

## BEHAVIOR OF METHANE-OXYGEN-NITROGEN MIXTURES NEAR FLAMMABILITY LIMITS

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Results of the detailed calculations using one-dimensional adiabatic premixed flame model for mixtures near inflammable compositions are reported. The effect of nitrogen as a diluent on the flame structure and speed are studied for stoichiometric and fuel-lean mixtures of methane and oxygen. The results indicate that while a fundamental limit in terms of a cut-off composition may not exist for the mathematical solution, the numerical solutions show an asymptotic limiting behavior as extreme compositions are reached. An attempt is made to explain the limits on the basis of rapid depletion of radical species and a steep increase in the flame thickness. Oscillations—which sometimes are said to indicate inflammability limits—are found to be of numerical origin.

### Introduction

Although the phenomenon of flammability limits is well established in mixtures of fuel and oxidizer under various conditions, the actual cause of these limits remains still a subject of considerable debate. Flammability limits are found in the laboratory for all fuel-oxidant systems that do not decompose themselves exothermically, eg. hydrazine or ozone. Almost all the existing theories on flammability limits rely upon the experimental conditions for explaining the limits. The explanations include various physical phenomena such as heat loss, preferential diffusion, natural convection, flame stretch and chemical kinetics. However, most investigators appear to favor the heat loss (conductive or radiative) to be the major factor for flame extinction. Many reviews are available on the subject.<sup>1,2,3</sup>

The explanations offered by different authors for flammability limits in the same apparatus differ from each other. While Bregeon et al<sup>4</sup> think that the extinction in a downward propagating flame is due to the formation of cellular flames and the heat loss from the cellular flamelets thereof, Strehlow<sup>5</sup> proposed the complex free convective mechanism wherein the gases close to the wall move downwards and gases in the center move upwards. Lewis and von Elbe<sup>6</sup> attributed flame stretch as the cause of a flammability limit. Spalding,<sup>7</sup> Mayer,<sup>8</sup> Berlad

and Yang<sup>9</sup> and Gerstein and Stine<sup>10</sup> have argued that heat loss is the primary cause for existence of limits. Clearly, views on the existence of a fundamental flammability limit for premixed gases independent of the experimental apparatus are divergent. A careful examination suggests that the literature is devoid of any strong theoretical results predicting the onset of an inflammable regime or the insolubility of equations for the classical one-dimensional adiabatic flame model. It is yet uncertain whether every combustible mixture for specified temperature and pressure has an intrinsic limiting composition just as for a given composition and environment it has a unique burning velocity, or the experimentally observed limit is only 'apparent.' Gerstein and Stine<sup>10</sup> integrated the flame equations assuming a single-step Arrhenius kinetics for diluted mixtures and found that a limiting concentration independent of the experimental apparatus, called the 'fundamental limit,' could not be defined. However, the authors appear to have stopped at fuel concentrations close to that of experimentally observed limits, (about 4% CH<sub>4</sub>) while it is in fact possible to calculate the flame structure using full kinetics for compositions considerably leaner than the observed lean-limit compositions. More recently, Carter, Cherian and Dixon-Lewis<sup>11</sup> have made detailed calculations of one-dimensional flame propagation of Hydrogen/Air mixtures and found the existence of an oscillatory solution beyond the rich flammability limit. Though they could not predict the point of extinction, they correlated the limit of flammability to the onset of unstable combustion.

Interestingly, most of the workers have devoted secondary importance to chemical kinetic effects for

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near-limit phenomena. It is known that chemistry indeed plays an important role in mixtures of extreme stoichiometry and investigations including full kinetics would certainly be rewarding. In the present paper, an attempt is made to study the behavior of methane-oxygen-nitrogen mixtures around their observed flammability limits considering realistic transport fluxes and a well established detailed chemistry scheme. The results are presented with the percentage of  $N_2$ , a diluent, as a parameter for stoichiometric and fuel-lean mixtures. Mixtures of dilution over a range including the flammable region to far above that of experimentally observed limits have been studied in an effort to understand whether a cut-off composition could be defined as a limiting point for flame propagation.

### The Governing Equations and Computational Procedure

In the classical flame theory, the assumptions and the corresponding equations describing the time-dependent propagation of a one-dimensional laminar premixed flame are now standard. The conservation equations for a reacting gaseous mixture consisting of  $N_s$  number of distinct chemical species are,

$$\text{Species: } \partial Y_i / \partial t = -\partial J_i / \partial \psi + \dot{\omega}_i'' / \rho \quad (i = 1, \dots, N_s) \quad (1)$$

$$\text{Energy: } \partial H / \partial t = \partial / \partial \psi [k\rho / c_p (\partial H / \partial \psi)] - \sum_{i=1}^{N_s} \partial / \partial \psi (h_{i1} [J_i + k\rho / c_p (\partial Y_i / \partial \psi)]) \quad (2)$$

where  $\rho$  is the mass density,  $T$  the temperature,  $k$  the thermal conductivity,  $c_p$  the specific heat at constant pressure, and  $H$  the total enthalpy of the mixture<sup>1</sup>.  $Y_i$ ,  $h_i$ ,  $J_i$  and  $\dot{\omega}_i''$  are respectively the mass fraction, enthalpy, diffusional mass flux and chemical reaction rate of the  $i$ -th species. Here the distance coordinate  $x$  has been transformed as  $\psi = \int \rho dx$ . The boundary conditions for Eqs. (1-2) are given at the burnt and the unburnt ends:

$$\psi \rightarrow -\infty : Y_i \rightarrow Y_{ib} \text{ and } T \rightarrow T_b \quad (3)$$

$$\psi \rightarrow +\infty : Y_i \rightarrow Y_{iu} \text{ and } T \rightarrow T_u \quad (4)$$

In the split operator method, the diffusional and chemical operators,  $\nabla_d$  and  $\nabla_r$  respectively, in Eqs. (1-2) are separately written as:

$$\partial Y_i / \partial t = \nabla_d Y_i + \nabla_r Y_i \quad (5)$$

$$\partial H / \partial t = \nabla_d H \quad (6)$$

The Eqs. (3-6) are integrated in two separate steps. First, the chemistry part is solved by an implicit scheme after quasilinearization to get the corrections due to reactions alone for  $Y_i$  and  $T$  from the following equations:

$$Y_i^{n+1/2} = Y_i^n + \nabla_r Y_i^{n+1/2} \Delta t \quad (7a)$$

$$H^{n+1/2} = H^n \quad (7b)$$

where the superscript  $n$  refers to the time level and  $\Delta t$  is the timestep. Then the diffusion part is solved by an explicit scheme to obtain the corrections due to diffusion process alone:

$$Y_i^{n+1} = Y_i^{n+1/2} + \nabla_d Y_i^{n+1/2} \Delta t \quad (8a)$$

$$H^{n+1} = H^{n+1/2} + \nabla_d H^{n+1/2} \Delta t \quad (8b)$$

Thus the solution is advanced to the next time level and the flame speed is computed from the new profiles. Starting from an assumed initial profile ( $n = 0$ ) for  $Y_i$  and  $T$ , the solution is time-marched until a steady state is reached i.e., the flame speeds of successive time levels are same. More details of the numerical scheme and its validation may be found in an earlier work.<sup>12</sup> The transport properties are calculated using the formulas taken from Brokaw's report<sup>13</sup> with the molecular parameters given by Warnatz.<sup>14</sup>  $N_2$  was treated as an inert and the chemical kinetics for the  $CH_4/O_2$  was represented by a complex kinetic scheme<sup>15</sup> involving a set of 14 species and 29 elementary, reversible reactions. The reverse reaction rates were obtained from the forward rates and the equilibrium constant calculated from the thermodynamic data of the species.

### Results and Discussion

The computations were made for a fixed volumetric ratio of  $CH_4/O_2$  and at different extents of dilution by varying the nitrogen percentage as a parameter. The unburnt mixture was taken at a temperature of 298 K and at atmospheric pressure. Calculations were made for two ratios of  $CH_4/O_2$ , 0.5 and 0.4 by volume, with  $N_2$  dilution varying from 71-92%. Figure 1 shows the variation of flame speed, flame thickness and adiabatic flame temperature as a function of nitrogen percentage in the mixture. The flame thickness was calculated as that spatial region which was within 2% of the temperatures between the hot and the cold ends. It may be seen that the flame thickness increases sharply after about 85%  $N_2$  and the flame speed decreases to very low values. For example, a 2% increase in dilution is found to produce an increase of 200% in flame thickness around 86%  $N_2$  while the same

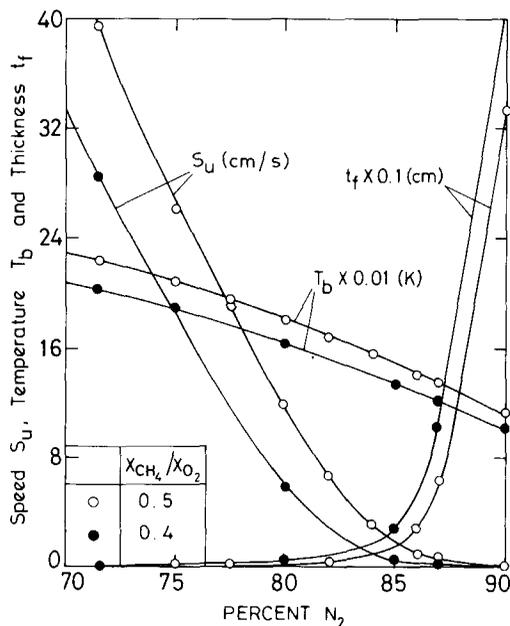


FIG. 1. Variation of Flame speed, Flame thickness and adiabatic flame temperature for different N<sub>2</sub> percentages.

amount of dilution increases the thickness by 1000% around 92% N<sub>2</sub>. This steep increase in the flame thickness calls for an increasingly large number of grid points to satisfy spatial resolution (for example, at 92% N<sub>2</sub>, about 500 equally spaced grids were required to obtain a solution independent of grid size) thereby imposing a limitation on numerical calculations for higher dilutions. This increase in thickness could be probably attributed to the very low reactivity of the mixture at high dilutions with the inability to sustain a reaction front and the domination of diffusion fluxes. Nevertheless, it was found that a steadily propagating flame could be computed to virtually any dilution of nitrogen although the flame speed becomes extremely low and no limiting phenomenon could be observed by further increasing the percentage of nitrogen.

One seemingly interesting and rather unexplored aspect of the near-limit flames is the behavior of intermediate species. In a complex chemical reaction, the reaction rates depend strongly on the concentrations of radical species present in the system. In the reaction scheme used for the current calculations, no direct reaction between CH<sub>4</sub> and O<sub>2</sub> is included. Hence, the reaction can occur only through the intermediate species. The initial profiles of most of the species were given a linear variation from cold boundary to the hot boundary values. No peaks were provided in the initial profiles for any species. However, the intermediate radicals

always picked up a peak in concentration around the flame zone, characteristic of the typical flame profile. It was found from the computations that the mass fractions of radicals decrease considerably with increase in dilution. Figure 2 shows the peak values of the mass fractions of all the intermediate species plotted at different nitrogen percentages. It can be seen that beyond about 82%, there is a tendency for sharp decrease in the mass fraction of most of the species, except H<sub>2</sub> and CO. Corresponding to the decrease in concentration of these species, a sharp increase in the flame thickness can also be noticed from the Fig. 1. It is important to note that this happens to be the range around which the limits are observed experimentally.<sup>4</sup> Probably, radical depletion might not be the single reason for extinction, but the current results indicate a steep drop in chemical activity beyond the apparent limit. Obviously, any secondary effect such as cellular flame formation is likely to perturb the weak flame front and promote extinction around this dilution of the mixture.

The profiles of H atom mass fraction as a function of nondimensional temperature  $\tau = (T - T_w)/(T_b - T_w)$  for various N<sub>2</sub> dilutions are shown in the Fig. 3. The profiles of other intermediate species

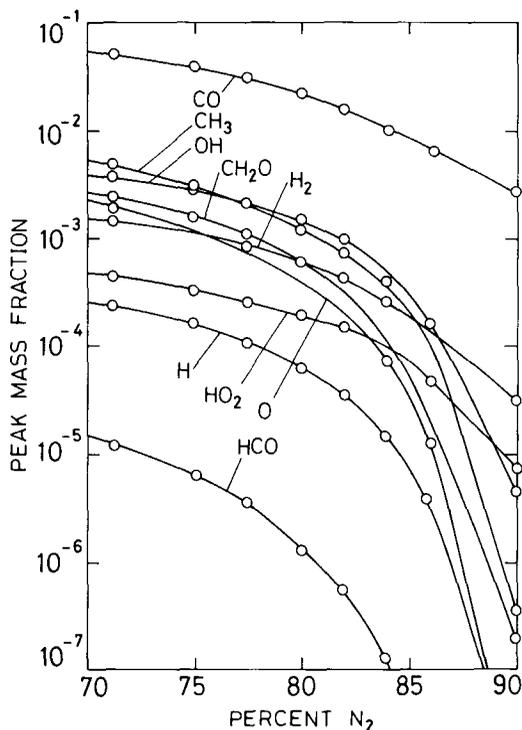


FIG. 2. Variation of peaks in the mass fraction profiles of each intermediate species as a function of nitrogen percentage.

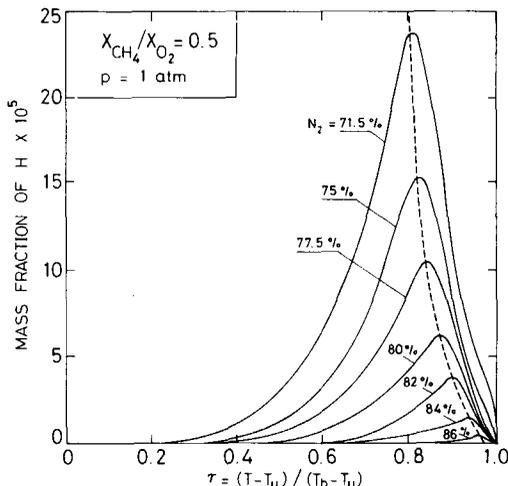


FIG. 3. Variation of the H atom species as a function of  $\tau$  at different nitrogen percentages.

were also found to behave similar to H, although the position of their peaks were slightly different. The peak shifts towards the hot boundary as the  $N_2\%$  increases indicating the transfer of reaction zone towards the hot end.

The chemical heat release rate as a function of  $\tau$  is shown in Fig. 4. The heat release rate may be thought of as a measure of the overall reaction rate of the entire mixture. An estimation of the overall activation energy may be obtained from a fit of the heat release profile. For example, if we assume

$$q = A(1 - \tau)^2 \exp(-E/RT) \quad (9)$$

where  $q$  is the chemical heat release rate,  $E$  the overall activation energy,  $R$  the universal gas constant and  $A$  is a dimensional constant, it is possible to compute the value of  $E$  from a knowledge of the temperature  $T_m$  at which  $q$  is maximum:

$$E = 2RT_m^2 / (T_b - T_m) \quad (10)$$

It is seen from the figure that the position of peak reaction rate shifts towards the hot boundary as the  $N_2$  content in the mixture is increased, indicating an increase in the apparent activation energy. A simple calculation using Eq. (10) showed that there is a tenfold increase in the overall activation energy as the nitrogen is increased from 71.5 to 86%. This suggests that the mixture demands increasingly more energy input to sustain a steady combustion as the dilution is increased near the limits.

During the initial stages in computation of extremely dilute mixtures, severe oscillations in the solution were observed. This was rather interesting since Carter et al<sup>11</sup> have reported such a behavior

for very rich hydrogen flames, and have concluded it as an indication of a flammability limit. But, on closer examination, the oscillations turned out to be of numerical origins. The oscillations did not disappear with a reduction in time step. However, a steady, nonoscillatory solution could be obtained in all the cases with a reduction in grid size. In fact, the grids needed to be refined several times (typically 3–4) on way to steady state. A simple linear interpolation of the solutions with grid-halving was found to reduce the amplitude of oscillations. Figure 5 shows the flame speed plotted against time for a stoichiometric mixture with 86%  $N_2$ . This is typical of the cases where the oscillations were particularly severe. It can be seen how the amplitude of oscillations has reduced after three grid refinements. This confirms the numerical origins of the oscillations, and that there may not be a direct correlation between flammability limits and the onset of any instability. Margolis<sup>16</sup> has obtained similar oscillations for a plain burner-stabilized flame, incorporating an implicit heat loss term by way of fixing the burner temperature. The present calculations indicate that the oscillations are not produced in one-dimensional flame calculations in the absence of any heat loss term.

## Conclusions

In summary, it has not been possible to actually predict a cut-off point in terms of nitrogen percentage for the mixture at the limits using the one-dimensional adiabatic flame model. Two major results of the present work that could further the knowledge about the observed limits are, (1) there is a steep increase in flame thickness and a vanishingly small flame speed as the limiting compositions are reached, indicating an asymptotic approach towards what may be termed as a 'fundamental' limit, and that (2) there is a sharp drop in the radical

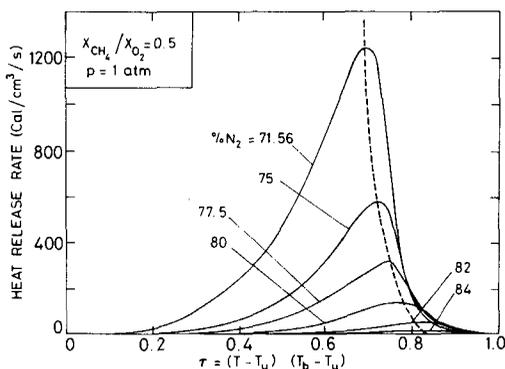


FIG. 4. Plots of heat release rate against  $\tau$  at different nitrogen percentages.

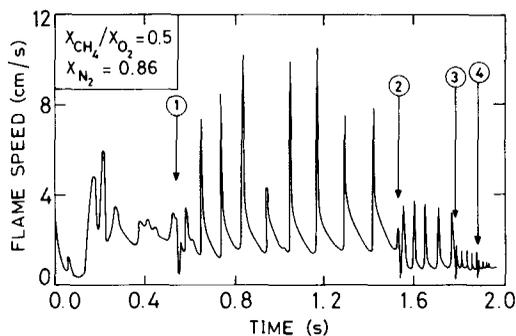


FIG. 5. Flame speed computed at successive time levels for a near-limit mixture ( $N_2 = 86\%$ ). Numbers inside circles refer to the steps at which grid refinement was done.

concentrations although they still show typical flame profiles. No oscillations in the solutions could be observed for near-limit mixtures of  $CH_4/O_2/N_2$  as has been reported by earlier workers. For a more comprehensive explanation of the phenomenon, it appears that other factors need to be taken into account. Perhaps solution of the flame propagation problem in 2- or 3-dimensions will predict the existence of cellular flames and it may still be possible to explain the flammability limits independent of external factors such as heat loss and buoyancy effects.

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#### COMMENTS

*M. Sibulkin, Brown Univ., USA.* I would like to suggest an alternative explanation for the existence of a flammability limit with a sharp cut-off composition and non-vanishing flame speed. We have recently completed calculations for methane-air flames which approximate the chemistry by a global reaction, but include the heat lost due to radiative band emission from carbon dioxide and water in the products of combustion. These calculated results show the experimentally observed sharp limit at a finite flame speed.

*Author's Reply.* We have examined in our paper the behavior of 1-*d* adiabatic flames near flammability limits, as our objective was to find whether there is any fundamental chemical limit. We could not find a clear limiting condition from these cal-

culations even though a sharp drop in radical concentrations were obtained around the observed limits. Some secondary mechanism such as heat loss (radiative or through other mechanism) is required to explain the limits.

*T. Niioaka, Tohoku Univ., Japan.* You considered the detailed reaction scheme and the detailed variable properties in your calculations, and you intended to find whether or not oscillation takes place. Do you think that the detailed reactions and/or variable properties may cause an oscillatory movement? I would like you to show an example which you expected if any.

*Author's Reply.* We were interested in finding the mechanism of flammability limits and whether a fundamental limit exists within the framework of 1-*d* adiabatic flame model. Oscillations near the observed flammability limits were reported by some

earlier workers (Reference 11). Though we found some oscillations during the calculations, they were traced to numerical origins. We do not believe oscillations are produced in the absence of other mechanisms such as heat loss (Reference 16).