

# EXPERIMENTAL AND NUMERICAL STUDY OF PREMIXED AMMONIA-METHANE-AIR FLAMES

C. F. Ramos<sup>1</sup>, R. C. Rocha<sup>1</sup>, P. M. R. Oliveira<sup>1</sup>, M. Costa<sup>1</sup>, X.-S. Bai<sup>2</sup>

1. IDMEC, Mechanical Engineering Department, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

2. Division of Fluid Mechanics, Lund University, P.O. Box 118, S-22100 Lund, Sweden

## ABSTRACT

The present work focuses on quantifying experimentally and numerically, using three chemical kinetic models available in the literature, the emissions of NO<sub>x</sub>, CO and NH<sub>3</sub> from premixed NH<sub>3</sub>-CH<sub>4</sub>-air flames as a function of the NH<sub>3</sub> mole fraction in the fuel mixture and the equivalence ratio. The experimental results showed that the NO<sub>x</sub> emissions for NH<sub>3</sub>-CH<sub>4</sub> flames are significantly higher than those for the pure CH<sub>4</sub> flames; they are not significantly affected by the NH<sub>3</sub> mole fraction in the fuel mixture, and decrease slightly as the equivalence ratio increases. In addition, measured CO and NH<sub>3</sub> emissions are below 60 and 10 ppm, respectively, for all operating conditions. The chemical kinetic models predicted similar NO<sub>x</sub> evolutions as a function of the NH<sub>3</sub> mole fraction and equivalence ratio, but well above the measurements for  $\phi = 0.8$  and  $0.9$ , but in good agreement for  $\phi = 1$ . In this latter case, however, the models over predicted significantly the measured CO emissions.

**Keywords:** NH<sub>3</sub>-CH<sub>4</sub>-air flames, NO<sub>x</sub>, experimental, numerical.

## 1. INTRODUCTION

Ammonia (NH<sub>3</sub>) has been considered one of the most viable candidates for substituting fossil fuels due to the absence of carbon in its structure and its versatility in terms of combustion applications [1]. Theoretically, NH<sub>3</sub> combustion emits only water and molecular nitrogen. However, in practice, significant amounts of nitrogen oxides (NO<sub>x</sub>) may be formed during its combustion so that there is a need of understanding the mechanisms behind the formation and destruction of NO in NH<sub>3</sub> flames.

On the experimental side, several studies have focused on characterizing the combustion of NH<sub>3</sub>. In the twentieth century, it was established that NH<sub>3</sub> presents very narrow flammability limits [2]. More recently, researchers have been focused on mitigating the difficulty of burning NH<sub>3</sub> due to its very low laminar flame speed, which is more than five times lower than that of methane [3].

To circumvent these difficulties, a number of fuels, e.g. CH<sub>4</sub> and H<sub>2</sub>, have been added to NH<sub>3</sub> in order to facilitate its combustion. Swirl burner combustors [4] and gas turbines [5] employing these mixtures were featured in investigations where the effect of equivalence ratio and amount of NH<sub>3</sub> in the fuel mixture were evaluated regarding the NO<sub>x</sub> emissions. The results pointed to a peak in NO<sub>x</sub> emissions for stoichiometric conditions, and to an increase in NO<sub>x</sub> emissions as the quantity of NH<sub>3</sub> in the fuel mixture increases, until a maximum is attained, decreasing afterwards.

On the numerical side, Okafor et al. [6] developed a mechanism for ammonia/hydrocarbon mixtures, validated against laminar flame speed data for NH<sub>3</sub>/CH<sub>4</sub>/air flames; Dagaut et al. [7] developed a mechanism for HCN oxidation containing sub-mechanisms for ammonia/methane combustion; and the UCSD combustion group [8] developed a mechanism for hydrocarbons with nitrogen-related sub-mechanisms.

Since  $\text{NO}_x$  emissions are one of the major concerns for a wide acceptance of  $\text{NH}_3$  as fuel, and in light of the limited work available on this matter, the main aims of this work are to extend the current database on  $\text{NO}_x$  emissions from  $\text{NH}_3$ - $\text{CH}_4$  flames, and to evaluate the performance of some of the most promising chemical kinetic mechanisms available in the literature.

## 2. EXPERIMENTAL

The experimental set-up used in this work consisted of a vertically oriented quartz tube with an inner diameter of 4 cm and a length of 50 cm, and a premixed laminar water-cooled burner operating at atmospheric pressure, mounted at the bottom end of the tube [9]. During the tests, the quartz tube was well-insulated with a 30-mm-thick ceramic fibre blanket. Ammonia and methane, from gas cylinders, were fed to the burner as fuel, and air, from a compressor, was supplied as oxidizer. The flow rates of  $\text{NH}_3$ ,  $\text{CH}_4$  and air were measured with digital flow meters.

Local mean gas temperature measurements along the centerline of the quartz tube were obtained using fine wire (27  $\mu\text{m}$ ) thermocouples of platinum/platinum: 13% rhodium. The uncertainty due to radiation heat transfer was estimated to be less than 5% by considering the heat transfer by convection and radiation between the thermocouple bead and the surroundings. Flue gas composition data were obtained using a stainless steel water-cooled probe, placed at a fixed position (30 cm above the burner), near the top end of the quartz tube. The analytical instrumentation included a magnetic pressure analyzer for  $\text{O}_2$  concentration measurements, a non-dispersive infrared gas analyzer for  $\text{CO}_2$  and  $\text{CO}$  concentration measurements and a chemiluminescent analyzer for  $\text{NO}_x$  concentration measurements. The  $\text{NH}_3$  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 a fixed fuel ( $\text{NH}_3$ - $\text{CH}_4$  mixtures) thermal input, 300 W, for three equivalence ratios, 0.8, 0.9 and 1, and  $\text{NH}_3$  mole fractions,  $x_{\text{NH}_3} = V_{\text{NH}_3}/(V_{\text{NH}_3} + V_{\text{CH}_4})$ , up to 0.7. For the conditions used in this study the Reynolds number of the reactants varied between 245 and 307.

## 3. NUMERICAL

The chemical kinetic simulations were made with Cantera [10], following the methodology used by Barbas et al. [9]. The flame region was modelled as an adiabatic, one-dimensional, premixed, laminar flame, held in place by the burner. The model was modified downstream from the flame front by considering heat losses through the introduction of the measured temperature profiles.

In a recent study [11], we evaluated the performance of various chemical kinetic mechanisms available in literature, based on which three mechanisms are considered in the present study. The chemical mechanisms considered are those developed by Okafor et al. [6], Dagaut et al. [7] and San Diego [8].

## 4. RESULTS AND DISCUSSION

Figure 1 shows the measured and predicted  $\text{NO}_x$  emissions as a function of the  $\text{NH}_3$  mole fraction,  $x_{\text{NH}_3}$ , for the three equivalence ratios considered. It is observed that the measured  $\text{NO}_x$  emissions for the  $\text{NH}_3$ - $\text{CH}_4$  flames are significantly higher than those for the pure  $\text{CH}_4$  flames, regardless of the equivalence ratio. Moreover, the measured  $\text{NO}_x$  emissions in the  $\text{NH}_3$ - $\text{CH}_4$  flames are not significantly affected by the value of  $x_{\text{NH}_3}$ , in contrast to the

predictions, although it is noticeable a maximum around  $x_{NH_3} = 0.5$  for  $\phi = 1$ , which is also not captured by the models. The measured  $NO_x$  emissions decrease slightly as  $\phi$  increases, whereas the opposite trend, in a much more accentuated way, is observed for the predicted  $NO_x$  emissions. It is, however, interesting to note the good agreement between measurements and predictions for  $\phi = 1$ . Overall, the three models predicted similar  $NO_x$  emissions as a function of  $x_{NH_3}$  and  $\phi$ , with the Okafor et al. model predicting the highest  $NO_x$  values, and the San Diego model the lowest ones.

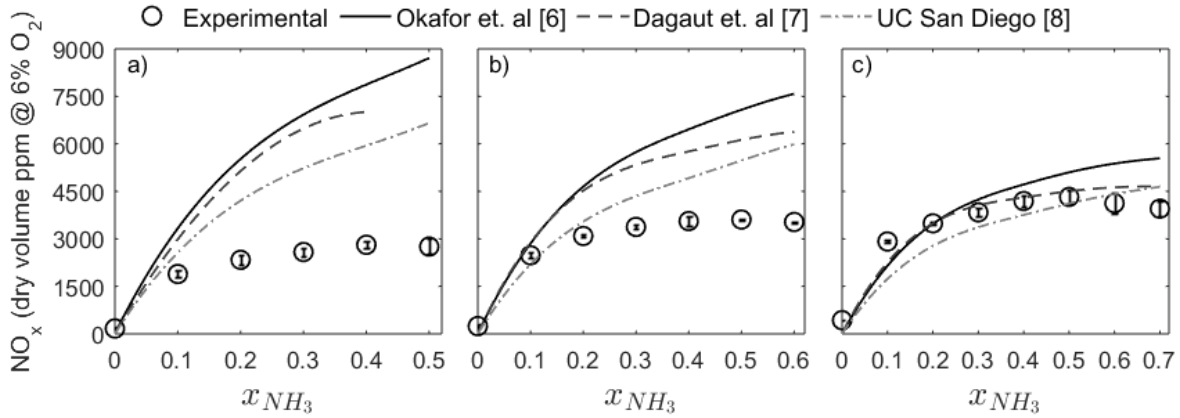


Figure 1 - Measured and predicted  $NO_x$  emissions as a function of the  $NH_3$  mole fraction,  $x_{NH_3}$ , for the three equivalence ratios considered. a)  $\phi = 0.8$ ; b)  $\phi = 0.9$ ; c)  $\phi = 1$ .

Figure 2 shows the measured and predicted CO emissions as a function of  $x_{NH_3}$  for the three equivalence ratios considered. It is seen that the measured CO concentrations were below 60 ppm, regardless of the operating condition, revealing the almost full oxidation of the  $CH_4$  present in the mixture. Consistently, the predicted CO emissions for  $\phi = 0.8$  and 0.9 were less than 10 ppm for all operating conditions, but for  $\phi = 1$  all mechanisms significantly over predicted the experimental results.

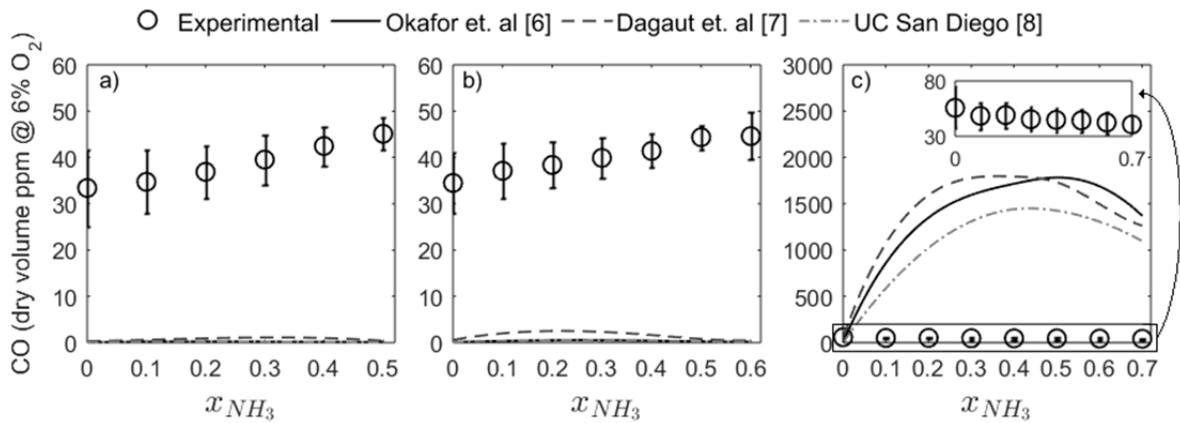


Figure 2 - Measured and predicted CO emissions as a function of the  $NH_3$  mole fraction,  $x_{NH_3}$ , for the three equivalence ratios considered. a)  $\phi = 0.8$ ; b)  $\phi = 0.9$ ; c)  $\phi = 1$ .

Finally, it is important to point out that the measured  $NH_3$  emissions (not shown) were below 10 ppm for all conditions, as also predicted by the three chemical kinetic models.

## 5. CONCLUSIONS

Measurements of NO<sub>x</sub>, CO and NH<sub>3</sub> emissions from premixed NH<sub>3</sub>-CH<sub>4</sub>-air flames are reported. Experiments were conducted for three equivalence ratios (0.8, 0.9 and 1) and NH<sub>3</sub> mole fractions up to 0.7. The study also includes a chemical kinetic study using three models (Okafor et al., Dagaut et al. and San Diego models) available in the literature. The main conclusions of this study are as follows.

- Measured NO<sub>x</sub> emissions for the NH<sub>3</sub>-CH<sub>4</sub> flames are significantly higher than those for the pure CH<sub>4</sub> flames.
- Measured NO<sub>x</sub> emissions for the NH<sub>3</sub>-CH<sub>4</sub> flames are not significantly affected by the NH<sub>3</sub> mole fraction in the fuel mixture.
- Measured NO<sub>x</sub> emissions decrease slightly as the equivalence ratio increases.
- Measured CO and NH<sub>3</sub> emissions are below 60 and 10 ppm, respectively, for all operating conditions.
- The three chemical kinetic models predicted similar NO<sub>x</sub> evolutions as a function of the NH<sub>3</sub> mole fraction and equivalence ratios.
- The predicted NO<sub>x</sub> emissions by the three models are well above the measurements for  $\phi = 0.8$  and  $0.9$ , but in good agreement for  $\phi = 1$ . In this case, however, the three models over predicted significantly the measured CO emissions.

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