

Combustion of NH_3 - CH_4 -air and NH_3 - H_2 -air mixtures in a porous burner: experiments and kinetic modelling

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ABSTRACT

This work focuses on the combustion of NH_3 - CH_4 -air and NH_3 - H_2 -air mixtures in a porous burner, studied using both experiments and kinetic modelling. Measurements of temperature within the porous burner and of NO_x , CO and NH_3 concentrations in the flue gas were obtained as a function of the NH_3 molar fraction in both fuel mixtures (NH_3/CH_4 or NH_3/H_2), maintaining constant equivalence ratio (0.8) and constant thermal input (1200 W). The kinetic modelling study included the use of the most recent NH_3 mechanisms reported in the literature. The measured NO_x emissions are significantly high for the two types of mixtures, reaching around 4000 ppm in both cases. The measured NH_3 emissions are also quite high for both types of mixtures, reaching values as high as 500 ppm for the NH_3/CH_4 /air flames, while the measured CO emissions are generally low. The predicted NO_x emissions for both fuel mixtures are significantly higher than the measured ones (up to 4 times), with the exception of the San Diego model for NH_3/H_2 /air flames. In general, the NO_x emission trends are well captured by the three models, but failures in the prediction of the unburned NH_3 and CO in the flue gas are substantial.

Keywords: Ammonia, methane, hydrogen, porous burner, experiments, chemical kinetic modelling

1. INTRODUCTION

Ammonia (NH_3) is a flammable substance that does not contain carbon in its chemical structure so that its combustion does not produce CO_2 . It can be used in a range of combustion systems, such as internal combustion engines and gas turbines [1]; it is relatively safe to store and use, being a stable hydrogen carrier. Ammonia combustion presents, however, a series of drawbacks, such as high minimum ignition energy, low flame speed and high NO_x emissions [1]; in addition, under certain conditions, it may produce significant NH_3 emissions [2]. Despite the recent progress, the mechanisms involved in the chemistry of the NH_3 oxidation and NO formation are still a matter of discussion, and more experimental, theoretical and numerical studies are needed to develop systems able to efficiently burn NH_3 .

To enhance the NH_3 flammability, its mixture with more reacting fuels, such CH_4 and/or H_2 , have been suggested. Some of the most relevant work on this issue came from the research groups at Cardiff University [1,3] and Tohoku University [2,4,5]. For NH_3 - CH_4 mixtures, Kurata et al. [2] showed that NO_x emissions in a laboratory gas turbine combustor increase with the addition of NH_3 , up to a given fraction of NH_3 in the fuel mixture, and that unburned NH_3 emissions may be significant for lower inlet reactant temperatures. For NH_3 - H_2 mixtures, with a NH_3 molar fraction of 0.5, Valera-Medina et al. [3] showed that NO_x emissions in a gas turbine are higher for lean conditions, decreasing for higher equivalence ratios. Interestingly, for high equivalence ratios, Nozari et al. [6] observed the same trend in a porous burner fired with mixtures of NH_3 - H_2 (NH_3 molar fraction equal to 0.8).

In terms of chemical kinetics, Okafor et al. [4] have established a mechanism, validated against laminar flame speeds, for $\text{NH}_3/\text{CH}_4/\text{air}$ flames; Tian et al. [7] have improved a previously developed mechanism for NH_3/CH_4 oxidation based on low pressure experiments; and the San Diego combustion group [8] has developed a nitrogen-related sub-mechanism for their full hydrocarbons mechanism, which is capable of describing the oxidation of NH_3 . For $\text{NH}_3/\text{H}_2/\text{air}$ flames, Rocha et al. [9] have examined the performance of various literature models and concluded that the mechanism of Otomo et al. [10] also predicts well the literature available experimental data.

In light of the limited work available in the literature, this work aims to augment the current understanding on NH_3 combustion. To this end, the combustion of $\text{NH}_3\text{-CH}_4\text{-air}$ and $\text{NH}_3\text{-H}_2\text{-air}$ mixtures in a porous burner is studied, using both experiments and kinetic modelling.

2. EXPERIMENTAL SETUP AND CONDITIONS

The porous burner used in this study is described in detail elsewhere [11,12]. It is made with four layers of alumina (Al_2O_3) and zirconia (ZrO_2) porous foams, with 80% of volumetric porosity, a diameter of 70 mm and a thickness of 20 mm. The porous burner is composed of two different regions, the preheating region that is made of two layers of 40 pores per inch (ppi) and the stable-burning region composed of two layers of 10 ppi. An insulation plate and a stainless steel plate with an injection hole with a diameter of 16 mm were placed upstream of the preheating region.

Ammonia (99.98% pure), methane (99.995% pure) and hydrogen (99.9% pure), from gas cylinders, and air, from a compressor, were supplied to the burner, being premixed in a chamber prior to being injected into the burner. The flow rates of NH_3 , CH_4 , H_2 and air were measured with digital flow meters.

The temperatures within the porous media were measured using 250 μm diameter wire platinum/platinum:13% rhodium thermocouples placed in a twin-bore alumina sheath with an external diameter of 1.59 mm. The 8 thermocouple beads were positioned in the center of the porous foams and were connected to a data acquisition system interfaced with a computer.

A chimney was placed at the top of the burner to homogenize the flue gas and to facilitate sampling through a stainless steel water-cooled probe. The analytical instrumentation included a magnetic pressure analyzer for O_2 concentration measurements, a non-dispersive infrared gas analyzer for CO_2 and CO concentration measurements and a chemiluminescent analyzer for NO_x concentration measurements. The NH_3 concentrations measurements were obtained with Gastec detector tubes, which have a minimum detection limit of 2 ppm. Repeatability of the flue gas data was, on average, within 10% of the mean value.

Experiments were conducted at atmospheric pressure for a fixed thermal input of 1200 W, an fixed equivalence ratio of 0.8, and NH_3 mole fractions, $x_{\text{NH}_3} = V_{\text{NH}_3}/(V_{\text{NH}_3} + V_i)$, i representing CH_4 or H_2 , from 0.3 to 0.8 for the NH_3/CH_4 mixtures and from 0.5 to 0.8 for the NH_3/H_2 mixtures.

3. NUMERICAL METHOD

The porous burner was modelled using Cantera [13] as a cylindrical burner in which a burner-stabilized, premixed flat flame is established by solving multicomponent transport equations using the measured temperature profiles along the axis. The mesh is one-dimensional, and correlations were made for the equivalent diameter, considering the porosity of the material.

The mechanisms of Okafor et al. [4], Tian et al. [7] and of the San Diego group [8] were chosen for both the $\text{NH}_3/\text{CH}_4/\text{air}$ flames and the $\text{NH}_3/\text{H}_2/\text{air}$ flames. The mechanism of Otomo et al. [10], despite the good performance for $\text{NH}_3/\text{H}_2/\text{air}$ adiabatic flames [9], does not converge well for the cases studied.

4. RESULTS AND DISCUSSION

Figure 1 shows the measured and predicted NO_x , CO and NH_3 emissions as a function of x_{NH_3} for $\text{NH}_3/\text{CH}_4/\text{air}$ flames and $\text{NH}_3/\text{H}_2/\text{air}$ flames. It should be pointed out that the measured NO_x and CO emissions for pure methane firing were 107 and 12 ppm, respectively, but for pure H_2 it was not possible to operate the present porous burner due to flame flashback. Fig. 1 reveals that the predicted NO_x emissions for both fuel mixtures are significantly higher than the measured ones (up to 4 times), with the exception of the San Diego model for $\text{NH}_3/\text{H}_2/\text{air}$ flames. For $\text{NH}_3/\text{CH}_4/\text{air}$ flames, the measured NO_x emissions present a maximum for $x_{\text{NH}_3} \approx 0.5$, as also captured by the predictions, although for different values of x_{NH_3} . The measured CO emissions for the $\text{NH}_3/\text{CH}_4/\text{air}$ flames are very low, below 50 ppm. Unlike the measurements, significant over prediction of CO is found with the present kinetic mechanisms, especially for low values of x_{NH_3} . The measured NH_3 emissions increase significantly as x_{NH_3} increases, reaching values of 500 ppm, while the predictions fail completely with values lower than 1 ppm for all conditions.

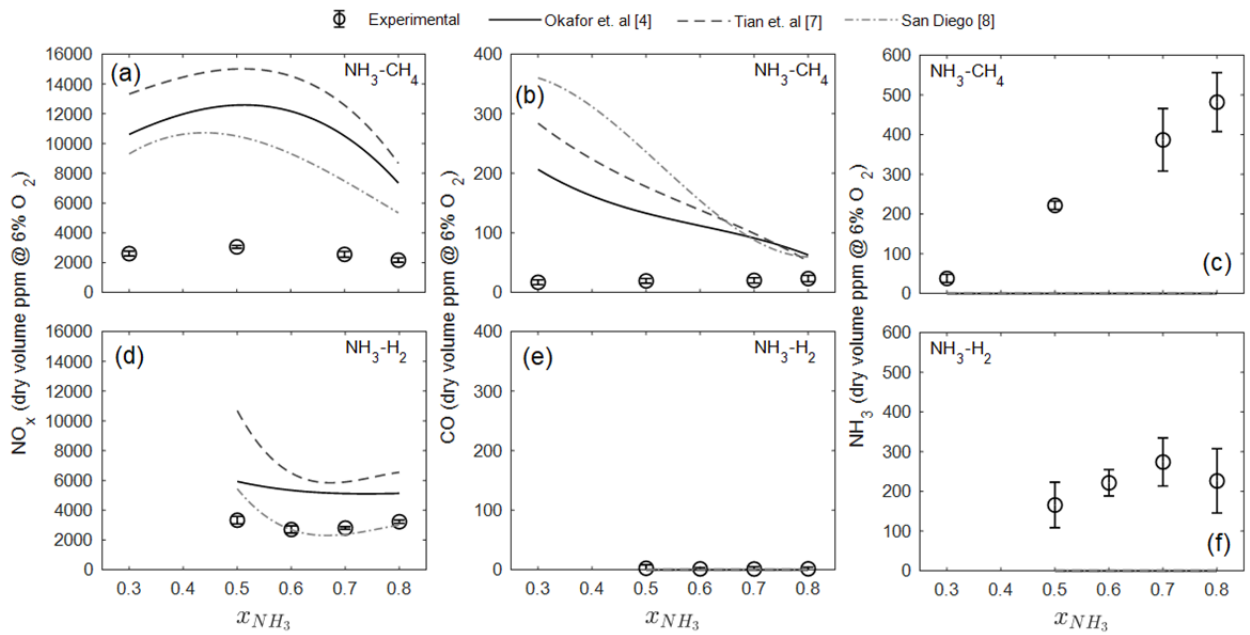


Figure 1 - Measured and predicted NO_x , CO and NH_3 emissions as a function of the NH_3 mole fraction, x_{NH_3} . (a-c) NO_x , CO and NH_3 emissions for mixtures of $\text{NH}_3\text{-CH}_4$ as fuel; (d-f) NO_x , CO and NH_3 emissions for mixtures of $\text{NH}_3\text{-H}_2$ as fuel.

For $\text{NH}_3/\text{H}_2/\text{air}$ flames, the measured NO_x emissions vary between 2000 and 4000 ppm, with a minimum located at $x_{\text{NH}_3} = 0.6$. The predictions show similar trends, with the mechanism of San Diego [8] giving values rather close to the measured ones. The measured and predicted CO emissions are obviously zero, owing to the absence of carbon in the fuel mixtures. Finally, the measured NH_3 emissions present a maximum at $x_{\text{NH}_3} = 0.7$, reaching almost 300 ppm, while the predictions indicate values below 1 ppm for all conditions.

5. CONCLUSIONS

Measurements of NO_x , CO and NH_3 emissions from the combustion of $\text{NH}_3\text{-CH}_4\text{-air}$ and $\text{NH}_3\text{-H}_2\text{-air}$ mixtures in a porous burner are reported for a wide range of operating conditions. The results indicate that the NO_x emissions are significantly high for the two types of mixtures, reaching around 4000 ppm in both cases. Unlike the low CO emissions, the experimental data also reveal that NH_3 emissions are an issue in the present burner for both types of mixtures, reaching values as high as 500 ppm for the $\text{NH}_3/\text{CH}_4/\text{air}$ flames. The work also included a chemical kinetic study

using three literature models. Overall, the predicted NO_x emissions for both fuel mixtures are significantly higher than the measured ones (up to 4 times), with the exception of the San Diego model for NH₃/H₂/air flames. In general, the NO_x emission trends are well captured by the three models, but failures in the prediction of the unburned NH₃ in the flue gas are substantial.

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