Analysis of Jet Ignition for Multistep Kinetics

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1 Background

It has been observed that in the event of a sudden release of high pressure hydrogen in the atmosphere, ignition may occur during the early, transient process. While according to Astbury & Hawksworth [1] there were earlier anecdotal reports, the first systematic study of the jet ignition phenomenon is due to Wolański & Wójcicki [2]. Jet ignition plays an ambiguous role in hydrogen safety, clearly increasing risks in some circumstances, but potentially lowering the risk of detonation.

Various ignition mechanisms have been suggested, the leading one being diffusion ignition. During the early part of the release, a complex shock structure is formed [3, 4]: the multidimensional equivalent to the shock tube problem. Here, the crucial feature is the contact surface initially present, separating shock-heated air from expansion-cooled hydrogen. In the near field, diffusion occurs, with heat conduction from hot air into cold hydrogen, with hydrogen diffusing into air, and air into hydrogen. Near the interface, there are concentration gradients and a temperature gradient, from pure cold hydrogen to pure hot air. Where fuel and reactant are both present, some reaction takes place, at a rate that depends upon concentrations and temperature, but is strongly temperature-dependent. Ignition at the interface has been analyzed by Liñán & Crespo [5] for unit Lewis number, and for arbitrary Lewis number by Liñán and Williams [6]. These studies considered uniform pressure (apart from an appendix in the latter). In the hydrogen jet, when in open air, because the shock structure grows in three dimensions, expansion occurs at the contact surface [7], which will lead to a decrease in temperature hence reactivity.

A previous study [8] extended the analysis [5, 6] to account for expansion, and led to identification of two thresholds, respectively a maximum fuel Lewis number, and a maximum expansion rate. However, that analysis considered a single step Arrhenius model, which is not realistic and does not account for chain branching. The current study extends the analysis to arbitrary multistep kinetics, as long as one key assumption is realistic: that initiation steps are much slower than the main reaction.

2 Formulation and the single step results

The formulation is as in Liñán & Crespo [5], plus a spatially uniform expansion. Mass, momentum and energy are conserved, including the effect of chemistry. A mass-weighted spatial coordinate is

introduced, satisfying continuity. Momentum leads to pressure being spatially uniform, since in a frame of reference instantaneously attached to the diffusion region, Mach numbers are small, and such a frame is approximately inertial. Thus expansion, absent in Liñán & Crespo's model, is also spatially uniform; indeed the diffusive length is small compared with the length scales associated with the shock structure. Initially, there is little chemistry and the problem is reduced to diffusion: the so-called (chemically) frozen solution. A perturbation added to the frozen solution accounts for the small effect of chemical reaction, which in the single step problem, is of the order of the inverse activation energy. A perturbation growing to infinity in finite time characterizes ignition. Otherwise ignition is inhibited.

In the absence of expansion, frozen flow is self-similar. However, expansion introduces a time hence a length scale. On a time scale smaller than the reaction time the planar frozen flow problem is reduced to the energy equation, and mass diffusion. For diffusivities inversely proportional to the square of density, using a density weighed spatial coordinate x related to the original coordinate \hat{x} by

$$x = \frac{1}{\rho\sqrt{\alpha}} \int_0^{\hat{x}} \rho d\hat{x} \tag{1}$$

in which α is the heat diffusivity, denoting the fuel and oxidant Lewis numbers as Le_F and Le_O , mass and momentum are satisfied. Introducing the similarity variable $\eta = x/2\sqrt{t}$ of the homogeneous problem, the frozen flow problem consists of diffusion of heat and species:

$$4t\frac{\partial y_k}{\partial t} - 2\eta\frac{\partial y_k}{\partial \eta} = \frac{1}{Le_k}\frac{\partial^2 y_k}{\partial \eta^2} \tag{2}$$

$$4t\frac{\partial T}{\partial t} - 2\eta\frac{\partial T}{\partial \eta} = \frac{\partial^2 T}{\partial \eta^2} + \frac{4t(\gamma - 1)T}{\gamma p}\frac{dp(t/t_0)}{dt}$$
(3)

in which y_k is the mass fraction of species k, Le_k is the Lewis number for species k, T is temperature, p is a dimensionless pressure, and t_0 is the ratio of the time scale associated with expansion to the yet arbitrary time scale otherwise used. At t = 0, p = 1. Boundary conditions for $\eta \to -\infty$ are $y_k \to 0$, except $y_F \to 1$ and $T \to T_F$. For $\eta \to -\infty$ the boundary conditions are $y_k \to 0$, except $y_O \to 1$, and $T \to T_O$. Initial conditions match the boundary conditions. The solution is

$$y_O = \frac{1 + \operatorname{erf}(\eta \sqrt{Le_O})}{2}, \quad y_F = \frac{1 - \operatorname{erf}(\eta \sqrt{Le_F})}{2}, \quad T = \left\{ T_O + \frac{(T_O - T_F)[\operatorname{erf}(\eta) - 1]}{2} \right\} p^{(\gamma - 1)/\gamma} \tag{4}$$

In the frozen flow solution, mass fractions of intermediate reactants remain zero.

For single step, summarizing previous results, [8] perturbations of the order of the inverse activation energy are added to the frozen solution. Because activation energy is high, the effect of temperature on the reaction rate overwhelms that of mass fractions. Focusing upon where temperature only departs from the hot side temperature by order of the inverse activation energy, η is rescaled by $[1 - \text{erf}(\eta)]/2 = \epsilon \xi/(1 - T_F/T_O)$, in which $\epsilon = T_O/T_a << 1$, with T_a being the activation temperature, where chemistry is fastest and where oxidant concentration is largest. However little fuel is present, slowing down chemistry, but not enough to compensate the effect of temperature in the exponential.

If $Le_F = 1$, the contribution of advection-diffusion to both fuel and temperature perturbations occur at order ϵ . For $Le_F < 1$ by order unity, fuel concentration brought in by diffusion in the region where temperature departs from the hot side temperature $O(\epsilon)$ is $O(\epsilon^{Le_F})$. Consumption by chemistry is then negligible. For $Le_F > 1$, fuel brought in by diffusion is still at order ϵ^{Le_F} , now of magnitude smaller than what chemistry at order ϵ would consume. Thus chemistry is limited to $O(\epsilon^{Le_F})$, even though in the Arrhenius exponential, the temperature drop due to diffusion remains $O(\epsilon)$. In all three cases, if



Figure 1: Solution T' for $\xi \to \infty$ to Eq. (5) for β less than 1, with values from 0 to 0.6 at intervals 0.1, from left to right. Turning points at the right end of each curve yield critical Δ values.

time is scaled such that chemistry and diffusion have the same magnitude, the transient term is small compared with diffusion. The perturbation equations become quasi-steady, with time only appearing as a parameter. For $Le_F - 1 = O(-1/\log \epsilon)$, the perturbation equations for temperature T' and fuel mass fraction can be combined [5]. in which Q is the heat release, b is the reaction order for fuel, and $\epsilon^{Le_F-1} = 1/l$ with l of order unity. Pressure has been assumed to drop slowly with respect to time scaled by τ , such that $p = 1 - \epsilon \alpha t + O(\epsilon^2)$ and $\alpha = -(\gamma - 1)dp/\gamma dt$. Thus $\alpha > 0$ if pressure drops. Defining $\beta = c_p(T_O - T_F)l/Q$, the ratio of the hot air temperature to the adiabatic flame temperature of the stoichiometric mixture initially at the cold fuel temperature, which is < 1, and introducing $\Delta = t \exp(-\alpha t)$, the problem becomes:

$$\frac{-\xi^2}{\Delta} \frac{d^2 T'}{d\xi^2} = (\xi - \beta T')^b \exp\left(T' - \xi\right)$$
(5)

Time is scaled by

$$\tau = \left(1 - \frac{T_F}{T_O}\right)^{bLe_F} \frac{(2\eta^*)^{2+b(1-Le_F)} Le_F^{b/2} \epsilon^{2-bLe_F}}{\pi^{b(Le_F-1)/2} Qk} \exp\frac{1}{\epsilon}, \quad \text{with} \quad \eta^{*2} = -\log\frac{2\eta^* \epsilon \sqrt{\pi}}{1 - T_F/T_O} \tag{6}$$

For $\xi = 0$, T'(0) = 0. Indeed far away no fuel is present hence no reaction. From matching with the main diffusion zone, $dT'/d\xi \to 0$ for $\xi \to \infty$. A second order ordinary differential equation in ξ follows in which time only appears as a parameter. If the rate of pressure drop is order unity, chemistry is exponentially small. If it is smaller than ϵ , its effect is negligible; the problem is reduced of Liñán & Crespo [5] for Le = 1. For an expansion rate of $O(\epsilon)$, Eq. (5) is as in Liñán & Crespo [5], but for Δ now equal to $t \exp -\alpha t$ instead of simply t. This two point boundary value problem with non-Lipschitz boundary condition at $\xi = 0$ is solved using a shooting method. As shown in Fig. 1 [5], for $\beta < 1$, two solutions exist to Eq. (5) as long as $\Delta < \Delta^*$ but for larger values there is no solution. However, the upper branch has no physical meaning [5]. For $\Delta \to \Delta^*$, chemistry becomes very fast, and the scaling leading to Eq. (5) breaks down. Ignition takes place at the finite time corresponding to Δ^* if such a time exists. If there is no expansion, ignition occurs at $t = \Delta^*$. For $\beta > 1$ there is no turning point. Instead, solutions exist for all values of Δ . A weak front moves from the hot side into cold hydrogen, eventually quenched by expansion. $\beta = 1$ determines a critical l, hence a critical fuel Lewis number:

$$Le_F^* = 1 - \frac{\log Q/c_P(T_O - T_F)}{\log \epsilon}$$
⁽⁷⁾

 $\Delta(t) = t \exp(-\alpha t)$ has a maximum $\Delta_{\max}(\alpha) = 1/\alpha e$, for $t = 1/\alpha$. No time exists resulting in a higher Δ^* . Thus, for $Le_F < Le_F^*$, ignition occurs only if $\Delta^*(Le_F) \le 1/\alpha e$. If expansion is faster than

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Figure 2: Left: Source term s due to initiation; right: positive eigenvalue of A.

this critical value, no ignition takes place. For $Le_F > Le_F^*$, expansion results in a temperature drop that becomes larger than the inverse activation energy before ignition can occur.

The reaction rate peaks on the hot side. For near unity fuel Lewis number, fuel consumption is of the same order as supply by diffusion. For smaller Lewis numbers, consumption is negligible compared with supply and temperature becomes the limiting parameter. For larger Lewis numbers, chemistry can consume more fuel than diffusion provides; the temperature increase is smaller than the inverse activation temperature. The current results are consistent with experiments showing a clear relationship between the size of the leak and the expansion rate, with a larger hole leading to a slower expansion [1,2].

3 Multistep kinetics

Generalization for complex kinetic schemes such as in Ref. [9] (used in results below) requires reformulating the perturbation problem for complex schemes, replacing high activation energy by a different approach. Before scaling time, conservation of species k is

$$\frac{\partial y_k}{\partial t} - \frac{\eta}{2t} \frac{\partial y_k}{\partial \eta} - \frac{1}{4tLe_k} \frac{\partial^2 y_k}{\partial \eta^2} = \frac{1}{\rho} \Sigma \omega_k \tag{8}$$

The frozen solution assumed time scaled such that source terms ω_k are negligible. At leading order there is only diffusion so that initially absent intermediate species remain absent. Thus reactants affect rates at leading order, while intermediate species, as a perturbation. Initiation steps depend only upon leading order temperature and reactant mass fractions. However these steps are slow compared with rates involving intermediate species, and the termination step involving H and OH is even faster. Writing rates $\omega_{ij} = K_{ij}y_i^m y_j^n$, perturbations are introduced of order $\epsilon = K_{il}/K_{ij} << 1$, in which *i* and *l* are reactants, and *j* is a typical intermediate for which n = 1. Then both ω_{ij} and ω_{il} are $O(\epsilon)$ and if time is scaled by $1/K_{ij}$, for intermediate species *k*:

$$\frac{\partial y_k^{(1)}}{\partial t} - \frac{\eta}{2t} \frac{\partial y_k^{(1)}}{\partial \eta} - \frac{1}{4Le_k t} \frac{\partial^2 y_k^{(1)}}{\partial \eta^2} = \frac{1}{\rho} \Sigma_i a_{ik} y_i^{(1)} + \frac{1}{\rho} a_t y_i^{(1)} y_j^{(1)} + \frac{s_k}{\rho}$$
(9)

in which index *i* refers to intermediate species and *r* to a reactant, with $a_{ik}(\eta) = K_{ik}y_r^{(0)}$, rates in which mass fraction perturbations occur at a power greater than unity have been omitted, a_k is the rate of the termination step and s_k corresponds to an initiation rate depending upon leading order reactant mass fractions, hence only of η . At infinity, boundary conditions are zero.

For typical mechanisms [9], source s is nonzero in only two equations, with value shown in Fig. 2, for a pressure ratio of 50 and ambient initial temperature. Only one of the eigenvalues $A = a_{ij}$ is positive in



Figure 3: Evolution of y_H (right peak) and y_{H2O} (left peak). Left: early times, middle: intermediate times, right: late times.



Figure 4: Evolution of y_O (interrupted) and y_{OH} . Left: early times, middle: intermediate times, right: late times.

an intermediate range of values of η shown on the right in Fig. 2. The positive eigenvalue corresponds to chain-branching. Figure 2 shows both chain-branching and the source due to initiation peaking in the warm air region.

Finally, for temperature, again with zero boundary conditions at infinity,

$$\frac{\partial T^{(1)}}{\partial t} - \frac{\eta}{2t} \frac{\partial T^{(1)}}{\partial \eta} - \frac{1}{4t} \frac{\partial^2 T^{(1)}}{\partial \eta^2} = \Sigma q_k + \frac{(\gamma - 1)T^{(0)}}{\gamma p} \frac{dp}{dt}$$
(10)

Equations (9) are solved numerically. They are coupled through the reaction terms, which are stiff. Matrix a_{ij} is a function of η only but not independently of time. It can be inverted once and for all for discretized values of η . The numerical solution uses a split scheme in which at each time step the coupled linear reaction problem is solved by projecting upon eigenmodes, advancing in time and reconstructing. The nonlinear term only involves two species. Is is solved using second-order backward integration, which is absolutely stable. Here backward integration only requires solving quadratics. The uncoupled diffusion problem is solved dividing into homogeneous and non-homogeneous parts. The latter has a solution proportional to time, while the former is expressed as a series solution using Hermite polynomials. This entails projecting the solution at t_n onto the Hermite base in function space, advancing in time, and reconstructing at t_{n+1} . That approach takes advantage of natural properties of Eq. (9), leading to an efficient and accurate overall solution.

4 **Results**

Results for the same case described above are shown in Figs. 3 and 4. They show initially only initiation, starting rapidly, for η around 1. Then chain-branching starts slowly to take place. While the latter grows approximately linearly, chain-branching approaches exponential growth, and peaks move left, initially

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close to $\eta = -1$, which is into cold hydrogen, and at later times, closer to $\eta = -0.5$. Initiation plays a key role in the overall ignition time, confirming the importance of the Lewis number of both H₂ and H, which is even lower. Indeed the latter plays a key role in shifting the reaction from the initiation region to the chain-branching region. That chain-branching is observed to peak in a range where η is somewhat negative may be associated with presence of OH radicals, which according to the figure are essentially absent for $\eta > 0$ at later times. For a pressure ratio of 500, $\eta = -0.5$ corresponds to a temperature of 780 K.

5 Conclusion

A previous analysis [8] pointed toward the fuel Lewis number as to why jet ignition only affects hydrogen but no hydrocarbon fuels. An extension of that analysis can handle arbitrary complex schemes, as long as initiation is slow compared with main reaction rates. The approach still considers whether initially incipient chemistry in the diffusion layer at the interface between cold hydrogen and warm air results in an increase in temperature, or if this increase is overwhelmed by expansion. results confirm the role of the high mass diffusivity of hydrogen, but also of that of radical H.

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References

- [1] Astbury, G. R. & Hawksworth S.J. (2007). Spontaneous Ignition of Hydrogen Leaks: A Review of Postulated Mechanisms. International Journal of Hydrogen Energy, 32:2178-2185.
- [2] Wolański, P. & Wójcicki, S. (1973). Investigation into the Mechanism of the Diffusion Ignition of a Combustible Gas Flowing into an Oxidizing Atmosphere. Proc. Combust. Institute, 14:1217-1223.
- [3] Radulescu, M. I. & Law, C.K. (2007). The Transient Start of Supersonic Jets. J. Fluid Mech., 578:331-369.
- [4] Liu, Y.F., Tsuboi, N., Sato, H., Higashino, F. & Hayashi, A. K. (2007). Numerical Analysis of Auto-ignition in High Pressure Hydrogen Jetting into Air. Proc. Combust. Inst., 31:1217-1225.
- [5] Liñán, A. & Crespo, A. (1976). An Asymptotic Analysis of Unsteady Diffusion Flames for Large Activation Energies. Combustion Science and Technology, 14:95-117.
- [6] Liñán, A. & Williams, F.A. (1993). Ignition in an Unsteady Mixing Layer Subject to Strain and Variable Pressure. Combustion and Flame, 95:31-46.
- [7] Maxwell. B. M. (2010). One-Dimensional Model for Predicting Ignition During an Accidental Release of Pressurized Hydrogen into Air, Master's Thesis, University of Ottawa.
- [8] Rezaeyan, N., Bauwens, L., Radulescu, M., Fachini, F.F. (2011). Influence of Lewis Number and Expansion on Jet Ignition, 23d ICDERS, Irvine, CA.
- [9] Saxena, P. and and Williams, F.A. (2006). Testing a small detailed chemical-kinetic mechanism for the combustion of hydrogen and carbon monoxide. Combustion and Flame, 145(1-2):316–323, 2006.