Numerical Analysis of Laminar Flame Speed for H₂-NH₃-Air mixtures in Premixed Jet Flames

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ABSTRACT: A numerical study of laminar flame speeds for premixed H₂-NH₃-air jet flames is carried out for 0 to 80% NH₃ in H₂ for different equivalence ratios from lean to rich conditions. Flame-speed predictions have been conducted by CHEMKIN package over a wide range of conditions. These data are then used to validate by experimental flame speeds in literature. The results demonstrated that these mechanisms perform well for H₂-air combustion. Differences in flame speeds and associated radical species concentrations (H, O, and OH) are found to be largest for higher levels of NH₃ and with increasing equivalence ratio. It is also revealed that OH is the key radical leading to NH₃ decomposition and is a likely source of deviation between model predictions. The numerical data show that GRI-Mech 3.0 mechanism is the capable of accurately projecting reductions in flame speed as much as 90 to 95% with NH₃ addition.

Keywords: Laminar Flame Speed, Premixed Flames, Ammonia, Hydrogen.

INTRODUCTION

The growing demand for viable alternative fuels with reduced pollutant has drawn significant attention towards hydrogen (H₂) combustion for heating, power, and transportation. However, there are still primary obstacles associated with hydrogen storage and distribution, leading to a wide range of research efforts that have suggested ammonia (NH₃) as a potential alternative fuel (Zamfirescu and Dincer, 2009). Ammonia is typically generated using the Haber-Bosch process, and it can also be generated via electrolysis of water from renewable sources. Once produced, NH₃ is a carbon-free fuel with a higher energy density than liquid H₂ and can easily be stored as a liquid at a pressure of about 8 bar at 21 °C, making it an ideal H₂ carrier. By comparison, liquid H₂ requires several hundred bar for effective storage.

Considering the potential for NH₃ to serve as an alternative fuel or as an H₂ carrier, a number of studies have investigated the flame stability and emissions characteristics of NH₃ for combustors or engine applications. This includes the combustion of pure NH₃ as well as NH₃ mixed with conventional fuels such as H₂ and methane (CH₄), among others (Miller and Bowman, 1989 and Bian, 1991). Reiter and Kong [2011], showed that NH₃ could replace 95% of the diesel fuel in a conventional diesel engine and reduce NOx emissions. Similarly, the effects of NH₃ substitution to improve the safety and performance of H₂ internal combustion engines were investigated and compared with results from computational modelling (Lee et al., 2010), which these studies show that NH₃ can potentially act as an alternative fuel. Recently, Mendiara and Glarborg, 2009, have extended a chemical kinetics model involving 97 species and 779 reactions for the oxidation of NH₃ in oxy-fuel combustion of CH₄/NH₃ in
a laminar flow reactor, which captured experimental trends fairly well. Furthermore, Konnov, 2009, as well as Tian et al., 2009, have developed chemical mechanisms for hydrocarbon/NH$_3$ and H$_2$/NH$_3$ reactions in a companion research with that of Mendiaro and Glarborg. Compared with the Miller and Bowman, these mechanisms have been expanded with more extensive reactions for NH$_3$ chemistry.

The Konnov mechanism was found to be in agreement with the measured NO concentrations in lean CH$_4$–NH$_3$–air premixed flames, but NO lean re-burning was not well predicted. Duynslaeger et al., 2009, utilized the Konnov mechanism to investigate the effects of initial H$_2$ content on NH$_3$–H$_2$–O$_2$–Ar flames. They were able to predict the effects of equivalence ratio on NO formation but found disagreement for NH$_2$ and N$_2$O species concentrations. Later, Shmakov et al., 2010, studied NO- and NH$_3$-doped H$_2$–O$_2$–N$_2$ flames experimentally and numerically using a derivative of the Konnov detailed reaction mechanism and provided modifications to the reaction chemistry based on the experimental data for better overall agreement. Tian et al., 2009, proposed a comprehensive kinetics mechanism based on the experimental and modeling study of 11 premixed NH3/CH4/O2/Ar flames at low-pressure, stoichiometric conditions. This mechanism has been employed for successfully predicting the structure of CH4–NH3 and nitro-methane flames. Because of comprehensive validation with experimental data over a range of conditions, this model is recently seeing wider use and is being substituted in some instances in place of the GRI-Mech 3.0 mechanism (Hansen and Glarborg, 2010). The combustion characteristics of near-stoichiometric NH$_3$-air mixtures have previously been modelled at elevated pressure and temperature conditions using a derivative of the Konnov mechanism in a flat, freely propagating flame model (Duynslaeger et al., 2009). Results indicate that both equivalence ratio and compression ratio have a substantial effect on the laminar burning velocity and the adiabatic flame temperature. Lee et al., 2010, have evaluated the unstretched laminar burning velocities and stretch effects for laminar, premixed H$_2$–NH$_3$–air flames in a freely propagating spherical configuration.

In the present work, a laminar premixed jet flame has been considered, since it is more convenient for a range of subsequent studies. Numerical laminar flame speeds for premixed H$_2$–NH$_3$–air jet flames are compared and validated with experimental measurements using the one-dimensional, laminar, freely propagating flame conditions. The accuracy of the current computational approach as well as each chemical mechanism is evaluated for various conditions.

**COMPUTATIONAL MODELLING**

A one-dimensional, laminar, freely propagating flame model is employed in CHEMKIN package with GRI-Mech 3.0 for predicting laminar flame speeds. Such flames, which are assumed to be free from external instabilities and wall effects, represent an idealized model for conducting fundamental studies. It is worth noting that, the GRI-Mech 3.0 has well established for predicting flame structure of pure CH$_4$ or CH$_4$ mixtures with other species such as H$_2$ and CO, among others.

A freely propagating adiabatic, premixed, unstretched planar flame was simulated by using PREMIX (Kee et al., 1985), a steady laminar one-dimensional flame code. PREMIX uses a hybrid time integrating/Newton iteration technique to solve the steady state mass, species and energy conservation equations and can simulate the propagating flame. Equations were solved
by using the TWOPNT, a boundary value problem solver in the CHEMKIN package (Kee et al., 1989). Also built in the CHEMKIN package are a transport property processor and a gas-phase interpreter, which provide the species transport properties and process the chemical reaction mechanism. One of the critical elements for simulation is the proper reaction mechanism that can describe the essential fundamental reaction paths followed by the overall reaction. GRI-MECH is an optimized detailed chemical reaction mechanism for the calculation of natural gas chemical reaction process and the latest version is GRI-MECH 3.0, which consists of 325 elementary chemical reactions with associated rate coefficient expressions and thermo chemical parameters for 53 species. It includes the detailed combustion reaction mechanism for hydrogen. The ranges of GRI-MECH 3.0 are 1000 to 2500 K in temperature, 10 Torr to 10 atm in pressure and 0.1 to 5.0 in equivalence ratio. The initial flow rate of the unburned mixture was chosen equal to 0.04 g/cm²s, according to the measurement of stoichiometric methane/air flame speed by Egolfopoulos et al., 1989. To start the iteration the temperature profile estimation obtained by Van Maaren et al., 1994, for a stoichiometric methane/air flame was adopted, as suggested by Uykur et al., 2001. The temperature profile resulting from the first simulation step was used for the next step. At the inlet boundary temperature, 298 K, pressure, 0.1 MPa, and composition of the unburned mixture were assigned. At the exit boundary, it was specified that all gradients vanish. It is observed that by using adaptive grid parameters GRAD=0.02 and CURV=0.1, the burning velocity obtained is grid independent. The length of calculations have been regarded 2 cm before the spot of reaction or generally equal to 12 cm. The conservation of mass is expressed by the general continuity equation as follows:

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \]  

(1)

Where, \( \rho \) is the mixture mass density and \( \mathbf{u} \) the gas mixture velocity. The conservation of momentum, with no body forces other than gravity, is covered by,

\[ \frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = \nabla \cdot \mathbf{\Pi} + \rho \mathbf{g} \]  

(2)

Where \( \mathbf{\Pi} \) is the stress-tensor, and \( \mathbf{g} \) is the acceleration due to gravity. The stress-tensor consists of a hydrodynamic and viscous part: \( \mathbf{\Pi} = -p \mathbf{I} + \tau \) in which \( p \) is the pressure, \( \mathbf{I} \) the unit tensor and \( \tau \) the viscous stress-tensor. The equation describing the conservation of energy is written in terms of specific enthalpy \( h \),

\[ \frac{\partial \rho h}{\partial t} + \nabla \cdot (\rho h \mathbf{u}) = \frac{\partial p}{\partial t} + \rho \mathbf{u} \cdot \mathbf{g} + \tau : \nabla \mathbf{u} - \mathbf{u} \cdot \nabla \mathbf{u} \]  

(3)

Where \( q \) is the total heat flux. The term \( \tau : (\nabla \mathbf{u}) \) represents the enthalpy production due to viscous effects. When chemical reactions are to be considered, conservation equations for the species mass fractions \( Y_i \) are used. They are defined as \( Y_i = \rho_i/\rho \) with \( \rho_i \) the density of species \( i \). The density of the mixture \( \rho \) is related to the density of the various species by \( \rho = \sum_{i=1}^{N_s} \rho_i \) with \( N_s \) the number of species. This leads to a conservation equation for every species mass fraction in the mixture,

\[ \frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho u_i Y_i) + \nabla \cdot (\rho U_i Y_i) = \omega_i, \quad i \in [1, N_s] \]  

(4)

With \( U_i \) is the diffusion velocity of species \( i \). The chemical source term \( \omega_i \) in this equation, is characteristic for the reactive nature of the flow. Note that Eq. (4) together with the continuity Eq. (1) gives an over-complete system, so instead of \( N_s \) only \( N_s - 1 \) equations in Eq. (4) have
to be solved. The mass fraction of one of the species can be computed using the following constraint,

$$\sum_{i=1}^{N_x} Y_i = 1$$

(5)

An abundant species, e.g. nitrogen, is commonly chosen for this species. By definition, chemical reactions are mass conserving, so therefore the following relations hold:

$$\sum_{i=1}^{N_x} \rho Y_i U_i = 0$$

$$\sum_{i=1}^{N_x} \omega_i = 0$$

(6)

Finally, state equations are needed to complete the set of differential equations (2) – (4). The first state equation introduces the specific enthalpy as a function of temperature $T$. This relation is given by,

$$h = \sum_{i} Y_i h_i \text{ with } h_i = h_i^{\text{ref}} + \int_{T_{\text{ref}}}^{T} c_{p_i}(T) dT$$

(7)

and holds for perfect gases. In this equation $h_i$ represents the enthalpy of species $i$ and $h_i^{\text{ref}}$ the formation enthalpy of species $i$ at a reference value for the temperature $T_{\text{ref}}$ and $c_{p_i}$ the specific heat capacity at constant pressure of species $i$. The mixture heat capacity is defined by,

$$c_p = \sum_{i=1}^{N_x} Y_i c_{p_i}$$

(8)

The species heat capacity $c_{p_i}$ is commonly tabulated in polynomial form. In most combustion problems, the mixture and its components are considered to behave as perfect gases. The ideal-gas law relates the density, temperature and pressure to each other by,

$$\rho = \frac{p \bar{M}}{R T}$$

(9)

With $R$ the universal gas constant and $\bar{M}$ the mean molar mass. This $\bar{M}$ can be determined from,

$$\bar{M} = \left( \sum_{i=1}^{N_x} \frac{Y_i}{M_i} \right)^{-1}$$

(10)

Where $M_i$ is the molar mass of species $i$.

**RESULTS**

Flame speeds are measured for each flame condition for equivalence ratios from 0.5 to 1.1 with flame speed predictions from a one-dimensional, laminar, freely propagating flame model in CHEMKIN-II package. The obtained results are then compared with flame speed predictions Kumar and Meyer, 2013, experimental study. The models are at standard temperature and pressure.
**H₂-air Flames** Fig. 1 shows the variations of the calculated laminar flame speed with increasing equivalence ratio and its comparison with experimental measurements of Kumar and Meyer. The flame speed predictions experimental data, and GRI-MECH 3.0 mechanisms follow similar trends and match closely with measured flame speeds for equivalence ratios from 0.5 to 0.9. It is notable that the current numerical data agree closely with experimental values of Kumar and Meyer, however, the experimental data are higher than the predictions at higher equivalence ratios. This discrepancy can be attributed to the assumption of an adiabatic flame for the one-dimensional, laminar, freely propagation flame model.

**Figure 1.** Comparison of computed and measured laminar flame speed variations with equivalence ratio for NH₃ addition at 0% by energy in H₂

**Figure 2.** Comparison of computed and measured laminar flame speed variations with equivalence ratio for NH₃ addition at 20% by energy in H₂

**H₂–NH₃–air Flames**

*NH₃ Addition 20% by Energy in H₂.* Variations in numerically calculated through GRI-MECH 3.0 mechanisms laminar flame speeds with respect to equivalence ratio are presented in Fig. 2. The computed flame speed for E%NH₃ = 20 increases gradually with improving equivalence ratio from 17 cm/s at φ = 0.5 to 186 cm/s at φ = 1.1. It can also be observed that the flame speed predictions by GRI-MECH 3.0 mechanisms are in close agreement with the Kumar and Meyer experimental data and both values follow the same upward trend.

*NH₃ Addition 50% by Energy in H₂.* Fig. 3 illustrate the computation and measurement values of laminar flame speed as a function of equivalence ratio for E%NH₃ = 50. The measured flame speeds increase from 12 to 54 cm/s as equivalence ratio increases from 0.55 to 1.1. These are somewhat difference than Kumar and Meyer, who reported unstretched flame speeds of 1, 27 and 53.5 cm/s at equivalence ratios 0.6, 0.8 and 1.1 respectively, for E%NH₃ = 50 in a spherical propagating flame. Given the nearly six-fold drop in flame speed from E%NH₃ of 0 to 50 and differences in heat losses between the two flame configurations, this agreement is roughly reasonable.

*NH₃ Addition 80% by Energy in H₂.* For the case of E%NH₃ = 80, the measured flame speeds for various equivalence ratios are demonstrated in Fig. 4. The flame speeds increase gently from 3.1 to 11 cm/s for equivalence ratio changes from 0.5 to 0.9. This is followed by a steep
increase from 0.9 to 1.1, reaching a peak flame speed of 16 cm/s. The unstrained laminar flame speeds measured by Kumar and Meyer for case E%NH₃ = 80 and at equivalence ratios 0.6, 0.8 and 1.0 are 1.7, 6.8 and 9.7 cm/s, respectively.

**Effects of Radicals on Flame Speed** From the flame speed analysis in the previous section, it is clear from Figs. 2–4 that the heat losses reduce the laminar flame speeds of the fuel–air mixtures. Heat loss from the flame reduces the flame temperature and, thereby, lowers the rate of radical formation reactions. To investigate the effects of heat loss on radical species and flame speed in the CHEMKIN models, the concentration profiles of H, O and OH radicals are plotted for adiabatic models in Fig. 5 at an equivalence ratio of 1.0 for E%NH₃ = 50.
To further investigate the effects of reduced radical concentrations on the rate of NH$_3$ decomposition at different equivalence ratios, the mole fractions of H, O and OH radicals are plotted in Fig. 6 for E%NH$_3$ = 50. As shown in Figs. 5 and 6, significant changes in OH and H radicals could lead to significant changes in flame speed with heat losses and changes in equivalence ratio. In particular, because OH has the greatest effect on NH$_3$ decomposition, the relatively high mole fraction of OH radicals leads to a higher flame speed at $\phi = 0.6$ and a greater increase in flame speed at higher equivalence ratio. Ultimately, the comparison of computation flame speed data at $\phi = 0.6$ and $\phi = 1.0$ is shown in Fig. 7.
Figure 7. Comparison of computation flame speed data at $\varphi = 0.6$ and $\varphi = 1.0$

CONCLUSIONS

Flame speed calculations are performed for $\text{H}_2$–$\text{NH}_3$–Air mixtures in a laminar jet flame configuration, and acquired data are compared with flame speed measurements of Kumar and Meyer. One-dimensional, laminar, freely propagating flame speed has been modelled in the CHEMKIN package. The equivalence ratio varied from 0.5, lean conditions, to 1.1, reach conditions, and also cases included NH$_3$ as a percent of the energy in H$_2$ of $E\%\text{NH}_3 = 0$ (pure H$_2$–air), 20, 50 and 80. The results showed that laminar flame speed predictions using GRI-MECH 3.0 are in good agreement with experimental values of Kumar and Meyer. It is also verified that the radical pool of OH, H, and O plays an important role in controlling the total rate of decomposition of NH$_3$, with OH having a more significant impact. From the current study, it is revealed that the radical mole fractions have strong implications on the predicted flame speeds. Similarly, the differences in radical mole fractions may be consequential for the NO formation in the flame. Hence, follow-on work will include investigation of the effects of radical species on the NO formation rates in H$_2$–NH$_3$–air flames.

REFERENCES

Bian, J. [1991], Experimental study of the formation of nitrous and nitric oxides in H$_2$–O$_2$–Ar flames seeded with NO and/or NH$_3$, Symposium (International) Combustion, Vol. 23, No. 1, pp. 379-386.


