearly will introduce inaccuracies in (10) and therefore in the resulting solution for φ . Even larger inaccuracies may be expected in the solution of (15) for y . In view of this situation, relatively little additional inaccuracy may be expected to arise from introducing an explicit approximation for $\varphi(\xi)$ into (15), to avoid the necessity of numerical integration. The value of a typically is sufficiently large that changes in y occur mainly in the region where φ is close to its minimum value. The expansion of φ about φ_m , namely $\varphi = \varphi_m + \xi^2/4$, therefore is introduced into (15), to enable the integration to be performed analytically. Application of the matching conditions then results in

$$a^{-1} = \sqrt{\pi} Z_b (1 - Z_b) (4/\pi + \ln 4 - b). \quad (16)$$

Equation (16) provides an expression for χ_b in that, use of the definitions, with $\Lambda = 2$, results in

$$\chi_b = \frac{Z_b T_a T_b^2}{a T_K^2 (T_b - T_0)} C \exp(-T_K/T_b). \quad (17)$$

Equations (14) and (16) imply that $T_b < T_m$, where

$$T_m = T^* [1 + (4/\sqrt{\pi} + \ln 4) T^*/T_K] \quad (18)$$

denotes the maximum value of T_b consistent with $\chi_b > 0$, through terms of order ϵ . If (6) and (16) are employed to eliminate Z_b from (17) in favor of T_b , then it is found that

$$\chi_b = \frac{\sqrt{\pi} T_a T_b^2 (T_b - T_1) (T_b - T_0) (T_m - T_b)}{T_K [2T_b - (T_0 + T_1)]^3 T^{*2}} C \exp(-T_K/T_b) \quad (19)$$

which shows that $\chi_b = 0$ at $T_b = T_0$ and at $T_b = T_m$, while $\chi_b > 0$ for T_b in the range $T_0 < T_b < T_m$. The value of χ_b achieves its critical maximum value, χ_c at $T_b = T_c$, the value of T_b at which $d\chi_b/dT_b = 0$ in this range. Differentiation then shows that, through first order in the small parameter ϵ ,

$$T_c = T^* [1 + (4/\sqrt{\pi} + \ln 4 - 1) T^*/T_K] \quad (20)$$

and

$$\chi_c = 4\sqrt{\pi} \exp(4/\sqrt{\pi} - 1) \frac{T_a T^{*2} (T^* - T_1) (T^* - T_0)}{T_K^2 [2T^* - (T_0 + T_1)]^3} C \exp(-T_K/T^*). \quad (21)$$

The maximum value of χ_b , given by (21), implies a minimum value of the droplet diameter [4] which can be compared with experiment.

8 Results

It has been shown in [4] the extinction diameter of the droplet, d_e is given by

$$(d_e)^2 = \frac{8D_{N_2} [\ln(1 - Z_b)]^4 (1 - Z_b)^2}{\chi_c [\ln(1 + B)]^2}. \quad (22)$$

Table 1: Comparison of measured and predicted values of extinction diameters d_e

Case #	pressure (atm)	O ₂ Vol %	B	T^* K	$\chi_c \text{ s}^{-1}$	d_e (mm) predicted	d_e (mm) measured
1	1	0.21	4.48	808	213	0.238	0.91
2	1	0.18	3.51	803	179	0.29	1.6
3	0.7	0.19	3.43	794	131	0.345	2.3

Here $D_{N_2} = 1.128 \times 10^{-4} \text{ m}^2/\text{s}$ is the coefficient of diffusion, and B is the transfer number. Table 1 shows comparison of predictions with measurements reported in [3]. In view of the aforementioned inaccuracies, numerical comparisons of extinction diameters exhibit significant discrepancies. Besides aforementioned effects, other processes beyond those analyzed here affect the extinction condition significantly. In particular, steady state of the first O₂ addition to the alkali radical has been assumed to be in partial equilibrium in developing the analysis [5], but, although the species formed by this addition, generally termed RO₂, is known to be in steady state at the higher temperatures in the vicinity of T^* , over which (13) applies, it is violated at the extinction point, which occurs at the lowest temperature at which the cool-flame chemistry can support a statically stable diffusion flame. That is, the extinction condition defining d_c occurs at the lowest temperature of the NTC range, where RO₂ formation is proceeding at a finite rate. It therefore would be desirable to extend the present analysis, to include that finite-rate steps, for better comparison with the experimental data on d_c . Since the rate of that step is proportional to [O₂], the resulting predicted dependence of d_c on [O₂] may be expected to be stronger than that obtained from the present theory. In other words, the fact that the rate of the RO₂ formation step is proportional to [O₂] may lead to a prediction that d_c is inversely proportional to [O₂] if that formation step is controlling.

References

- [1] E. Ranzi, P. Gaffuri, T. Faravelli, and P. Dagaut, “A wide-range modelling study of *n*-heptane oxidation,” *Combustion and Flame*, vol. 103, pp. 91–106, 1995.
- [2] A. Cuoci, M. Mehl, G. Buzzi-Ferraris, T. Faravelli, D. Manca, and E. Ranzi, “Autoignition and burning rates of fuel droplets under microgravity,” *Combustion and Flame*, vol. 143, pp. 211–226, 2005.
- [3] V. Nayagam, D. L. Dietrich, P. V. Ferkul, M. C. Hicks, and F. A. Williams, “Can cool flames support quasi-steady alkane droplet burning?” *Combustion and Flame*, vol. 159, pp. 3583–3588, 2012.
- [4] G. Paczko, N. Peters, K. . Seshadri, and F. A. Williams, “The role of cool-flame chemistry in quasi-steady combustion and extinction of *n*-heptane droplets,” *Combustion Theory and Modelling*, vol. 18, pp. 515–531, 2014.
- [5] N. Peters, G. Paczko, R. Seiser, and K. Seshadri, “Temperature cross-over and non-thermal runaway at two-stage ignition of *n*-heptane,” *Combustion and Flame*, vol. 128, pp. 38–59, 2002.
- [6] A. Liñán, “The asymptotic structure of counterflow diffusion flames for large activation energies,” *Acta Astronautica*, vol. 1, pp. 1007–1039, Jul. 1974.