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Effects of Variable Specific Heats on Markstein Lengths and Flamefront Stability

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We develop a variable-property, hydrodynamic theory for freely propagating premixed flames that allows for differing, temperature dependent, specific heats of fuel and product. The influence of this effect on the Markstein number and planar flame stability is explicitly determined.

1. Introduction

Hydrodynamic models of premixed flame propagation have contributed a great deal to the development of combustion theory. They have led to an understanding of the role of thermal expansion on flamefront stability, and have provided a rigorous description of the sensitivity of flame propagation speed to local flow conditions and flamefront curvature, *i.e.*, stretch. These models date back to Darrieus [1] and Landau [2] who, in order to investigate flamefront stability, treated the flame as a front of density discontinuity, propagating with constant velocity relative to the underlying flow. Markstein [3] later suggested a linear dependence of flame speed on curvature, with the sensitivity of that dependence characterized by a phenomenological constant which later came to be known as the Markstein length. Then in the 1980's multi-scale analysis was employed to systematically derive hydrodynamic models from the general conservation laws [4, 5]. These models revealed a linear dependence of flame speed on both curvature and strain, with the combined effects known as flame stretch. The derived Markstein length, as well as the conditions relating the hydrodynamic variables across the flame, exhibit an explicit dependence on the parameters fundamental to flame propagation, such as Lewis number and activation energy, and are free of phenomenological parameters. More recently, these asymptotic models have been extended to account for additional realistic features in order to provide more quantitative accuracy for comparison with experiments. Effects of stoichiometry, non-unity reaction orders and variable transport coefficients were included in [6], and volumetric heat loss was considered in [7]. A model allowing for the interaction of premixed flames with acoustic waves was derived in [8]. These models have been effectively used in a variety of contexts, such as laminar flame speed measurement [9–12], turbulent combustion analysis [13–16], and flame stability under various conditions [17–19].

While several of the most recent models have considered variable conductivity, mass diffusivity and viscosity, none have specifically considered the effects of variable specific heat. Indeed,

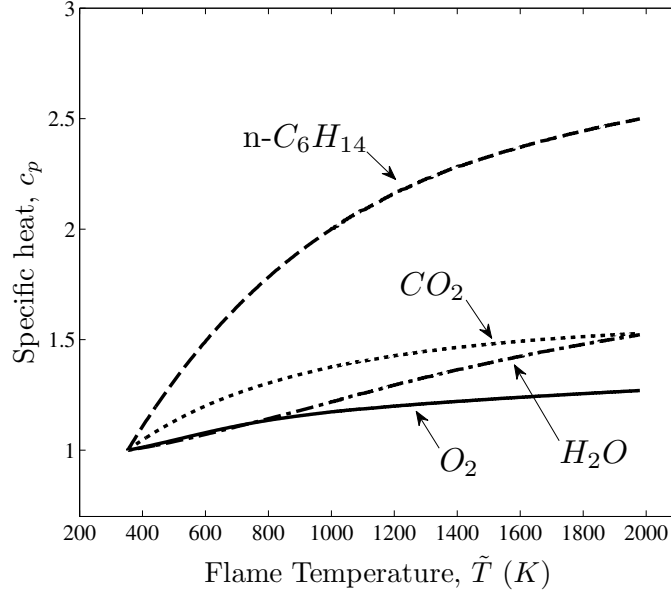


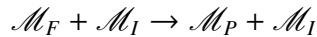
Figure 1: Specific heats for typical gases in combustion, in the unit of the values at an reference temperature of 353 K. Data were computed using thermodynamic database in a detailed chemical reaction mechanism, JetSurf 2.0 mechanism [20]

like the transport properties, the specific heats $c_{p,i}$ of species may vary significantly through the flame as shown in Figure 1, computed using chemkin for a mixture of n-hexane in air. It is seen that specific heat generally increases with temperature, with the values of large-molecule hydrocarbons increasing substantially more than lighter species. Variations in these thermodynamic properties alter the diffusive transport during combustion, which in turn modifies the flame temperature, and hence all of the fundamental flame properties. The importance of being able to accurately prescribe the specific heats of the reactants and products is therefore essential for a satisfactory quantitative description of flame structure, propagation and stability.

With the above considerations, the aim of the present analysis is to extend the hydrodynamic models to account for realistic variations in specific heats. Our results demonstrate the influence of variable specific heats on the flame dynamics in two ways. First, it results in a new effective thermal diffusivity in the expressions relating hydrodynamic variables. Secondly, it modifies the Lewis number effect as a result of the diffusive imbalance caused by the upstream product diffusion, which is a factor seldom addressed in previous studies. We examine these effects on Markstein number as well as the stability of a planar flame front.

2. Formulation

We consider a single-reactant system, *i.e.*, the case when the mixture strength is away from stoichiometry,



where \mathcal{M}_F denotes the fuel, \mathcal{M}_P the product and \mathcal{M}_I the inert. We assume the concentration of the inert is much higher than that of \mathcal{M}_F and \mathcal{M}_P , which is frequently the case in typical combustion system. Under this assumption, the diffusion of \mathcal{M}_I can be neglected, while only the binary diffusion of \mathcal{M}_F and \mathcal{M}_P with respect to \mathcal{M}_I needs to be considered. Therefore, only one variable is needed to represent the mixture composition, *i.e.*,

$$\tilde{Y} \equiv \tilde{Y}_F = \text{constant} - \tilde{Y}_P$$

$$\tilde{D} \equiv \tilde{D}_F = \tilde{D}_P$$

where \tilde{Y}_i and \tilde{D}_i respectively denote the mass fraction and diffusivity of species i .

Following a previous 1-D formulation allowing for variable specific heats by Rogg and Williams [21], we assume the thermal enthalpy (not including chemical enthalpy) of fuel and product to be different from that of the inert, and define the mean thermal enthalpy

$$\tilde{h} = \tilde{Y}_F \tilde{h}_F + \tilde{Y}_P \tilde{h}_P + \tilde{Y}_I \tilde{h}_I$$

where \tilde{h}_i denotes the thermal enthalpy of species i . Here, \sim is used to denote dimensional quantities. Using the identity,

$$\tilde{\nabla} \tilde{h} = (\tilde{h}_F - \tilde{h}_P) \tilde{\nabla} \tilde{Y} + \tilde{c}_p \tilde{\nabla} \tilde{T}$$

where \tilde{T} is temperature, \tilde{c}_p is the mean specific heat, the energy equation written in terms of thermal enthalpy becomes,

$$\tilde{\rho} \frac{D\tilde{h}}{D\tilde{t}} - \tilde{\nabla} \cdot \left(\frac{\tilde{\lambda}}{\tilde{c}_p} \tilde{\nabla} \tilde{h} \right) + \tilde{\nabla} \cdot \left[\left(\frac{\tilde{\lambda}}{\tilde{c}_p} - \tilde{\rho} \tilde{D} \right) (\tilde{h}_F - \tilde{h}_P) \tilde{\nabla} \tilde{Y} \right] = \tilde{q} \tilde{\omega}$$

where $\tilde{\rho}$ and $\tilde{\lambda}$ are the density and thermal conductivity of the mixture, and $\tilde{\omega}$ and \tilde{q} are the reaction rate and heat release of the global one-step reaction.

In the present formulation we adopt an equation of state for the thermal enthalpy. For constant specific heat, it is known that the product of density and thermal enthalpy remains nearly constant under isobaric conditions, *i.e.*

$$\tilde{P} \propto \tilde{\rho} \tilde{h},$$

where the proportionality constant depends on both the ratio of specific heats and the mean molecular weight of the mixture. As combustion proceeds, both these quantities vary with temperature through the flame. Variations of the mean molecular weight through the flame for an n-hexane/air mixture are depicted in Figure 2. The combined effect, as shown in the figure is that the above equation is reasonably valid and is therefore employed as the equation of state in the present formulation. We note that the trend observed in Figure 2, while appropriate for heavy hydrocarbon fuels, is less likely to remain valid for light fuels, such as hydrogen.

The thermal conductivity, viscosity, mean specific heat of the mixture are all allowed to vary, but their ratios, *i.e.*, Lewis number Le and Prandtl number Pr are assumed to be constant, a realistic assumption in general. Previous flame theories have considered constant Lewis number, but with specific heat also assumed constant. However, allowing for variations in specific heat may be more consistent with a constant Lewis number assumption. This is the case for example in a n-hexane flame, as shown in Figure 3, which was generated for a 1-D flame with detailed mechanism. Finally, we assume constant pressure and a low Mach number flow.

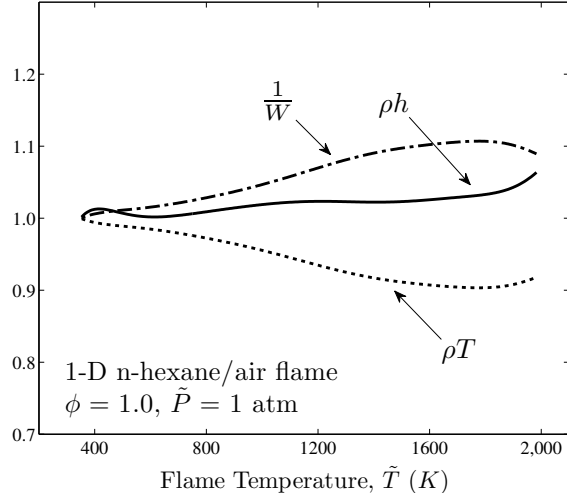


Figure 2: Variation of nondimensional values (*w.r.t* unburned state) of ρh , ρT and $1/W$ in a realistic flame. Data were computed with detailed chemical kinetic mechanism (JetSurf 2.0) using the Premix Code

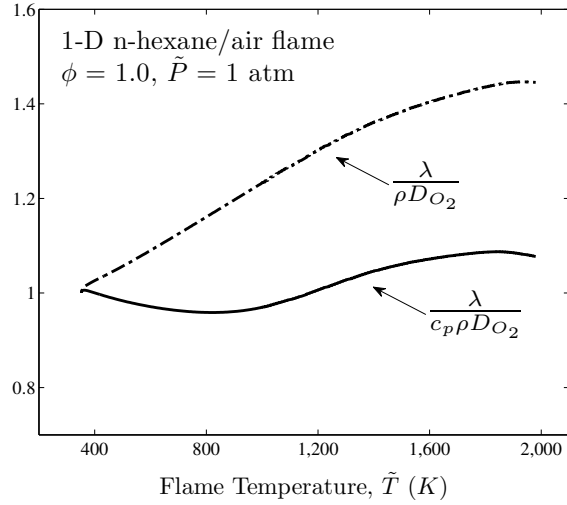


Figure 3: Variation in Lewis number of O_2 in a realistic 1-D n-hexane flame with and without assuming a constant specific heat. Data were computed with detailed chemical kinetic mechanism (JetSurf 2.0) using the Premix Code.

Starting from the full set of conservation laws of combustion, we nondimensionalize thermodynamic variables, species concentrations, and transport properties with respect to their values at the unburned state. The laminar flame speed, \tilde{s}_u^0 , defined as the speed with which a planar flame propagates into the unburned gas is used as a characteristic speed. We employ the multi-scale approach in [5, 6] by nondimensionalizing equations with a hydrodynamic length scale \tilde{L} , and time scale \tilde{L}/\tilde{s}_u^0 . The hydrodynamic scale, \tilde{L} , is typically much larger than flame thickness \tilde{l}_T , defined by $\tilde{\lambda}/\tilde{c}_{p,u}\tilde{\rho}_u\tilde{s}_u^0$ (where subscript u denotes values evaluated at far upstream). The ratio of the two, $\delta = \tilde{l}_T/\tilde{L}$, is typically $\sim 10^{-2}$.

The resulting nondimensional governing equations may be written,

$$\begin{aligned}\rho h &= 1 \\ \frac{D\rho}{Dt} + \rho(\nabla \cdot \vec{v}) &= 0 \\ \rho \frac{DY}{Dt} - \frac{\delta}{Le} \nabla \cdot \left(\frac{\lambda}{c_p} \nabla Y \right) &= -\omega \\ \rho \frac{Dh}{Dt} - \delta \nabla \cdot \left(\frac{\lambda}{c_p} \nabla h \right) + \left(1 - \frac{1}{Le} \right) \delta \nabla \cdot \left[\frac{\lambda}{c_p} Q \nabla Y \right] &= q\omega \\ \rho \frac{D\vec{v}}{Dt} &= -\nabla p + \nabla \cdot \left\{ \frac{\lambda}{c_p} \left[\nabla \vec{v} + (\nabla \vec{v})^T - \frac{2}{3} \mathbf{I}(\nabla \cdot \vec{v}) \right] \right\}\end{aligned}$$

where

$$\begin{aligned}\frac{D}{Dt}() &= \frac{\partial}{\partial t}() + \vec{v} \cdot \nabla() & q &= \frac{\tilde{q}\tilde{Y}_u}{\tilde{h}_u} & Q &= \frac{(\tilde{h}_F - \tilde{h}_P)\tilde{Y}_u}{\tilde{h}_u} & h - 1 &= \frac{\tilde{c}_{p,u}\tilde{T}_u}{\tilde{h}_u} \int_1^T c_p dT' \\ \omega &= Da_c T^\alpha \rho^n Y^n \exp\left(-\frac{T_a}{T}\right) & Da_c &= \frac{\tilde{B}_c \tilde{L}}{\tilde{Y}_u \tilde{\rho}_u \tilde{s}_u^0} \tilde{T}_u^\alpha \tilde{\rho}_u^n \tilde{Y}_u^n & T_a &= \frac{\tilde{E}_a}{\mathcal{R} \tilde{T}_u}\end{aligned}$$

with boundary conditions,

$$\begin{aligned}Y &= 1, \quad h = 1 && \text{far upstream} \\ Y &= 0, \quad h = 1 + q && \text{far downstream.}\end{aligned}$$

We define a total enthalpy,

$$H = h + qY$$

and sum the species and energy the equations we arrive at an reaction-free equation for H ,

$$\rho \frac{DH}{Dt} - \delta \nabla \cdot \left(\frac{\lambda}{c_p} \nabla H \right) = \left(\frac{1}{Le} - 1 \right) \delta \nabla \cdot \left[\frac{\lambda}{c_p} (q + Q) \nabla Y \right]$$

The above equations differ from the formulation by Matalon et al. [6] in two respects. First, it is more convenient in the present formulation to work with an energy equation in terms of thermal enthalpy, rather than temperature. Note also the nondimensional transport coefficient λ/c_p in place of λ . Second, we note an additional term, Q , in the equation for total enthalpy, H , which arises as a result of the imbalance caused by the diffusion of fuel and product.

3. The Hydrodynamic Model

On the hydrodynamic scale \tilde{L} the entire flame is confined to a surface that separates burned gas from unburned gas. A consistent model requires conditions relating the fluid variables across the flame surface, which may be derived using a multi-scale approach. Details of such analyses may be found in [4–6], and therefore only the key features and results of the analysis are presented here.

The analysis assumes a one-step overall reaction characterized by a large activation energy, *i.e.* large Zeldovich number, defined as $Ze = E(\tilde{T}_{ad} - \tilde{T}_u)/\mathcal{R}\tilde{c}_{p,f}\tilde{T}_{ad}^2$ (where \tilde{T}_{ad} is the adiabatic flame temperature and subscript f denotes values evaluated at the flamefront). This limit permits the resolution of the reaction zone, a layer much thinner than the flame thickness, of the order of $O(\delta/Ze)$, as demonstrated in [22]. Integration of conservation equations across the flame zone is also possible by considering the limit $\delta \ll 1$, resulting in conditions relating flow variables across the flame zone [4–6].

Incorporating the effects of variable specific heats, the hydrodynamic model that results may be written

$$S_f = 1 - \delta \left(\gamma_1 + \frac{Ze(Le - 1)}{2} \gamma_2 \right) K$$

$$\llbracket \rho S_f \rrbracket = \delta \frac{\sigma - 1}{\sigma} \gamma_1 K$$

$$\llbracket \vec{n} \times (\vec{v} \times \vec{n}) \rrbracket = \delta \left\{ - \left(\frac{\lambda_f}{c_{p,f}} Pr + \gamma_1 \right) \llbracket \vec{n} \times (\vec{\nabla} \times \vec{v}) \rrbracket + 2Pr \left(\frac{\lambda_f}{c_{p,f}} - 1 \right) (\vec{n} \times (\mathbf{E} \cdot \vec{n}) \times \vec{n}) \right\}$$

$$\llbracket p + \rho(\vec{v} \cdot \vec{n}) S_f \rrbracket = \delta \left\{ \gamma_1 \llbracket \vec{n} \cdot \nabla p \rrbracket + \frac{\sigma - 1}{\sigma} \gamma_1 V_f K + \Gamma \kappa + 2Pr \left(\frac{\lambda_f}{c_{p,f}} - 1 \right) (\vec{n} \cdot \mathbf{E} \cdot \vec{n}) \right\}$$

with right hand side evaluated at the upstream boundary of the flamefront and $\llbracket \rrbracket$ denoting the jump in a quantity across the flame, *i.e.* burned minus unburned values. In the above model, S_f is the flame speed relative to the upstream gas, $\sigma = \tilde{\rho}_u/\tilde{\rho}_b$ the thermal expansion ratio, $K = -\nabla \cdot \vec{n} - \vec{n} \cdot \mathbf{E} \cdot \vec{n}$ the stretch rate, \vec{n} the unit normal to the flame surface pointing towards the burned gas, and \mathbf{E} the strain rate tensor. The constants, γ_1 , γ_2 , γ_3 and Γ , are defined as,

$$\gamma_1 = \frac{\sigma}{\sigma - 1} \int_1^\sigma \frac{\lambda}{c_p z} dz$$

$$\gamma_2 = \frac{1}{\sigma - 1} \int_1^\sigma \frac{\lambda}{c_p z} \left(\int_z^\sigma \frac{\sigma - 1 + Q(z')}{(\sigma - 1)(z' - 1)} dz' \right) dz$$

$$\gamma_3 = \int_1^\sigma \frac{\lambda}{c_p} dz$$

$$\Gamma = (\sigma - 1)\gamma_1 - (2Pr - 1)\gamma_3 + 2Pr(\sigma - 1) \frac{\lambda_f}{c_{p,f}}$$

Comparing the above expressions to those derived previously [6] in two ways. First, the λ in [6] is replaced by a new effective thermal diffusivity term λ/c_p . In most gasses, c_p is known to increase with temperature, resulting in a reduced magnitude of such terms. Second, by allowing different specific heats for fuel and product, the constant γ_2 is further modified: it increases with

Q . Since γ_2 directly represents the effect of Lewis number, this result suggests that when $Q > 0$, *i.e.*, the specific heat of fuel is greater than that of product, the effect of Lewis number is amplified; and vice versa. Additionally, the present result reduces to that in [6] by setting $c_p = 1$ and $Q = 0$, as well as the result in [5] by further setting $\lambda = 1$.

Markstein Number

The expression for Markstein number may be written

$$Ma = \frac{\sigma}{\sigma - 1} \int_1^\sigma \frac{\lambda}{c_p z} dz + \frac{Ze(Le - 1)}{2(\sigma - 1)} \int_1^\sigma \frac{\lambda}{c_p z} \left(\int_z^\sigma \frac{\sigma - 1 + Q(z')}{(\sigma - 1)(z' - 1)} dz' \right) dz.$$

If fuel and product have equal specific heats, then $Q = 0$ and the only modification to the result obtained in [6] is a new effective diffusivity λ/c_p suggesting a decrease in magnitude. However, when fuel and product have different specific heats, $Q \neq 0$, an additional modification to the Lewis number effect is observed. In particular, the Markstein number becomes more sensitive to Lewis number when the specific heat of the fuel is larger than that of the product, $Q > 0$, while the reverse is true when specific heat of fuel is less than that of the product, $Q < 0$.

$$Ma_b = \frac{1}{\sigma - 1} \int_1^\sigma \frac{\lambda}{c_p z} dz + \frac{Ze(Le - 1)}{2(\sigma - 1)} \int_1^\sigma \frac{\lambda}{c_p z} \left(\int_z^\sigma \frac{\sigma - 1 + Q(z')}{(\sigma - 1)(z' - 1)} dz' \right) dz.$$

Flamefront Stability

The above hydrodynamic model has been used to investigate the linear stability analysis of a planar flame yielding the following dispersion relation for the growth rate $\hat{\omega}$ for small disturbances

$$\hat{\omega} = \hat{\omega}_0 k - \delta \{B_1 + Ze(Le - 1)B_2 + PrB_3\} k^2$$

where k is the wavenumber and the coefficients are given by

$$\begin{aligned} \hat{\omega}_0 &= \frac{1}{\sigma + 1} \left(\sqrt{\sigma^3 + \sigma^2 - \sigma} - \sigma \right) \\ B_1 &= \frac{\sigma [\gamma_1(2\hat{\omega}_0 + \sigma + 1) + \gamma_3]}{2(\hat{\omega}_0(\sigma + 1) + \sigma)} \\ B_2 &= \frac{\gamma_2 [\sigma(\hat{\omega}_0 + 1)(\hat{\omega}_0 + \sigma)]}{2(\hat{\omega}_0(\sigma + 1) + \sigma)} \\ B_3 &= \frac{\sigma \left[(\sigma - 1) \frac{\lambda_f}{c_{p,f}} - \gamma_3 \right]}{\hat{\omega}_0(\sigma + 1) + \sigma}, \end{aligned}$$

which are all positive. The expressions above are identical to those previously derived in [6], and thus influence of variable specific heats are contained solely in the re-defined integral expressions for γ_i . Thus, the leading order term $\hat{\omega}_0$ is the Darrieus-Landau instability, and the correction terms, all proportional to k^2 , correspond to thermal, mass and viscous diffusion. The smaller magnitude of B_1 , B_2 and B_3 which result from increased values of c_p , suggests that variable specific heat can destabilize the flame, consistent with the numerical study by Mukunda and Drummond [23].

As with the Markstein number, different values of specific heats of fuel and product only serve to modify the Lewis number effect. In particular, when $\tilde{h}_F > \tilde{h}_P$, the effect of Le is enhanced, and when $\tilde{h}_F < \tilde{h}_P$, the effect of Le is diminished.

4. Concluding Remarks

We have extended the hydrodynamic model of premixed flames to allow for variable specific heat, providing a more realistic description of flame propagation. Expressions for the Markstein length and the dispersion relation for a planar flame have been derived, and their dependence on variable specific heats was explicitly determined. When the fuel and product have the same specific heat, variations in this thermodynamic property are found to reduce the magnitude of the Markstein number, and de-stabilize planar flames in mixtures with Lewis number exceeding a value substantially less than unity. For very small Lewis numbers, variable specific heat may have a stabilizing effect. When the specific heats of fuel and product differ, further modification of the Lewis number effects arise due to a diffusive imbalance. In particular, if the fuel has a larger specific heat than the product, the effect of the Lewis number becomes more significant on both Markstein length and flamefront stability. The reverse is true when specific heat of product exceeds that of fuel.

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