

BLENDING AMMONIA INTO HYDROGEN TO ENHANCE SAFETY THROUGH REDUCED BURNING VELOCITY

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ABSTRACT

Laminar burning velocities (S_L) of hydrogen/ammonia mixtures in air at atmospheric pressure were studied experimentally and numerically. The blending of hydrogen with ammonia, two fuels that have been proposed as promising carriers for renewable energy, causes the laminar flame speed of the mixture, S_L , to decrease significantly. However, details of this have not previously available. Systematic measurements were therefore performed for a series of hydrogen/ammonia mixtures with wide ranges of mole fractions of blended ammonia (X_{NH_3}) and equivalence ratio using a heat flux method based on heat flux of a flat flame transferred to the burner surface. It was found that the mixture of $X_{\text{NH}_3} = 40\%$ has a value of S_L close to that of methane, which is the dominant component of natural gas. Using three chemical kinetic mechanisms available in the literature, i.e., the well-known GRI-Mech 3.0 mechanism and two mechanisms recently released, S_L were also modelled for the cases studied. However, the discrepancies between the experimental and numerical results can exceed 50% with the GRI-Mech 3.0 mechanism. Discrepancies were also found between the numerical results obtained with different mechanisms. These results can contribute to an increase in both the safety and efficiency of the co-utilization of these two types of emerging renewable fuel and to guiding the development of better kinetic models.

1. INTRODUCTION

Both hydrogen and ammonia have been proposed as renewable energy carriers [1, 2]. It is therefore important to develop efficient and cost-effective methods to safely utilise, store and transport these two fuels, either together or separately. However, the physical and combustion characteristics of these two gases are quite different from each other, so that their blending can be expected to introduce new challenges and opportunities. Hydrogen has wide flammability limits (0.04 - 0.75, the mole fraction of hydrogen in hydrogen/air mixtures at 1 atm) [3], a high diffusion coefficient (0.756 cm²/second, at 20 °C and 101.325 kPa) [4] in air and a low ignition energy. It is also colourless and non-toxic. On the other hand, ammonia has narrow flammability limits (0.15 - 0.28) [3], a high ignition energy and a relatively low diffusion coefficient (0.228 ± 0.0012 cm²/s at 1atm and 25 °C) [5]. Furthermore, ammonia can be easily separated from hydrogen by cooling and pressurizing the mixture. The complementary properties of hydrogen and ammonia, together with their ease of separation, inspire us to assess the feasibility of blending ammonia into hydrogen to enhance the safety in hydrogen transport and storage. Blending has the potential to reduce both the probability of ignition of gases in case of a leak and the dissipation velocity of any leaked gas. However, while the physical properties of a hydrogen/air mixture (e.g. density, heat capacity and diffusion rate) can be predicted theoretically with acceptable accuracy from the values of each gas, the combustion properties cannot due to nonlinear dependences of the chemical reactions on the mole fractions of reactants. This is particularly true for the burning velocity, which is a critical parameter needed to manage the fuel safely. Since only a few detailed investigations of the burning velocity of hydrogen blended with ammonia are available, the aim of the present investigation is to expand the experimental data to meet this need.

Previous investigations of the burning velocity of hydrogen/ammonia mixtures have been motivated mostly by the desire to increase the burning velocity of ammonia by co-burning it with hydrogen [6-8]. However, despite a few previous investigations of this topic, the amount of experimental data is very

limited. Insufficient numbers of blending ratio and equivalence ratio have been reported for designs to be performed reliably. In addition, insufficient knowledge is available of the accuracy of the available chemistry mechanisms in the prediction of ammonia-fuelled combustion. For example, the widely used and well-known GRI mechanism (GRI-Mech 3.0) [9] has been developed to predict NO_x production from methane flames. Hence, even though both ammonia and hydrogen are both involved in this mechanism, their very different concentrations in ammonia/hydrogen blended fuels raises the question as to whether this mechanism may be less accurate in predicting ammonia/hydrogen/air flames. In addition, two more recent kinetic mechanisms, namely the Okafor-mechanism [10] and the San Diego-mechanism [11], have been developed specifically for ammonia-fuelled combustion. However, insufficient experimental data are available with which to validate these models across a wide range of flame conditions. Hence the second aim of the paper is to meet this need.

In the light of the above discussion, the specific aims of the present work are (1) to measure the laminar burning velocities of series of hydrogen/ammonia mixtures in air at atmospheric pressure for a range of blend ratios and mixture fractions and (2) to assess the validity of the three available chemical mechanisms in predicting flame speed across the range of new data. The feasibility of co-transporting and co-storing the two renewable fuels is also discussed briefly.

2. EXPERIMENT

Laminar burning velocities were measured using the heat flux method based on a flat flame burner. Details of the method can be found in a previous work [12]. Briefly, the radial profile of temperature on the burner plate was measured using thin thermocouples attached to the plate. The radial temperature profile on the surface of the burner plate became flat when the velocity of the premixed gases (fuel and air) equals the burning velocity of the mixture. This method has the advantage over some methods in that the flames are stretchless, one-dimensional and quasi adiabatic, and the measurement uncertainty was estimated as ± 1 cm/s for results obtained in the present work. Figure 1 shows a schematic diagram of the experimental setup, which comprises a heat flux burner and a gas supply system [13]. In the present work, synthetic air was produced by mixing 20.9% (mole fraction) oxygen with nitrogen. All gases (Hydrogen, Ammonia, Oxygen and Nitrogen) have a purity of 99.99% and the gas-supplying pipes are made from stainless steel.

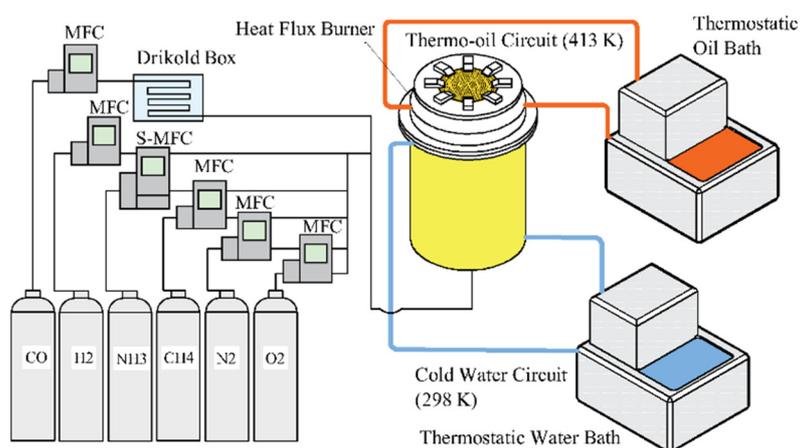


Figure 1. Schematic diagram of the experimental setup

3. KINETIC MODELLING

Three chemical mechanisms were used in the kinetic modelling of the mixtures, namely the GRI-mech 3.0 [9], the Okafor mechanism [10] developed for $\text{NH}_3/\text{CH}_4/\text{air}$ flames based on the GRI-mech 3.0 and

the San Diego mechanism [11] used for modelling NH_3 ignition processes. All the kinetics modelling was performed using the ChemKin-PRO software and the PREMIXED module was adopted.

4. RESULTS AND DISCUSSION

Figure 2 presents the laminar burning velocities measured and calculated for the H_2/NH_3 mixtures with different blending ratios (X) of NH_3 . The equivalence ratio of fuel/air was kept stoichiometric. Both experimental and numerical results consistently present a trend that blending ammonia reduces the burning velocity of the mixture, which decreases significantly from that of more than 200 cm/s for H_2/air to only around 20 cm/s with a 65% NH_3 concentration. The effect of blending ammonia on reducing burning velocity is particularly significant in the range of $X_{\text{NH}_3} < 0.3$, in which the predictions obtained from three mechanisms are consistent and agree well with previous experimental results. Figure 1a also shows that blending 10% ammonia reduces the burning velocity to approximately 170 cm/s, which further decreases to approximately 100 cm/s with 20% blending. This indicates that no large amount of ammonia is needed to halve the burning velocity of the fuel mixture. From the numerical and previous experimental data at approximately $X_{\text{NH}_3} = 0.4$, it is also found that the burning velocity approaches to 50 cm/s. This S_L value is close to that of the methane burned in air under stoichiometric condition at atmospheric pressure, which has been widely studied regarding to natural gas safety.

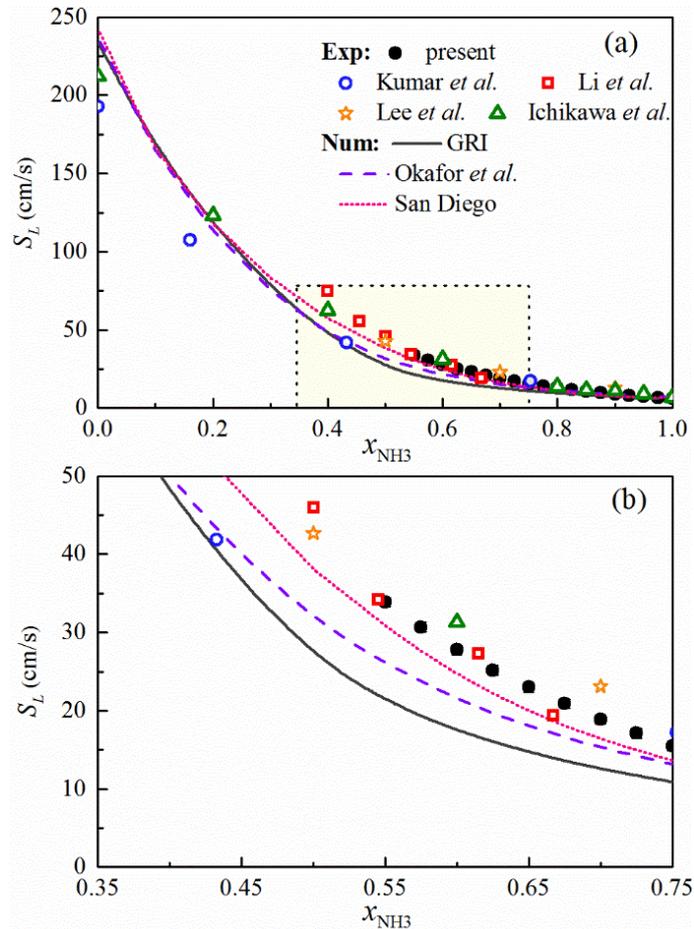


Figure 2. (a) Laminar burning velocities of stoichiometric $\text{H}_2/\text{NH}_3/\text{air}$ flames as a function of the blending ratio of NH_3 in the fuel; (b) a zoomed-in figure for the blending ratios between 0.35 and 0.75. Experimental results include those from Kumar *et al.* [14], Li *et al.* [15], Lee *et al.* [16] and Ichikawa *et al.* [17].

Figure 2 also presents large discrepancies between the measured results and those predicted using the three chemistry mechanisms. Particularly in the range of $0.35 < X_{\text{NH}_3} < 0.75$, which is interest for fuel

safety because of the low S_L values, large discrepancies remain between the measured and numerical results, as shown in Fig. 2b. The experimental data obtained from different methods have a good agreement between them, but all the numerical data are lower than those from experiments. The relative discrepancies between the experimental and numerical data are even more than 50% for the concentrations around $X_{NH_3} = 50\%$. Furthermore, in the range $0.45 < X_{NH_3}$, the numerical results based on the well-developed GRI-3.0 mechanism have a greater discrepancy than both that based on the Okafor-mech and on the San-Diego mech. This suggests that further development of the chemical mechanism is needed prior to its use in ammonia-related ignition and combustion, even though the mechanism has been widely used for hydrocarbon fuels.

Figure 3 further highlights the large discrepancies between the numerical and experimental results for the flames with different equivalence ratios but for a constant blend ratio of 0.6. None of the mechanisms tested can accurately predict the burning velocities quantitatively, with the poor performance again being worst for the well-known GRI-mech 3.0. While most of fire accidents are diffusion combustion processes, accurate prediction of the burning velocities for a wide range of fuel/air ratios is also necessary.

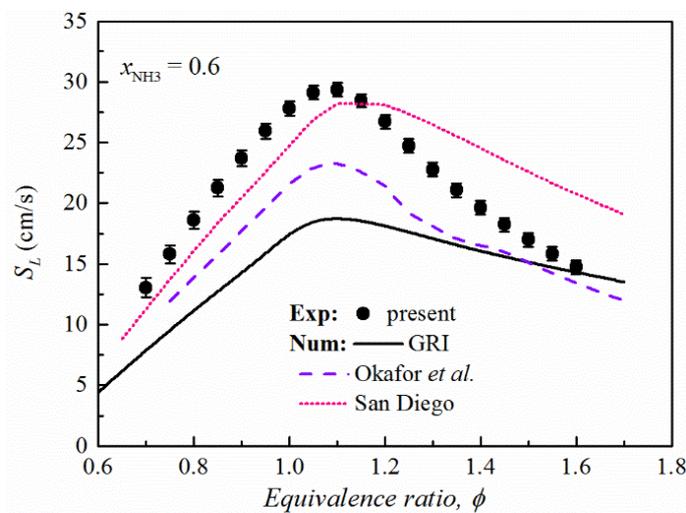


Figure 3. Laminar burning velocities of H_2/NH_3 /air flames with equivalence ratio ranging from 0.7 to 1.6. The blending ratio of NH_3 in the fuel was kept constant as 0.6.

In addition to the burning velocity, other studies are also needed to assess the feasibility of the proposed method, for example the optimal blending ratio of ammonia and the suitable materials for fuel pipelines. Anhydrous ammonia has moderately high vapour pressures. It is 429.4 kPa at 0 °C, 728.3 kPa at 15 °C and 857.1 kPa at 20 °C [18]. Therefore, it is feasible to blend gaseous ammonia into pressurised pipelines that have already been built for hydrogen transportation, while the maximum blending ratio of ammonia depends on the operation pressure. So that ammonia liquefaction in the gas pipe is avoided. Both polyethylene (PE) and polyvinyl chloride (PVC) have good chemical resistance for ammonia, while stainless steel (316L) has excellent chemical resistance. These materials are already used in natural gas pipelines nowadays.

5. CONCLUSIONS

New information has been obtained of the influence of pure hydrogen and ammonia on flame speed. Trends are consistent with previous work showing that the blending of ammonia into hydrogen reduces the burning velocity of the fuel mixture, although the present measurements reduce the uncertainty in the measured data. The results identify conditions in which the laminar flame speed of the blends is similar to that methane, although other combustion performance parameters also need to be assessed. Significant discrepancies were identified between the present experimental results and those calculated based on three chemistry mechanisms available in the literature, indicating that the mechanisms still

need further improvement to accurately predict of the burning velocities related to hydrogen/ammonia mixed fuel. These mechanisms should also be assessed against other performance parameters, such as radiation heat transfer and pollutant emissions.

REFERENCES

1. Crabtree, G.W. and M.S. Dresselhaus, The Hydrogen Fuel Alternative. MRS Bulletin, 2008. 33(4): p. 421-428.
2. Service, R.F., Liquid sunshine: Ammonia made from sun, air, and water could turn Australia into a renewable energy superpower. Science, 2018. 361(6398): p. 120-123.
3. Chung K. Law, *Combustion Physics*. 2006: Cambridge University Press.
4. CRC handbook of chemistry and physics: a ready-reference book of chemical and physical data. 95th ed. ed. 2014: CRC Press.
5. Spiller, L.L., Determination of Ammonia/Air Diffusion Coefficient Using Nafion Lined Tube. Analytical Letters, 1989. 22(11-12): p. 2561-2573.
6. Kobayashi, H., A. Hayakawa, K.D.Kunkuma A. Somarathne, and Ekenechukwu C. Okafor, Science and technology of ammonia combustion. Proceedings of the Combustion Institute, 2019. 37(1): p. 109-133.
7. Morgan, E., J. Manwell, and J. McGowan, Wind-powered ammonia fuel production for remote islands: A case study. Renewable Energy, 2014. 72: p. 51-61.
8. Zamfirescu, C. and I. Dincer, Ammonia as a green fuel and hydrogen source for vehicular applications. Fuel Processing Technology, 2009. 90(5): p. 729-737.
9. Gregory P. Smith, David M. Golden, Michael Frenklach, Nigel W. Moriarty, Boris Eiteneer, Mikhail Goldenberg, C. Thomas Bowman, Ronald K. Hanson, Soonho Song, J. William C. Gardiner, Vitali V. Lissianski, and Z. Qin. Available from: http://www.me.berkeley.edu/gri_mech/.
10. Okafor, E.C., Y. Naito, S. Colson, A. Ichikawa, T. Kudo, A. Hayakawa, and H. Kobayashi, Experimental and numerical study of the laminar burning velocity of CH₄-NH₃-air premixed flames. Combustion and Flame, 2018. 187: p. 185-198.
11. The San Diego Mechanism: Chemical-Kinetic Mechanisms for Combustion Applications. Available from: <http://web.eng.ucsd.edu/mae/groups/combustion/mechanism.html>.
12. Bosschaart, K.J. and L.P.H. de Goey, Detailed analysis of the heat flux method for measuring burning velocities. Combustion and Flame, 2003. 132(1): p. 170-180.
13. Wang, Z.H., W.B. Weng, Y. He, Z.S. Li, and K.F. Cen, Effect of H₂/CO ratio and N₂/CO₂ dilution rate on laminar burning velocity of syngas investigated by direct measurement and simulation. Fuel, 2015. 141: p. 285-292.
14. Kumar, P. and T.R. Meyer, Experimental and modeling study of chemical-kinetics mechanisms for H₂-NH₃-air mixtures in laminar premixed jet flames. Fuel, 2013. 108: p. 166-176.
15. Li, J., H. Huang, N. Kobayashi, Z. He, and Y. Nagai, Study on using hydrogen and ammonia as fuels: Combustion characteristics and NO_x formation. International Journal of Energy Research, 2014. 38(9): p. 1214-1223.
16. Lee, J.H., J.H. Kim, J.H. Park, and O.C. Kwon, Studies on properties of laminar premixed hydrogen-added ammonia/air flames for hydrogen production. International Journal of Hydrogen Energy, 2010. 35(3): p. 1054-1064.
17. Ichikawa, A., A. Hayakawa, Y. Kitagawa, K.D. Kunkuma Amila Somarathne, T. Kudo, and H. Kobayashi, Laminar burning velocity and Markstein length of ammonia/hydrogen/air premixed flames at elevated pressures. International Journal of Hydrogen Energy, 2015. 40(30): p. 9570-9578.
18. Lange's Handbook of Chemistry. 10th ed. McGraw-Hill Education LLC