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Experimental and numerical study of the laminar burning velocity of CH_4–NH_3–air premixed flames

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ABSTRACT

With the renewed interest in ammonia as a carbon-neutral fuel, mixtures of ammonia and methane are also being considered as fuel. In order to develop gas turbine combustors for the fuels, development of reaction mechanisms that accurately model the burning velocity and emissions from the flames is important. In this study, the laminar burning velocity of premixed methane–ammonia–air mixtures were studied experimentally and numerically over a wide range of equivalence ratios and ammonia concentrations. Ammonia concentration in the fuel, expressed in terms of the heat fraction of NH_3 in the fuel, was varied from 0 to 0.3 while the equivalence ratio was varied from 0.8 to 1.3. The experiments were conducted using a constant volume chamber, at 298 K and 0.10 MPa. The burning velocity decreased with an increase in ammonia concentration. The numerical results showed that the kinetic mechanism by Tian et al. largely underestimates the unstretched laminar burning velocity owing mainly to the dominance of $HCO\ (+H, OH, O_2) = CO\ (+H_2, H_2O, HO_2)$ over $HCO = CO + H$ in the conversion of HCO to CO. GRI Mech 3.0 predicts the burning velocity of the mixture closely however some reactions relevant to the burning velocity and NO reduction in methane–ammonia flames are missing in the mechanism. A detailed reaction mechanism was developed based on GRI Mech 3.0 and the mechanism by Tian et al. and validated with the experimental results. The temperature and species profiles computed with the present model agree with that of GRI Mech 3.0 for methane–air flames. On the other hand, the NO profile computed with the present model agrees with Tian et al.'s mechanism for methane–ammonia flames with high ammonia concentration. Furthermore, the burned gas Markstein length was measured and was found to increase with equivalence ratio and ammonia concentration.

1. Introduction

Interest in ammonia as a hydrogen carrier has recently been kindled in a search for safer and cheaper means of hydrogen transportation and storage. In comparison to the advanced materials for hydrogen storage such as metallic hydrides, ammonia has a relatively high hydrogen density, being made up of 17.8% by weight of hydrogen [1,2]. Ammonia, being one of the world's most produced chemicals, has a well-established production, transportation and storage infrastructure. Similar to hydrogen, ammonia is synthesised from fossil fuels and the CO_2 produced during the synthesis can be captured and sequestered [2]. On the other hand, ammonia can be produced from renewable CO_2 free energy sources [3]. Ammonia can be easily liquefied and stored at about 8.5 bar at room temperature or cooled to −33 °C and stored at ambient pressure. This makes its storage much less expensive than hydrogen storage, which requires about 350–700 bar for its storage at room temperature or −252.8 °C for its storage as a liquid at ambient pressure [4].

On the other hand, following the kindled interests in ammonia as a hydrogen carrier is a renewed interest in ammonia as a fuel. Ammonia is combustible and, being a carbon-free molecule, burns without carbon oxides emission. Ammonia is therefore considered a promising carbon-neutral fuel that offers great potentials of mitigating greenhouse gas emission. However, earlier applications and studies of ammonia as a fuel reported challenges associated with ammonia combustion [5,6]. Ammonia has a low burning velocity that is about five times lower than that of methane, a narrow flammable range, a high minimum ignition energy and a nitrogen atom in its molecule. These may result to low heat release rate, poor flame stabilisation characteristics, low combustion efficiency and high fuel NO emission etc. [6,7]. Nonetheless, our research team has recently demonstrated efficient application of ammonia for power generation in a micro gas turbine plant [8]. Other

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means of employing ammonia as a fuel in internal combustion engines include the use of mixtures of ammonia and other fuels such as hydrogen [9–11], methane [12] and diesel [13,14].

Stabilisation of flames of ammonia containing mixtures on gas turbine combustors and the reduction of the high fuel NO emission from the flames are among the most important challenges in the development of gas turbine combustors for the fuels. Therefore, for the development of combustors for ammonia and blends of ammonia and other fuels, chemical kinetic mechanisms that accurately model the burning velocity of the mixtures and NO emissions from the flames are very relevant.

The laminar burning velocity is one of the most important properties of a mixture governing its combustion behaviour. It can serve as a parameter for characterising many premixed flame phenomena such as flashback, blow off or flame stabilisation on gas turbine combustors. It is also relevant in the validation and optimisation of reaction mechanisms. The laminar burning velocity is defined based on an adiabatic planar unstretched flame. However most practical laminar flame experience curvature and/or stretch, which results in the deviation of their burning velocities from those of the unstretched planar flames. Consequently, a method that correlates the stretched burning velocity with stretch and curvature needs to be used to extrapolate the laminar burning velocity of the stretched flame to that of an unstretched planar one [15].

The Markstein length, which is another important combustion property of a fuel, quantitatively expresses the sensitivity of the laminar burning velocity to flame stretch rate due to thermo-diffusive effects. It is an important parameter in the modelling of turbulent flames. Bradley et al. [16] concluded in their studies that the turbulent burning velocity may be affected by thermo-diffusive effects, hence may depend on the Markstein number i.e. the Markstein length normalised with the flame thickness. Although the Markstein number may correlate linearly with the Lewis number, which is easier to evaluate, the Markstein number is the preferred parameter to the Lewis number in turbulent flame modelling [17]. The Markstein length or the Markstein number is a more comprehensive expression of the phenomenon of response of a flame to stretch [18].

The present study focuses on measurement of the laminar burning velocity and development/optimisation of chemical kinetic mechanisms to accurately model the laminar burning velocity and NO emission from methane–ammonia mixtures. The fundamental combustion characteristics of methane have been well studied and numerous studies of methane flame chemistry have resulted to the development, optimisation and validation of kinetic mechanisms for modelling methane combustion, such as GRI Mech 3.0 [19], ARAMCO Mechanism v1.3 [20], University College San Diego Mechanism [21], etc. On the other hand, ammonia is an unconventional fuel, which has not been given much attention as a fuel for combustion applications. Therefore, even though several studies on ammonia oxidation chemistry have led to the development of ammonia oxidation mechanisms, there is limited data on some key combustion properties of ammonia mixtures for optimising and validating the mechanisms [7]. Hayakawa et al. [7] compared their measured unstretched laminar burning velocity of NH_3–air flames with numerical results obtained using the chemical kinetic mechanisms by Miller et al. [22], Lindstedt et al. [23], Konnov [24], Tian et al. [25], all of which were developed for ammonia combustion, and GRI Mech 3.0 [19]. They concluded that the mechanisms could not satisfactorily reproduce the measured burning velocity.

Similarly, there are limited experimental data on the laminar burning velocity of methane–ammonia flames. Most previous experimental studies on the fundamental combustion characteristics of methane–ammonia fuel concentrated mainly on the measurement of species profiles, being motivated by the need to understand and predict NO formation from the combustion of nitrogen-containing fuels. These studies provided important information on the structure of the flames and also resulted to the development of chemical kinetic mechanisms for the mixtures [24–29]. Tian et al. [25] developed a detailed reaction mechanism for methane–ammonia flames based on their experimental and numerical study of the structure of premixed $NH_3/CH_4/O_2/Ar$ stoichiometric flames at 4 kPa using tuneable synchrotron vacuum ultraviolet photoionisation and molecular-beam mass spectrometry. The mechanism has a detailed methane and ammonia oxidation chemistry, consisting of 84 species and 703 elementary reactions. The study by Hayakawa et al. [7] showed that the laminar burning velocity of ammonia flames obtained using the mechanism by Tian et al. [25] was closer to the experimental result than were those obtained using the mechanisms by Miller et al. [22], Lindstedt et al. [23], and Konnov [24]. However, due to very limited experimental data on the laminar burning velocity of methane–ammonia flames, the available methane–ammonia reaction mechanisms, including Tian et al.'s [25], have not been validated or optimised for modelling the laminar burning velocity of the mixtures. So far, the only reported laminar burning velocity data on methane–ammonia flames are for trace quantities of ammonia in methane i.e. ammonia volume fractions less than or equal to 0.05 [26]. Furthermore, data on the Markstein length of methane–ammonia flames have not been reported so far.

In this study therefore, the unstretched laminar burning velocity of methane–ammonia–air flames were carefully measured for varying concentrations of ammonia in the binary fuel over a wide range of equivalence ratios. A detailed kinetic mechanism was developed to satisfactorily model the laminar burning velocity and NO concentration in the flames. Furthermore, the Markstein length of the mixtures was measured and its variation with equivalence ratio and ammonia concentration was investigated.

2. Experimental and numerical procedures

Figure 1 schematically shows the experimental setup used in this study. Experiments were carried out using a cylindrical constant volume combustion chamber. The inner diameter and length of the chamber were 270 mm and 410 mm, respectively. Two oppositely faced quartz glass windows of 60 mm in diameter allowed for optical access into the chamber. The combustible mixture quantities were prepared in the chamber according to the required partial pressures of the component gases using a GE UNIK 5000 silicon pressure sensor with an enhanced premium accuracy. The mixtures were ignited at a point along the central axis of the cylindrical chamber using capacitor discharge ignition (CDI). The diameter of the spark electrodes was 1.5 mm and the spark gap was set to 1 mm. The electrostatic energy, which was charged in the capacitor in the CDI circuit, was set to 0.3 J.

Flame propagation up to a diameter of 60 mm was observed and recorded by Schlieren photography via the quartz windows of the chamber with a high-speed digital camera (Photron, FASTCAM Mini UX100), while the pressure rise inside the chamber during flame propagation was measured using a Kistler pressure transducer. The pixel setting for the camera was 768 × 768 and the framing rates adopted ranged from 2500 to 6000 f/s, depending on the flame speeds. In addition, direct colour photographs were taken using the high-speed camera. The pixel resolution and frame rate of the colour imaging were 1024 × 1024 and 2500 f/s, respectively while the spatial resolution of the images was approximately 0.16 mm/pixel.

The studied conditions and properties of the mixtures are summarised in Table 1. The mixture temperature, T_u, and pressure, P_i, were 298 K and 0.10 MPa, respectively. Variations in the temperature of the mixtures were kept within ±3 K. As Fig. 2 shows, there was no pressure rise in the chamber during the period of record-