Laminar Burning Velocity Measurement of Ammonia Fuel Blends at Elevated Temperature and Pressures

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1   Introduction

Ammonia, a carbon-free chemical, offers to be a clean alternative fuel to widely used hydrocarbon-based transportation fuels secondary to hydrogen. The focal point of Sustainable Development Summit 2015 was to encourage the easy access to clean energy globally by 2030 to mitigate the negative impact of hydrocarbon-based fuels. Currently, both hydrogen (H_2) and ammonia (NH_3) are promising carbon-free, green fuels. Low values of boiling point and volumetric energy density (8.4 MJ/l) with wide flammability limits, and high combustion instabilities poses a serious concern in the storage and transportation of H_2 [1]. NH_3 on the other hand has a high boiling point of 240 K with a volumetric energy density of 11.2 MJ/l, and is being commercially used for fertilization, and refrigeration due to the ease in storing and transporting. Hence, making NH_3 a potential candidate as a carbon-free fuel for different practical combustion systems.

Laminar Burning velocity (LBV), a fundamental combustion property is used in the development/validation of a reaction mechanism and determining heat release rate [1]. It also plays a key role in the investigation of flame characteristics, such as flame stabilization, flashback, blow off and flame extinction. For any fuel, commonly used LBV measurement techniques are spherically expanding combustion chamber, heat-flux method, and counterflow stagnation method [1]. With a low LBV (0.07 m/s) of NH_3 at atmospheric conditions [2], various approaches have been suggested such as fuel blending, preheating air, and ammonia cracking. Hayakawa et al. [3] experimentally demonstrated a decrement in the LBV of pure NH_3/air mixtures as the constant volume combustion chamber pressurized. NH_3 flame propagation was observed to be clearer at high pressures. However, for pressures up to 0.5 MPa, LBV was found to be less than 7 cm/s at 298 K mixture temperature. Furthermore, NO formation/reduction species participated in pure NH_3 flames and reported a decrease in NO mole fraction as the mixture turned richer ($\phi \geq 1.1$) at high pressures (up to 0.3 MPa) due to excess NH_i (i=0,1,2) radicals [4]. In the context of enhancing NH_3 LBV, blending with methane (CH_4) and H_2 have been conducted separately. Henshaw et al. [5] observed a LBV reduction of 17 % - 23 % for CH_4-air mixture (with 4 % NH_3 addition) from lean to rich mixture conditions. A non-linear decreasing trend of CH_4 LBV was reported by Okafor et al. [6] with NH_3 addition (up to 50%) and developed a reaction mechanism for CH_4-NH_3 flames. For CH_4/NH_3-air flames, presence of OH radical resulted in the formation of NH_2 molecules with an increase in NOx emissions. Okafor et al. [6] reported high pressure (up to 0.5 MPa) LBV measurements of blends (NH_3/CH_4) using constant volume combustion chamber at 298 K mixture temperature. The NH_3 mole fraction ranged between 0 and 0.52 in the CH_4/NH_3 fuel blend for an equivalence ratio of 0.7-1.3. The obtained unstretched LBV tend to reduce with the rise in both pressure and NH_3 concentration. For the H_2/NH_3 blends, Lee et al. [8] reported 84 % increment in the NH_3 LBV as the H_2 volume fraction increased from 30 % to 50 % in the spherical flame propagation

method. The reason being high diffusivity of H_2 [9]. Similar behavior was observed in the study of Lhuillier et al. [10] for the H_2 addition (X_{H2}) up to 60 % in the premixed mixture of NH_3/H_2. However, unstable flames were evident for $X_{H2} < 20$ % and $X_{H2} > 50$ %. Recently, investigations of Ji et al. [11] and Mei et al. [12] focused on the effect of partial cracking of NH_3 to H_2 and N_2 on the LBV of NH_3-air mixtures. The partial cracking (≥ 40 %) of NH_3 contributed in higher LBV of the mixture. Further, high H_2 concentration gave rise to cellular instabilities. In the study of Ichikawa et al. [13] at elevated pressures (up to 0.5 MPa)in the constant volume combustion chamber, the LBV of NH_3/H_2 flame with 40% H_2 (by vol.) was found to be 31.2 cm/s (similar to other hydrocarbons). Interestingly, wrinkled flames were formed at 0.5 MPa with 40% H_2 (by vol.) in fuel-air mixture due to thermal-diffusive instability. Xiao et al. [14] assessed the efficacy of 12 kinetic models using the available experimental data of NH_3/H_2/air mixtures on the basis of flame speed, NOx emissions and ignition delay.

This work investigates the effect of NH_3 concentration (0-30%) on the LBV of $NH_3/H_2/CH_4$-air mixtures. The measurements are performed using the externally heated diverging channel technique (EHDCM) for temperatures and pressures up to 750 K and 0.3 MPa respectively. The outcomes of this work will be crucial in advancing the expedition in proposing alternate fuel blends of NH_3 with a comparable laminar burning velocity and low carbon emissions compared to methane. For an equivalence ratio ($\phi = 0.7$-1.4), current measurements are compared with the detailed kinetic models of Li et al. [15], Shrestha et al. [16], and Okafor et al. [6].

2   Experimental set up

For this high-pressure study, the externally heated diverging-channel method is appropriately adapted to measure LBV inside a cylindrical pressure chamber (40 L) as shown in Fig. 1 [17]. A quartz made diverging channel with the 10^0 divergence and 50 mm^2 (25 mm × 2 mm) inlet area is used primarily because of its high heat capacity, low thermal conductivity, and optical access for flame visualization. The top flange of the chamber is carefully designed to have a provision for toughened glass (visual access) along with a pressure relief valve and a pressure gauge. The divergence assists in establishing a negative velocity gradient along the mixture flow direction. An ignition system is stationed near the channel exit for igniting the premixed fuel-air mixture at high-pressure conditions. The high aspect ratio (12.5) at the channel inlet creates a uniform flow field and subsequently stabilizes planar flames (Fig.2) followed with LBV determination at distinct operating conditions. A positive temperature gradient is formed in the direction of mixture flow using an external heater distanced at 2 cm below the quartz channel. This heater also helps achieving adiabaticity. The channel and heater are aligned parallel to each other with an overlap distance of 4 cm. The position of a stabilized flame is fixed by the balance between the negative and positive velocity gradient. The flow rates of fuel and air are monitored using the mass flow controllers (MFC) for different experimental conditions (equivalence ratio and mixture velocity).

Air is used as an oxidizer for the different mixtures of methane, hydrogen, and ammonia for the present measurements. The MFC's for methane (0-2 slpm), hydrogen (0-0.5 slpm), ammonia (0-0.2 slpm), and air (0-5 slpm) have an accuracy of ±1% of the full-scale flow and are controlled via computer using a command module. A K-type thermocouple is used for temperature measurements. All the LBV measurements were repeated thrice, and the final values have an uncertainty of ±5%. The LBV is calculated using Eq. (1) (obtained from the continuity equation and equation of state):

$$S_u = U_{inlet} \times \frac{A}{A_f} \times \frac{T_u}{T_{u,o}} \tag{1}$$

Following correlation (Eq. (2)) was obtained between LBV and temperature ratio using the power-law curve fitting to calculate the temperature exponent:

$$\frac{S_u}{S_{u.o}} = \left(\frac{T_u}{T_{u,o}}\right)^{\alpha} \tag{2}$$

The current measurements are compared with the reaction mechanisms of Li et al. [15], Okafor et al. [6], and Shrestha et al. [16]. The predictions of the kinetic models are evaluated using Chemkin-Pro software tool.
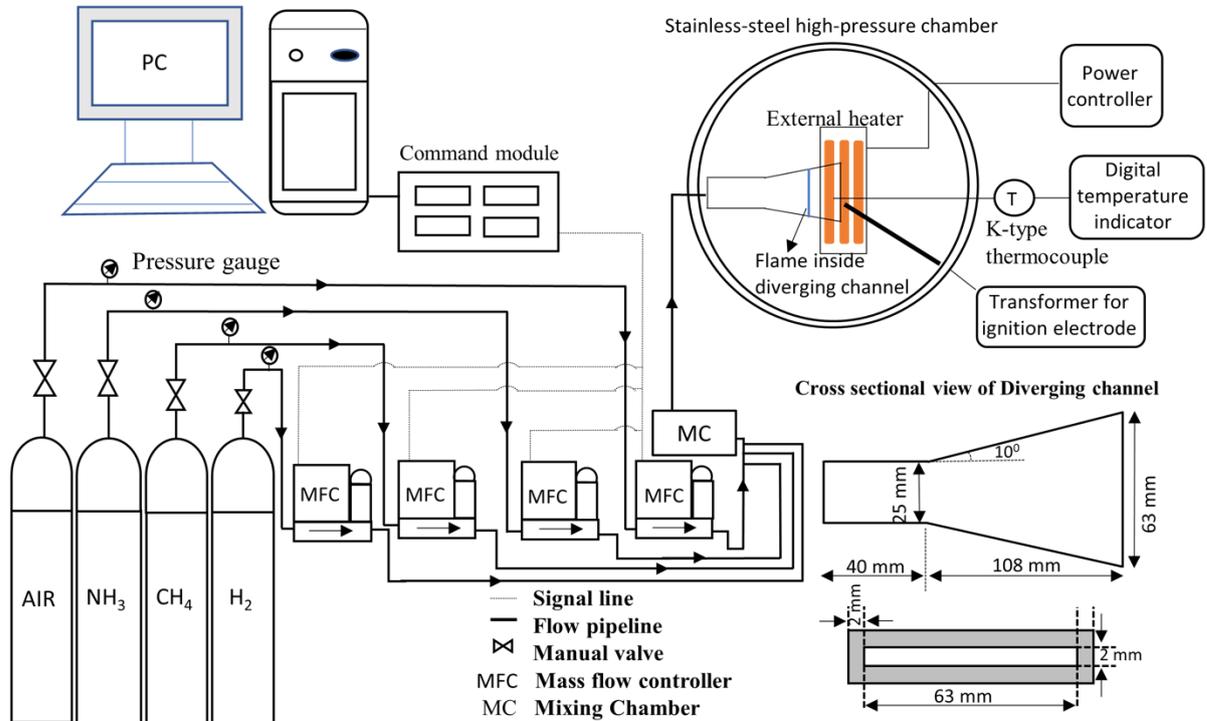
Figure 1: Experimental set up schematics
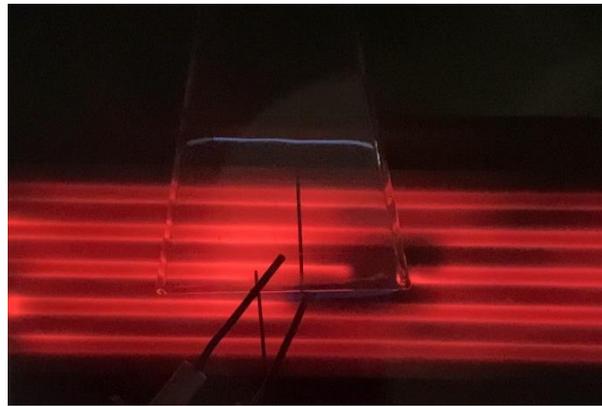
Figure 2: Stabilized planar flame of $NH_3/H_2/CH_4$-air mixture under 0.3 MPa at stoichiometric condition

3   Results and Discussion

In this study, laminar burning velocity (LBV) measurements of $NH_3/H_2/CH_4$-air premixed mixtures are carried out using the externally heated diverging channel method. For an equivalence ratio ($\phi = 0.7$-1.4) at mixture temperature (300 – 750 K) and elevated pressures (0.1-0.3 MPa), the mole fraction of NH_3 (X_{NH3}) is varied between 0.1 and 0.3 in CH_4/H_2 (4:1) fuel mixture. The influence of varying experimental conditions on the LBV of the proposed ternary blend have been discussed and compared with pure CH_4-air mixtures in the following subsections. The measurements being novel in terms of the blend

composition, no literature data is available for comparison. Therefore, mechanism predictions of Li et al. [15], Okafor et al. [6], and Shrestha et al. [16] has been used in this investigation.

Figure 3 illustrates the LBV variation of $NH_3/H_2/CH_4$-air mixtures with X_{NH3} = 0.1, 0.3 and pure CH_4 with temperature ratio ($T_u/T_{u,0}$) for lean, stoichiometric, and rich conditions. The data is compared for 0.1 and 0.3 MPa. A consistent decrease in the LBV is evident with increase in pressure at all mixture conditions. Interestingly, LBV for the composition with X_{NH3}= 0.1 is higher in comparison to CH_4/natural gas irrespective of the pressure. This clearly shows the efficacy of the ternary blend as an alternative for natural gas with lower carbon emissions (~ 25%). Also, LBV increases with the rise in temperature ratio, and the temperature exponent (calculated using Eq. 2.) tends to increase with pressure rise.
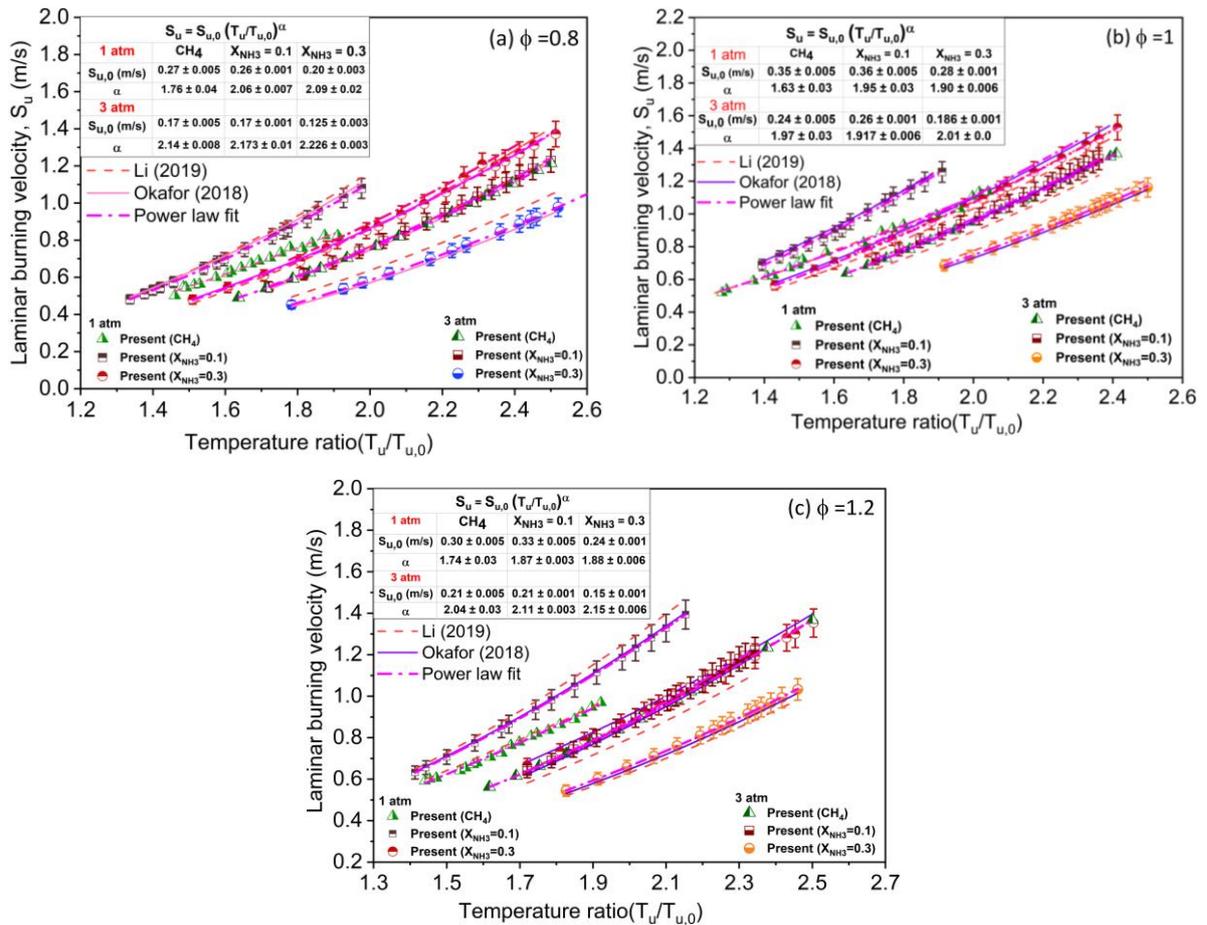
Figure 3. Variation of LBV with temperature ratio at (a) ϕ = 0.8, (b) ϕ = 1 and (c) ϕ = 1.2

Figure 4 shows the LBV variation with equivalence ratio at mixture temperatures of 300 K and 750 K for 0.1 and 0.3 MPa. At ϕ = 1 and 0.3 MPa pressure, LBV decrease by ~33% and ~27% at mixture temperatures of 300 K and 750 K respectively. This highlights the diminishing effect of pressure at higher mixture temperature. LBV of X_{NH3} = 0.1 is higher than pure CH_4 at 0.1 MPa and is comparable at higher pressure (0.3 MPa). A good consistency is observed on comparison with the predictions of Okafor [6] and Li [15] kinetic models. Higher LBV predictions are observed for Shrestha [16] reaction mechanisms at stoichiometric and rich conditions.

(a)   (b)
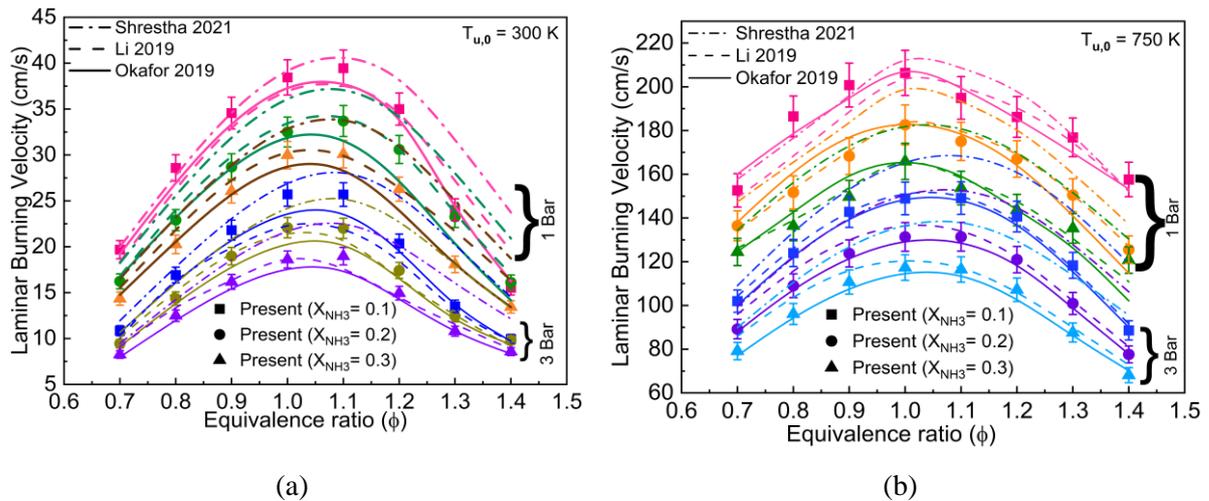
Figure 4: Variation of LBV with equivalence ratio at 0.1 and 0.3 MPa for temperatures (a) 300 K and (b) 750 K

4   Conclusion

Fundamental investigations on ammonia fuel blend have been reported to investigate a ternary blend composition with either higher or comparable laminar burning velocity (LBV) with methane. The key findings of this work include:

- A higher LBV of $NH_3/H_2/CH_4$-air mixture is observed in comparison to pure CH_4 at higher mixture temperatures of 500 K.
- At high pressure, the LBV of $NH_3/H_2/CH_4$-air mixtures ($X_{NH3} = 0.1$) comply well with pure CH_4.
- $NH_3/H_2/CH_4$ ternary blend can be proposed as a potential alternative fuel to natural gas and extensive research can be further performed at engine relevant conditions to mitigate NOx emissions.

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