Laminar flame speed and minimum spark-ignition energy measurements of ammonia in airgon

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1 Introduction

Ammonia, a carbon-free compound, has been recently identified as a potential alternative to conventional fuels in applications such as transportation and power generation. A deep understanding of the behavior of ammonia at various combustion conditions is of utmost importance for the implementation of this fuel in practical applications and thus, research activities are needed on various scientific fronts.

Characterization of the oxidation of this promising fuel has recently been the target of several works available in the literature, covering ignition delay time measurements [1,2], speciation experiments [3–6] and laminar flame speed measurements. Flame speed measurements of ammonia at room temperature were first reported in the early works by Zakaznov et al. [7], Ronney et al. [8] and Pfahl et al. [9], who also analyzed flame behavior of blends of ammonia, nitrous oxide, methane and hydrogen. Takizawa et al. [10] studied mixtures of neat ammonia in air at atmospheric pressure and room temperature, while Hayakawa et al. [11] studied ammonia/air mixtures at various pressures up to 5 atm. More recently, Han et al. [12] reported ammonia/air measurements together with blends of ammonia with hydrogen, methane and carbon monoxide. Mei et al. [13] reported the flame speeds of oxygen enriched mixtures of ammonia up to 5 atm. Efforts by Lhuillier et al. [14], Kanoshima et al. [15] have reproduced the room temperature and atmospheric pressure experiment, while also pushing the limits of unburned gas temperatures up to 500 K.

Identification of the minimum spark ignition energy of fuel mixtures is valuable for the design of new combustion systems and the identification of fire hazards during storage or transportation. Ignition energies of ammonia and its blends can be found in the works of Pfahl et al. [9], Sadaghiani et al. [16], where mixtures with carbon monoxide were also studied, Lesmana et al. [17] and Fernández-Tarrazo et al. [18], who focused on hydrogen ammonia/blends.

Studies of the impact of argon as the bath gas on ammonia flame speeds are scarce in literature. These include the works of Andrews and Gray [19], who analyzed the influence of mixing helium, nitrogen and argon on flame speed at low pressures; and Karan et al. [20], where a mixture of argon and helium was used to stabilize the flames.

Herein, flame speeds of ammonia in airgon (79% argon, 21% O_2) are measured in a cylindrical, constant-volume section of a shock tube across a range of equivalence ratios (0.75-1.2) and pressures (0.5-2 atm), at room temperature. A survey of minimum spark-ignition energy at these conditions is presented. The

shock tube flame speed method [21] is additionally used for the measurement of laminar flame speeds at high temperatures.

2   Experimental Methods

Room-temperature laminar flame speed measurements of ammonia/airgon mixtures were performed in the cylindrical, constant-volume section of the Imaging Shock Tube (IST) at Stanford University. The chamber has an internal diameter of 11.53 cm and a total length of 39.5 cm. High temperature measurements were performed behind reflected shock waves using the shock tube flame speed method at the same facility, described in detail in [22]. In both sets of experiments, flames were initiated by a laser-induced spark ignition system, which consists of a pulsed, frequency-doubled Nd:YAG laser emitting at 532 nm. The beam was introduced through a slot window and was focused at the center of the test section. In order to study minimum spark ignition energies, the incident laser power was controlled using a variable attenuator consisting of a half-wave plate and a polarizer. Further information about the ignition system can be found in [22]. A dual-camera, high-speed imaging approach is employed to analyze the morphological evolution of each flame and measure its speed of propagation. An OH* chemiluminescence diagnostic, comprised of a Phantom V710 high-speed camera coupled with a LaVision HS-IRO and a 310 nm bandpass filter, allows for the visualization of emission from the endwall perspective, giving a complete view of the circular cross-section of the tube. A sidewall schlieren system is used to track the advancement of the flame front into the unburned gas mixture and it consists of a pair of off-axis parabolic mirrors and a Phantom V2012 camera. Two opposed, cemented-doublet windows permit a complete view of the evolution of the flame before confinement effects become dominant. An area-averaged linear curvature approach, described in detail by Susa et al. [22], is used to extract unstretched, burned flame speeds from the processed images and the density ratio of the reactants and products is then applied to translate these results to unburned flame speeds.

Ignition energy was estimated using differential energy measurements performed by two Ophir 3A-FS laser power sensors, The first measurement is taken before the laser beam enters the test section and the second after the beam has passed through the gas mixture. Energy losses through all the optics are considered in the calculations of deposited energy.

The mixtures studied in this work are summarized in Table 1 and span three different equivalence ratios: $\varphi = 0.75, 1, 1.2$. Ammonia gas (45% NH_3 in Ar), oxygen (99.99%) and argon (99.9%) cylinders were provided by Linde Gas Equipment, Inc. Each experiment was repeated 3 times in order to test repeatability and increase the accuracy of minimum ignition energy measurements.

Table 1. Ammonia mixtures used in flame speed and minimum spark ignition energy experiments.

Fuel	Oxidizer	ϕ	X_{Fuel} [%]	X_{O2} [%]	X_{Ar} [%]	T [K]
Ammonia	Airgon (79% argon, 21% O_2)	0.75	17.35	17.35	65.3	295
		1	21.9	16.4	61.7	295, 477-747
		1.2	25.9	15.6	58.5	295

3   Results

Room-temperature (295 K) laminar flame speeds of ammonia mixtures ($\varphi = 0.75, 1, 1.2$) at pressures varying from 0.5-2 atm are shown in Fig. 1. Experimental measurements are compared with simulated flame speeds computed with the models of Okafor et al. [23], Shrestha et al. [24], Glarborg et al. [25] and Otomo et al. [26]based on a 1-D freely propagating flame model with a domain size of 10 cm. Measured flame speeds can be seen to decrease with increasing pressure at all the equivalence ratios, a characteristic also observed in the trends predicted by the various chemical kinetic models.

In the lean case ($\varphi = 0.75$), the measured flame speeds agree very well with the models of Okafor et al. [23] and Shrestha et al. [24] at pressures below 1 atm; [24][25]at pressures above 1.5 atm, the Okafor et al. [23] and Otomo et al. [26] models almost overlap up to 2.5 atm and are close to the measurements at 2.0 atm. While these three mentioned models agree with each other within 2 cm/s, the model by Glarborg et al. [25] is seen to clearly overpredict both the measurements and simulations.

In the stoichiometric case ($\varphi = 1$), the measured room-temperature flame speeds agree reasonably well with the model by Okafor et al. [23], while Shrestha et al. [24] overpredicts the experimental values, having the highest deviation close to atmospheric pressure. The model by Otomo et al. [26] underpredicts the results across all pressures, though shows better agreement at 1 and 1.5 atm. As in the lean case, the model by Glarborg et al. [25] overpredicts the experimental values and all the simulated values generated using other models. It should be mentioned that the measurement at 2 atm falls within the experimental uncertainty of the measurement at 1.5 atm, thus the predicted trend of flame speed with pressure is not compromised.

No model is successful in accurately predicting the measured flame speeds for the rich case ($\varphi = 1.25$), where a large spread in the simulated values is observed. At these conditions, the measurements fall in between the lines simulated with Glarborg et al. [25] and Shrestha et al. [24],while the models by Okafor et al. [23] and Otomo et al. [26] largely underpredict the experiments. Uncertainty bounds are also presented in Fig. 1 and include contributions from the uncertainty in the pressure, temperature and mixture composition, in addition to the error related to the fit parameters from linear regression used in the extrapolation of the measurements to zero-stretch flame speed. Uncertainty related to the selection of the linear curvature extrapolation model has not been included for this data set, as a reliable method of error quantification for these specific mixtures and conditions is not currently available.
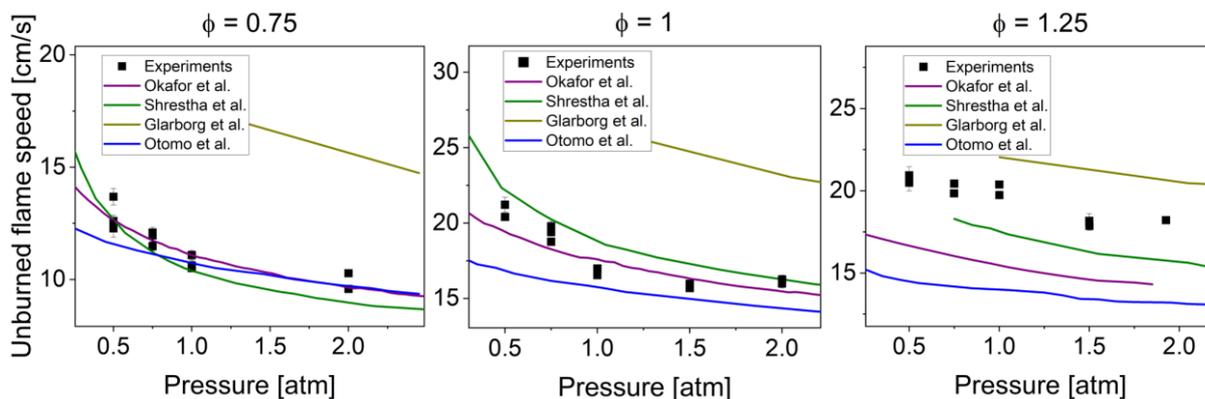
Figure 1: Room-temperature (295 K) laminar flame speed measurements of lean, stoichiometric, and rich mixtures of NH$_3$/Airgon. Solid lines are simulations using various chemical kinetic models.

In order to understand the effect of the equivalence ratio and pressure on the minimum required spark ignition energy for flame development, several experiments were carried out where the incident laser power was attenuated before entering the test section. For this, a low-energy pulse was selected and increased gradually until a flame was successfully formed and confirmed by high-speed imaging diagnostics. The ignition energies for these experiments are plotted in Fig. 2 for the mixtures studied herein. As pressure increases, it is evident that the amount of spark energy needed for successful ignition decreases, ranging from 15.4 mJ at 0.5 atm to 1.6 mJ at 2 atm for the lean case, from 26.1 mJ at 0.5 atm to 2.7 mJ at 2 atm for the stoichiometric case, and from 47 mJ at 0.5 atm to 4.5 mJ at 2 atm for the rich case. This observation is expected as the density of molecules, and hence electrons, is higher at higher pressure and thus facilitates the inverse bremsstrahlung process, a mechanism associated with laser-induced spark ignition [27]. The lean mixture, having the highest concentration of oxygen and the lowest concentration of ammonia, is recognized as the easiest to ignite at all studied pressures, followed by the

stoichiometric and rich mixtures, respectively. Notably, sub-atmospheric flames require a significant amount of energy input to successfully sustain a propagating flame, with the lowest energy value used in a successful ignition being 47 mJ for φ = 1.25.
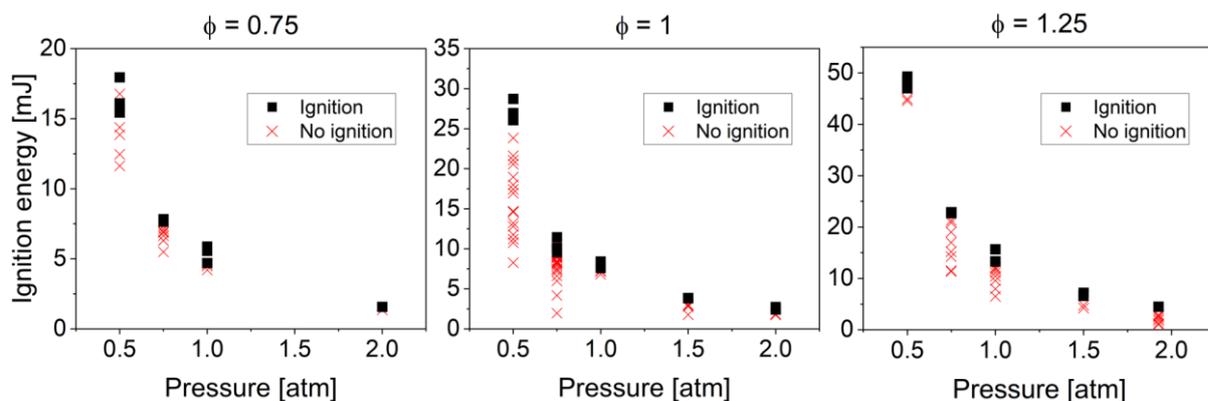
Figure 2. Spark ignition energy needed for flame initiation. Crosses indicate cases where ignition was unsuccessful and squares indicate cases where flame propagation was observed.

In addition to the room-temperature static experiments, a high-temperature survey of flame speeds is presented in Figure 3. At lower temperatures (below 400 K), the models of Shrestha et al. [24], Okafor et al.[23] and Otomo et al. [26] predict similar values of laminar flame speeds, with a clear deviation observed above 500 K. The measurements at high temperatures show good agreement with the model of Okafor et al. [23], while Otomo et al. [26] slightly underpredicts the experimental results. Measurements are overpredicted by Shrestha et al. [24] and Glarborg et al. [25], with the latter showing a larger deviation from both the data and the other models. Figure 3 also includes the experimental uncertainty of the experiments performed with the shock tube flame speed method. Here, contributions from the uncertainty in the determination of temperature and pressure behind reflected shock waves, uncertainty in mixture composition, error in the linear regression fitting and the uncertainty related to the implementation of the linear curvature model [28] are included.
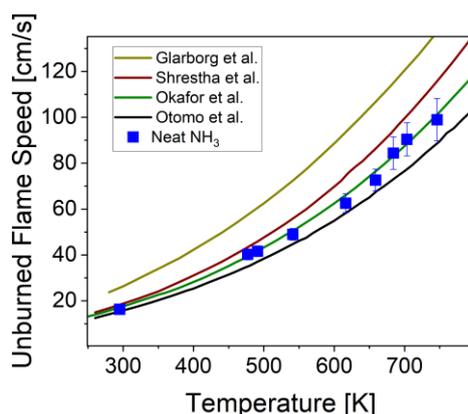
Figure 3. Laminar flame speed measurements of stoichiometric NH_3/airgon at atmospheric pressure and high temperatures. Solid lines are simulations using various chemical kinetic models.

4   Conclusion

Laminar flame speed measurements of ammonia/airgon mixtures were performed at room temperature using a constant volume chamber and at high temperatures using the shock tube flame speed method.

Lean, stoichiometric and rich mixtures were used in room-temperature measurements at pressures ranging from 0.5-2 atm. To our knowledge, these results comprise the first dataset of ammonia flame speeds using argon as the bath gas. An inversely proportional relationship between pressure and flame speed was observed in all the studied cases. The rich case showed the highest flame speeds at all pressures, followed by the stoichiometric and lean mixtures, respectively. Results were compared against simulations using various available models for ammonia oxidation. The model by Okafor et al. [23] was found to have the best agreement with flame speed measurements for the lean and stoichiometric mixtures, while all the models failed to accurately predict the experimental data at rich conditions. A study of the minimum spark ignition energy necessary for successful ignition was performed, facilitated by a variable attenuator in the employed optical setup. The required energy was observed to decrease with increasing pressure. Equivalence ratio was found to have a strong impact on minimum ignition energy, with a lean composition facilitating the onset of ignition at much lower spark energies. High-temperature laminar flame speeds were measured behind reflected shock waves for a stoichiometric mixture of ammonia/airgon at atmospheric pressure. At these conditions, the model by Okafor et al. was identified to best describe the flame speed dependence on temperature. Future work will focus on the study of ammonia/air mixtures at comparable conditions to investigate the influence of bath gas on flame speed and minimum ignition energy.

5   Acknowledgments

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