Ammonia as an alternative to carbon-based fuels: experimental and modelling analysis of its oxidation process

M. Abián, Á. de Goñi, Á. Millera, R. Bilbao, M.U. Alzueta

Aragón Institute of Engineering Research (I3A) – Department of Chemical and Environmental Engineering, University of Zaragoza - Spain

Abstract

Combustion of fossil fuels is typically considered as one of the main responsible of the emission to the atmosphere of greenhouse CO_2 gas and important atmospheric pollutants, such as soot. To go towards a decarbonisation of energy, ammonia has been identified as a promising fuel for transport and power applications. Besides technical aspects on NH_3 utilization, a key issue arising from this approach is its proper combustion in relation to the minimization of NO_x and NH_3 emissions in the flue gases. In this context, the present work is focused on the analysis of the ammonia conversion process and the formation of main nitrogen oxides (NO, NO_2 and N_2O) over a wide range of temperatures (800-1400 K) and O_2 reaction environments (different air excess ratios, λ).

Introduction

Ammonia (NH_3) is reported as a carbon-free fuel for both internal engine combustion and industrial gas turbines to face the grand challenge of Climate Change. To go further on the implementation of this alternative fuel, besides the technical issues on the given technologies, there exists the necessity of increasing the knowledge on its combustion process and, particularly, on pollutant emissions [1]. There are some fundamental studies in the literature addressing the conversion of NH_3 in different reactors and under different experimental conditions of temperature and pressure (e.g. [2-4]). From these works, it can be drawn that the formation of a specific pollutant (NO, NO_2 or N_2O) from NH_3 conversion depends strongly on the given experimental conditions considered. Therefore, there is a clear need of extending the experimental work of ammonia oxidation to increase the knowledge on how burning ammonia with minimum emissions.

In this context, the present work accomplishes an experimental and modelling study, at atmospheric pressure, of the conversion regime of ammonia at different operating conditions (temperatures and stoichiometries) of interest for combustion applications.

Methodology

Experiments are performed at atmospheric pressure in a laboratory tubular flow reactor, covering the temperature range of 800 to 1400 K and for different air excess ratios (from pyrolysis to very oxidizing conditions). The air excess ratio (λ) is defined as function of reaction (r.1).

$$NH_3 + \frac{3}{4}O_2 \leftrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2O \qquad \text{(r.1)}$$

Specifically, the study includes the analysis of the conversion of NH_3 (0.1 %) at λ = 0, 0.75, 2, 5, 11 and 22, using N_2 as bath gas. A detailed description of the experimental installation can be found in [5]. The analysis of the product gas is performed by means of a gas chromatograph equipped with TCD detectors and continuous infrared NO and chemiluminescence NO_x analyzers.

corresponding author: please indicate here name and email of the corresponding authors

The experimental results are used to update a gas-phase chemical kinetic mechanism for describing NH_3 oxidation process. This mechanism is based on previous works by the authors [6] and the software used for calculations is Chemkin. The mechanism is being updated in relation to the recent review of Glarborg et al. [7] on the modeling of nitrogen chemistry in combustion.

Results

Figures 1 and 2 show, respectively, the conversion of NH_3 and the formation of H_2 and NO (ppm) as function of the reaction temperature and for the different air excess ratios considered. In this study, neither NO_2 nor N_2O were detected at any of the conditions analyzed.

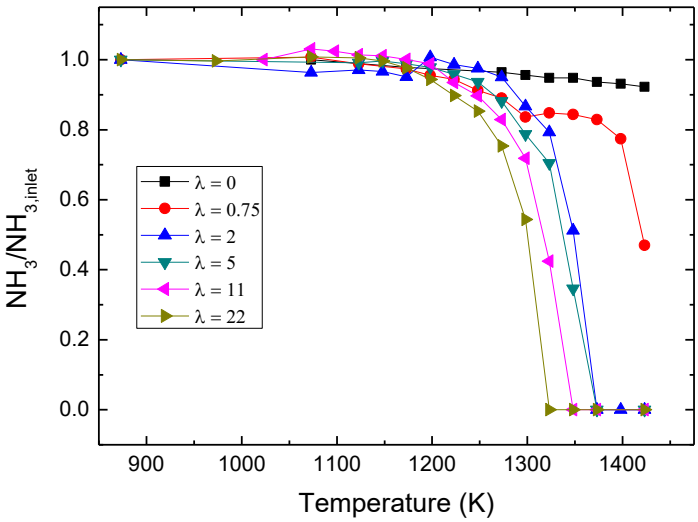

Figure 1. Conversion of NH_3 as a function of the reaction temperature for λ=0 to λ=22.

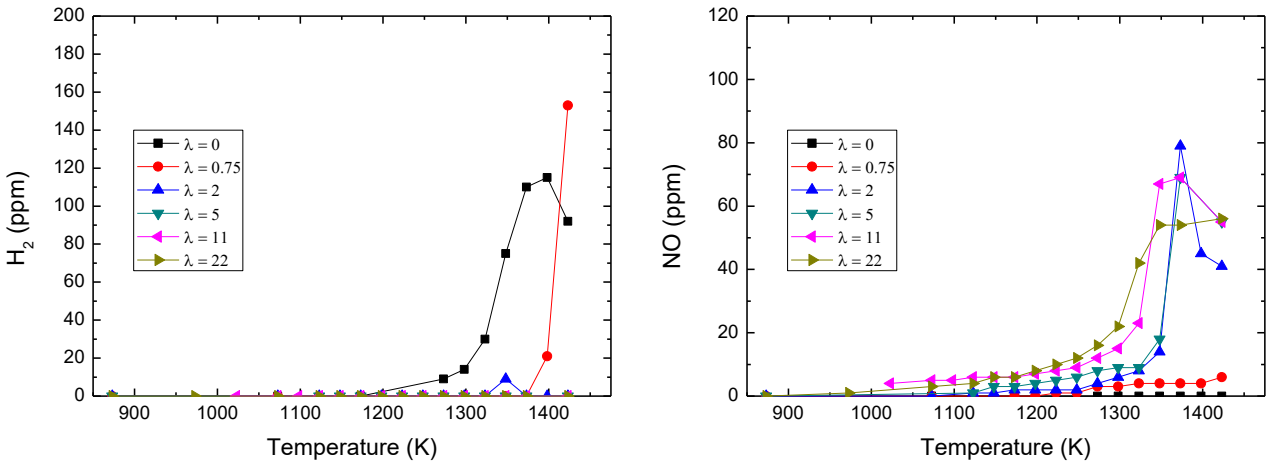

Figure 2. Concentration (ppm) of H_2 and NO as a function of the reaction temperature for λ=0 to λ=22.

First results indicate that the oxygen availability is a key factor in the process. The higher the O_2 level in the reaction environment, the lower the temperature necessary for the complete conversion of NH_3. However, the excess of O_2 favors the formation of NO, as compared with oxygen-lean conditions. The maximum yield to NO is attained at around 1375 K for oxidizing

conditions, with a value lower than 7 %. H_2 was only detected for $\lambda \leq 2$, and shows an increasing concentration tendency when the deficit of oxygen increases.

Conclusions

This work is being performed on the basis of contributing to broader the knowledge on the environmentally friendly use of NH_3 as an alternative to carbon-based fuels in different energy applications.
First results indicate that the oxygen availability is a key factor in the process that prompts the complete conversion of NH_3, but also the formation of NO. Nor NO_2 neither N_2O were quantified at any of the conditions of the present work. Additionally, the experimental results are used to develop/update a reaction kinetic mechanism for describing the conversion of ammonia under a variety of operating conditions.

Acknowledgements

The authors express their gratitude to Aragón Government and European Social Fund (GPT group), and to MINECO and FEDER (Project CTQ2015-65226) for financial support.

References

[1] Valera-Medina A., Marsh R., Runyon J., Pugh D., Beasley P., Hughes T., Bowen P. Ammonia–methane combustion in tangential swirl burners for gas turbine power generation. Applied Energy, 185, 1362-1371, 2017.
[2] Song, Y., Hashemi, H., Christensen, J.M., Zou, C., Marshall, P., Glarborg, P. Ammonia oxidation at high pressure and intermediate temperatures. Fuel, 181, 358-365, 2016.
[3] Tian, Z., Li, Y., Zhan, P., Glarborg, P., Qi, F. An experimental and kinetic modeling study of premixed $NH_3/CH_4/O_2$/Ar flames at low pressure. Combustion and Flame, 156, 1413-1426, 2009.
[4] Hayakawa A., Goto T., Mimoto R., Kudo T., Kobayashi H. NO formation/reduction mechanisms of ammonia/air premixed flames at various equivalence ratios and pressures. Mechanical Engineering Journal, 2, 1-10, 2015.
[5] Alzueta M.U., Glarborg P., Dam-Johansen K. Low temperature interactions between hydrocarbons and nitric oxide: An experimental study. Combustion and Flame, 109, 25-36, 1997.
[6] Abián M., Millera A., Bilbao R., Alzueta M.U. Effect of CO_2 atmosphere and presence of NO_x (NO and NO_2) on the moist oxidation of CO. Fuel, 15, 615-621, 2019.
[7] Glarborg P., Miller J.A., Ruscic B., Klippenstein S.J. Modeling nitrogen chemistry in combustion. Progress in Energy and Combustion Science, 67, 31-68, 2018.