Propagation and Emissions of Ammonia-substituted Hydrogen/Air Flames

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ABSTRACT

In order to evaluate the potential of partial ammonia (NH_3) substitution to improve the safety of hydrogen (H_2) use in general and the performance of internal combustion engines in particular, the propagation and nitrogen oxide (NO_x) and nitrous oxide (N_2O) emissions of laminar premixed H_2/NH_3/air flames were studied experimentally and computationally. Freely propagating spherical laminar premixed flames at normal temperature and pressure were considered for a wide range of global fuel-equivalence ratios, flame stretch rates and the extent of NH_3 substitution. Ammonia substitution does not generate any carbon dioxide, carbon monoxide and unburned hydrocarbons compared with hydrocarbon substitution. Results also show substantially reduced laminar burning velocities and low NO_x and N_2O emissions in fuel-rich H_2/air flames. These observations support the potential of NH_3 as a carbon-free, clean additive for improving the safety of H_2 use.

Keywords: hydrogen combustion, ammonia, flame propagation, laminar burning velocity, nitrogen oxide

1 INTRODUCTION

Because of the high reactivity of hydrogen (H_2), there has always been substantial interest in its use as an additive to hydrocarbon fuels for improved performance, including extended flammability limits and enhanced burning rates, and recently there is also increasing interest in the use of pure H_2 as a carbon-free, clean fuel, in either combustion devices or fuel cells [1,2]. Attractive as it is, the use of H_2 also imposes considerable technological challenges, particularly those associated with storage, safety and the performance of internal combustion engines. The high reactivity and diffusivity of H_2 are directly responsible for the potential of explosion hazards in storage due to either slow leakage or puncturing of the storage tank. Hydrogen flames are practically non-luminous, which renders visual detection difficulty and optical monitoring challenging. Furthermore, H_2-fueled internal combustion engines could also be susceptible to substantial nitrogen oxide (NO_x) and nitrous oxide (N_2O) emissions as well as knock-limited operation. In order to overcome the technological challenges, the use of hydrogen/hydrocarbon mixtures in combustion devices was suggested [3].

We propose herein an alternative approach towards enabling H_2 utilization and diminishing the associated safety and emission problems: the use of carbon-free ammonia (NH_3)/hydrogen mixtures in combustion devices. Reaction of NH_3/H_2/air mixtures involves only water vapor and nitrogen (and small amount of NO_x and N_2O) as the final products. Thus, no carbon dioxide emission is still maintained, compared with the use of hydrocarbon-added H_2/air mixtures. Furthermore, NH_3 is easily storable: a saturated pressure of 8.8 atm at 21ºC [4]. The combustion of NH_3/H_2/air mixtures also appears to possess some potentially beneficial characteristics as follows. First, since the need for supercharging is reduced due to the high-energy density of liquefied NH_3, limitation due to knock is correspondingly reduced. Second, since H_2/NH_3 flames are luminous, even with trace amount of NH_3 doping, visual and optical detection of potentially disastrous small-scale fires are facilitated. Third, there is the potential that the presence of NH_3 in H_2/air flames could diminish the propensity of the mixture to detonate. Specifically, flames are subjected to inherent preferential-diffusion instability [5], in that a flame tends to be cellularly unstable if the limiting reactant is the more mobile one, and stable otherwise. Development of preferential-diffusional cells over the flame surface greatly increases the flame surface area and thereby the flame propagation rate, which could in turn lead to self-turbulization of the flame and the eventual transition to detonation, possibly within a confinement. Lean H_2/air flames are preferential-diffusionally unstable, and have been found to develop cells profusely [5]. Recognizing that although lean NH_3/air flames are also preferential-diffusionally unstable, they are less so than the highly diffusive H_2/air flames, its addition to H_2/air flames could reduce the propensity of the mixture to become diffusionally unstable. In addition to modifying the flame instability characteristics, the addition of NH_3 to H_2/air mixtures also lowers the flame speed.

In the present investigation we aim to study the potential of improving H_2 safety and engine performance by adding NH_3 to H_2/air mixtures, with the following specific objectives. The first is to measure and predict the laminar burning velocities of NH_3/H_2/air flames in order to quantify the extent of burning rate reduction due to NH_3 addition. The second is to measure and predict the Markstein numbers, which represent the sensitivities of flame response to stretch, and are related to the onset of preferential-diffusion instabilities. We shall also examine the effects of NH_3 substitution on the NO_x and N_2O formation.

2 EXPERIMENTAL AND COMPUTATIONAL METHODS

The outwardly propagating spherical flame was adopted as the model flame for the present investigation. Experimental and computational methods are similar to past work for various laminar premixed flames and will be described only briefly, see [5,6] for more details.

The experiments were conducted in a spherical windowed chamber having an inside diameter of 312 mm. The combustible mixture was spark-ignited at the center of the chamber. The flame propagation sequence was imaged with shadowgraphy and recorded using high-speed digital camera, up to 8000 frames/s. Present measurements were limited to flames having diameters larger than 10 mm to avoid ignition disturbances and smaller than 60 mm to limit pressure increases during the measuring period to values less than 1.0% of the initial pressure. Measurements were limited to the ratio of flame thickness to radius $\delta_D/r < 2\%$ ($\delta_D \equiv D_u/S_L$ where D_u and S_L are the mass diffusivity of the unburned gas and the laminar burning velocity, respectively) so that effects of curvature and transient phenomena associated with large flame thicknesses were small. For these conditions, the local (stretched) laminar burning velocity and flame stretch rate are given as follows [5]:

$$S_L = \left(\rho_b/\rho_u\right) dr/dt, \qquad K = \left(2/r\right) dr/dt \qquad (1)$$

where r, t and ρ_b/ρ_u are the flame radius, time and the density ratio of burned to unburned gases, respectively. At the aforementioned thin-flame limit conditions, the relationship between laminar burning velocity and flame stretch rate can be conveniently represented by the "local conditions" hypothesis [5], to yield:

$$S_{L\infty}/S_L = 1 + MaKa \qquad (2)$$

where $S_{L\infty}$ is the unstretched downstream laminar burning velocity, Ma is the Markstein number (representing the sensitivity of flame response to stretch) and Ka is the Karlovitz number (the normalized flame stretch). The Karlovitz number is defined KD_u/S_L^2 where D_u is the binary mass diffusivity of NH_3 into nitrogen. Fortuitously, both existing measurements and numerical simulations yield a linear correlation between $S_{L\infty}/S_L$ and Ka, for values of Ka not too near quenching conditions, which implies constant Markstein numbers for each reactant condition [5,6]. Experiments were conducted on H_2/air mixtures with NH_3 addition. The composition of the mixture was defined by its global fuel-equivalence ratio ϕ and the stoichiometric fraction of the NH_3 in the fuel gases SFA, which is defined as the volumetric fraction of H_2 replaced by the NH_3. The use of SFA instead of a more direct and convenient parameter such as the mole fraction of the NH_3 in the fuel gas, $x_a = X_{NH3}/(X_{H2} + X_{NH3})$ where X_{H2}

and X_{NH3} are the mole fractions of H_2 and NH_3, respectively, will be discussed in Section 3. Experiments were carried out for ϕ = 0.60-1.67 and SFA = 0-0.367 (x_a = 0-0.3) and at a mixture temperature of 298±3 K and atmospheric pressure (NTP). Experimental uncertainties (95% confidence) are as follows: $S_{L\infty}$ less than 10% and |Ma| less than 25% for |Ma| > 1 and less than 25%/|Ma| for |Ma| < 1.

The outwardly propagating spherical laminar premixed flames were simulated using the unsteady one-dimensional laminar flame computer code COSILAB [7], developed by Rogg. This code was used to calculate $S_{L\infty}$ and Ma for comparison with the measured values. This algorithm allows for mixture-averaged multicomponent diffusion, thermal diffusion, variable thermochemical properties, and variable transport properties. The numerical simulations were analyzed similar to the measurements. All the calculations were carried out with the detailed NH_3 oxidation mechanism of Miller and Bowman [8], involving 19 species and 73 reversible reactions.

3 RESULTS AND DISCUSSION

3.1 Unstretched Laminar Burning Velocities

Figure 1 shows the measured and predicted $S_{L\infty}$, as well as the predicted laminar burning flux f, as a function of SFA for the NH_3-substituted H_2/air flames. All the results show significant reduction of $S_{L\infty}$ with NH_3 substitution. Furthermore, the following interesting trends are observed. First, fuel-lean and stoichiometric flames show nearly the same relative amount of reduction in $S_{L\infty}$ with NH_3 substitution, while reduction for the rich flames is more substantial. This difference can be explained from the $S_{L\infty}$ profiles of the pure fuels, which was discussed in the earlier investigations [3,6]. Specifically, while the maximum $S_{L\infty}$ for the NH_3/air flames occur around ϕ = 1.1, for the H_2/air flames it occurs around ϕ = 1.8 as a result of the high diffusivity of H_2. Consequently, the difference between the NH_3 and H_2 flames is larger for fuel-rich conditions, particularly around ϕ = 1.8. Second, the above trend was also observed for the laminar premixed methane (CH_4)-substituted H_2/air flames [3]. Compared with the earlier investigation of the effects of hydrocarbon substitution on H_2/air flames, however, it is seen that for the same SFA and the stoichiometric fraction of the hydrocarbon in the fuel gases $SFHC$, which is defined as the volumetric fraction of hydrogen replaced by the hydrocarbon [3], the reductions in $S_{L\infty}$, are more significant for the NH_3-substituted flames. This is reasonable because of the smaller laminar burning velocity for the less reactive NH_3. As discussed in the earlier study [3], for the same SFA and $SFHC$, the amount H_2 replaced is the same for all the NH_3- and CH_4-substituted mixtures, and therefore allows comparison of effects of substitution on the same basis. On the other hand, comparing the effects of substitution on mole basis could provide a distorted implication on the effects of substitution,

yielding larger effects for larger molecules. Third, the experimental and predicted $S_{L\infty}$ generally shows good agreement. Finally, the decreasing trends of f with NH$_3$ substitution are similar to those in $S_{L\infty}$. This implies that the density effect on the decreasing trends in $S_{L\infty}$, due to the change in molecular weights, is not significant for the present range of SFA studied. Consequently, the reduction in $S_{L\infty}$ is indeed caused by modifications of the flame structure and propagation process due to NH$_3$ substitution, instead of the change in density.
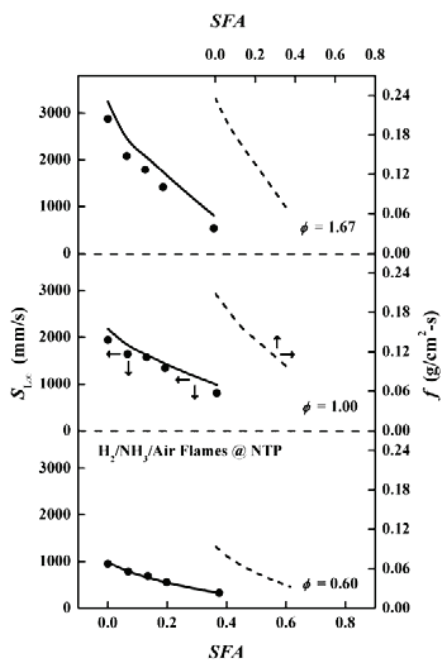

Figure 1: Measured and predicted $S_{L\infty}$ and f as a function of SFA for NH$_3$-substituted H$_2$/air flames of $\phi = 0.6$, 1.0 and 1.67 at NTP: symbols for measurements and lines (solid: $S_{L\infty}$; dashed: f) for predictions using the kinetics of Miller and Bowman [8].

3.2 Markstein Numbers

The Markstein number quantifies the sensitivities of the flame response to stretch. Together with $S_{L\infty}$, they are the two most important global properties of a laminar flame subjected to aerodynamic stretching [3,5,6]. Furthermore, Ma is also directly related to the occurrence of the flamefront preferential-diffusion instability. Figure 2 shows the measured and predicted Ma for the same mixtures as those of Fig. 1. In contrast to the consistent reduction in $S_{L\infty}$ with NH$_3$ substitution, the dependence of Ma on the nature and extent of substitution varies substantially. Specifically, for fuel-rich conditions, flames show that Ma is positive for all SFAs and decreases with increasing SFA, implying less stabilized (but still stable) flames with NH$_3$ substitution. This observation showing positive Ma for all SFAs is reasonable because rich H$_2$ flames are preferential-

diffusionally stable. Also, this observation is similar to that as in the case of CH$_4$ substitution [3], which was somewhat expected since NH$_3$ and CH$_4$ have similar molecular weights (lighter than oxygen) and hence are assumed to have similar flame response to stretch and the preferential-diffusion of fuel and oxidizer. The reduced flame stability with NH$_3$ substitution implies that the minimal destabilizing effect of NH$_3$ addition is overweighed by the destabilizing effect caused by the correspondingly reduced H$_2$ concentration which tends to render the flame to be more unstable. However, this tendency is different from that in the case of CH$_4$ substitution [3]. Rich H$_2$ flames are preferential-diffusionally stable, while the substitution with small amounts of CH$_4$ asserts minimal destabilizing effect. This opposite tendency with between NH$_3$ and CH$_4$ substitution seems to be caused by the different pools of radicals produced via different paths respectively by NH$_3$ and CH$_4$ substitution. An earlier investigation shows that light radical (such as H and OH) production and transport are important aspects of preferential-diffusion/stretch interactions in view of the unusually large diffusivities and strong effects on S_L of these light radicals [5].
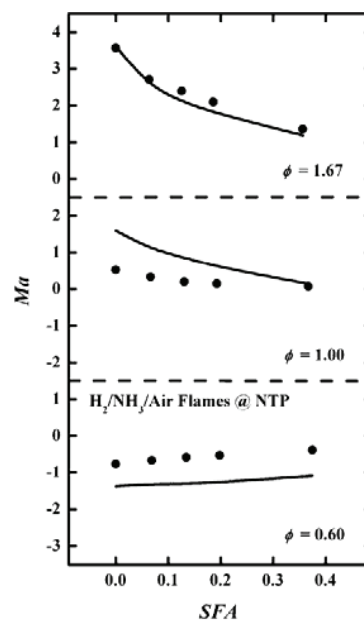

Figure 2: Measured and predicted Ma as a function of SFA for NH$_3$-substituted H$_2$/air flames of $\phi = 0.6$, 1.0 and 1.67 at NTP: symbols for measurements and lines for predictions using the kinetics of Miller and Bowman [8].

For stoichiometric conditions, flames show that Ma approaches zero with increasing ammonia substitution, implying that the flames become neutral, i.e., less stabilized. The reduced flame stability implies that the minimal destabilizing effect of NH$_3$ addition is overweighed by the destabilizing effect caused by the correspondingly reduced H$_2$ concentration which tends to render the flame to be more unstable. This opposite trend is somewhat expected

from the different responses of Ma with between the pure H_2/air and pure NH_3/air flames: almost linear increase with increasing ϕ for the latter [6] but rapid increase across moderately fuel-lean to stoichiometric conditions and then a plateau profile over fuel-rich conditions for the former [5]. Consequently, the destabilizing effect due to the reduced H_2 concentration dominates the flame response for this stoichiometric mixture. This tendency is also observed in the case of CH_4 substitution [3]. For fuel-lean conditions, all values of Ma are negative and hence all flames are unstable. Ammonia substitution tends to render the flame less unstable; however, it is not significant. This result implies that the minimal destabilizing effect of NH_3 addition and the destabilizing effect caused by the correspondingly reduced H_2 concentration which tends to render the flame to be more unstable are comparable to each other and hence the net effect is not remarkable. This tendency is somewhat different from that in the case of CH_4 substitution [3]. Again, this different tendency with between NH_3 and CH_4 substitution can be attributed to the different pools of radicals produced via different paths respectively by NH_3 and CH_4 substitution. Finally, the experimental and predicted Ma shows fairly good agreement, though it is somewhat worse than $S_{L\infty}$. This agreement to the present extent is considered to be satisfactory in the determination and prediction of $S_{L\infty}$ and Ma.

3.3 NO_x/N_2O Formation

Effect of NH_3 substitution on the NO_x and N_2O (one of strong green house gases) formation was predicted.
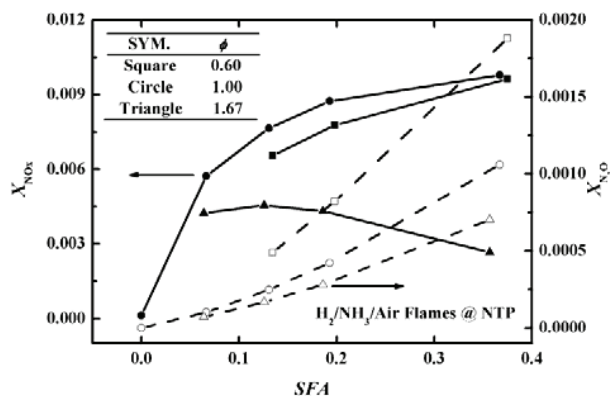

Figure 3: The predicted maximum mole fractions of NO_x and N_2O as a function of SFA for NH_3-substituted H_2/air flames of $\phi = 0.60$, 1.00 and 1.67 at NTP. Based on the kinetics of Miller and Bowman [8].

Figure 3 compares the maximum mole fractions of NO_x and N_2O as a function of SFA for various fuel-equivalence ratios. In most cases, NH_3 substitution enhances the NO_x and N_2O formation. At fuel-rich conditions, however, the amount of NO_x emissions decreases with NH_3 substitution

and the increased amount of N_2O emissions with NH_3 substitution is much lower than that under fuel-lean conditions. This observation along with the earlier observation that the relative amount of decrease in $S_{L\infty}$ with NH_3 substitution is more substantial for fuel-rich conditions supports the potential of NH_3 as an additive for improving the safety performance with low NO_x and N_2O emissions particularly in fuel-rich H_2/air flames. The different NO_x and N_2O emission behavior for various fuel-equivalence ratios indicates that NO_x and N_2O are produced via different paths for each mixture condition.

4 CONCLUTIONS

Effects of partial NH_3 substitution on H_2/air flames were studied, motivated by safety considerations in hydrogen usage. Ammonia is all capable to significantly reduce the laminar burning velocities of H_2/air flames, particularly for fuel-rich conditions, without any CO and CO_2 generated. In most conditions, the potential of significant NO_x reduction due to the substantially reduced temperature with NH_3 substitution is overweighed by the enhanced NO_x formation effect caused by the NH_3-containing N. At fuel-rich conditions, however, the amount of NO_x emissions decreases with NH_3 substitution and the increased amount of N_2O emissions with NH_3 substitution is much lower than that under fuel-lean conditions. These observations support the potential of NH_3 as a carbon-free, clean additive for improving the safety performance with low NO_x and N_2O emissions particularly in fuel-rich H_2/air flames.

REFERENCES
[1] S.R. Bell and M. Gupta, Combust. Sci. Tech. 123, 23-48, 1997.
[2] J.M. Gomes Antunes, R. Mikalsen and A.P. Roskilly, Int. J. Hydrogen Energy 34, 6516-6522, 2009.
[3] C.K. Law and O.C. Kwon, Int. J. Hydrogen Energy 29, 867-879, 2004.
[4] G. Thomas G and G. Parks, World Wide Web location http://www.hydrogen.energy.gov/pdfs/nh3_paper.pdf, 2006.
[5] O.C. Kwon and F.M. Faeth, Combust. Flame 124, 590-610, 2001.
[6] J.H. Lee, J.H. Kim, J.H. Park and O.C. Kwon, Int. J. Hydrogen Energy 35, 1054-1064, 2010.
[7] SoftPredict, COSILAB: Combustion simulation laboratory, ROTEXO GmbH & Co. KG., Germany, Document SP-D-0005, 2007.
[8] J. Miller and C.T. Bowman, Prog. Energy Combust. Sci. 15, 287-338, 1989.