Ammonia Oxidation at High Pressure as a Carbon Free Fuel

X JORNADA DE JÓVENES INVESTIGADORES DEL I3A

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BACKGROUND AND OBJECTIVES

Objective: Increasing knowledge on the conversion of NH_3 at high pressures, as well as its mixtures with CH_4 and H_2 under different operating conditions

Advantages: NH_3-CH_4 can emit less NOx than a NH_3-air blend [7] and higher ratio of H_2 in NH_3-H_2 mixtures improves its reactivity without effects in its emissions [8].

Ammonia oxidation

Directly [3] without CO_2 emissions

Mixed with H_2 [5] and CH_4 [6] enhancing its combustion characteristics

Turning NH_3 into a suitable alternative fuel

Security of energy supply and existing facilities for its transportation.

Study of NH_3 as an alternative fuel for several applications including energy storage, transportation and gas turbines [1, 2]

Global chemical reactions for the formation of N_2 and NO_x.

$$NH_3 + \frac{3}{4}O_2 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2O \quad r1$$

$$NH_3 + \frac{5}{4}O_2 \rightleftharpoons NO + \frac{3}{2}H_2O \quad r2$$

Disadvantage: nitrogen oxides (NO_x) can be formed from NH_3 oxidation [4]

EXPERIMENTAL RESULTS AT HIGH PRESSURE

Conditions: 40 bar of pressure, temperatures from 500ºC to 900ºC, gas flow = 1000 mln/min, residence time = 0.524 min and (1)Lambda (λ) = 3.

Case A) 1000 ppm of pure NH_3: oxidation reaction of NH_3 started at 875ºC.

Case B) & C) NH_3-CH_4 and NH_3-H_2 mixtures (1000 ppm for each component): oxidation reaction of NH_3 started at 530ºC.

$$(1)\ \lambda = \left[\frac{O_{2_{feed}}}{O_{2_{stoic}}}\right]$$

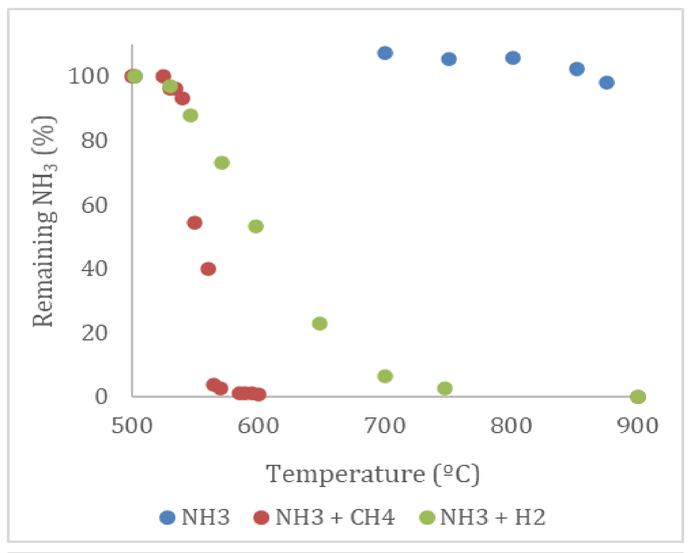


Figure 1: case A (pure NH_3) most of ammonia does not react more than 10% at 900 ºC, case B (NH_3-CH_4 mixture) full conversion of NH_3 approximately at 600ºC and case C (NH_3-H_2 mixture) fully reaction at 850ºC.

The oxidation reaction of NH_3 at 40 bar started at 875ºC for pure NH_3 and at 530ºC for NH_3 mixtures for the selected conditions.

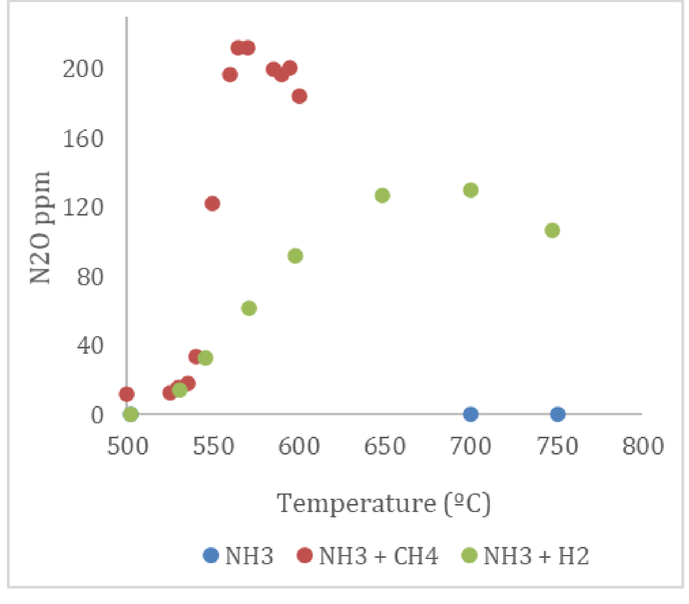
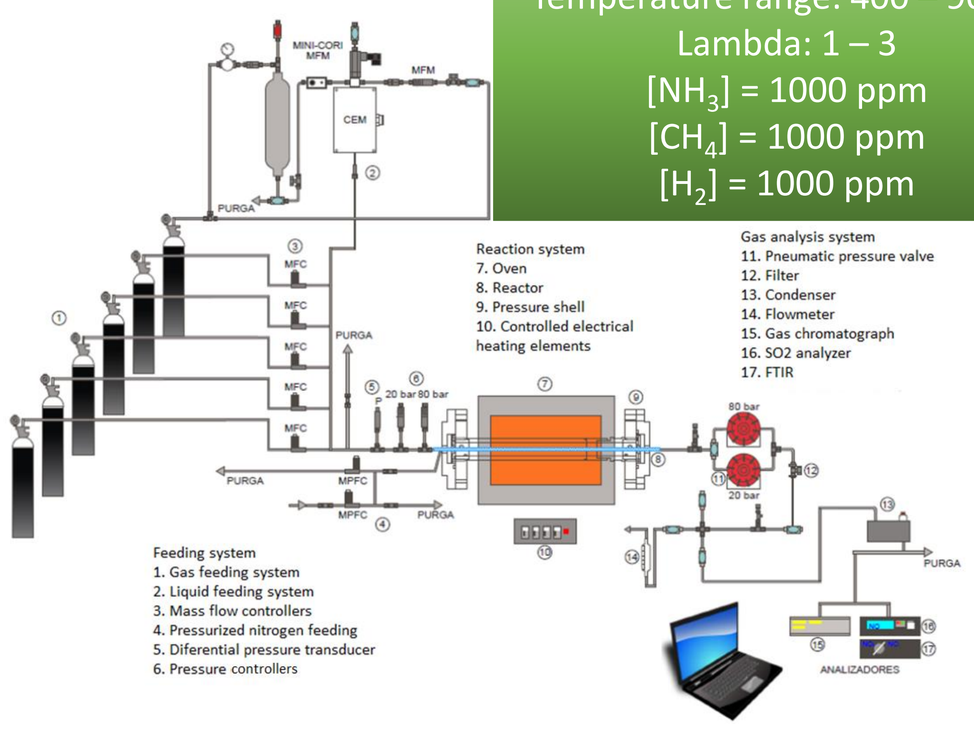


Figure 2: case B (NH_3-CH_4 mixture), produced 212 ppm of N_2O at 570ºC that is approximately twice as much N_2O produced compared to case C (NH_3-H_2 mixture), which produce 61 ppm of N_2O at the same temperature.

Methodology

Experimental Conditions
Pressure: 10 – 40 bar
Temperature range: 400 – 900ºC
Lambda: 1 – 3
[NH_3] = 1000 ppm
[CH_4] = 1000 ppm
[H_2] = 1000 ppm



CONCLUSIONS

- NH_3 oxidation starts at lower temperatures, about 355ºC before, for both NH_3-CH_4 and NH_3-H_2 (cases B and C) mixtures compare to pure NH_3 (case A).
- Mixing NH_3 with CH_4 or H_2 improves reaction behaviour, consuming practically all the NH_3 at temperatures at which the oxidation of pure NH_3 has not yet started, but this mixtures oxidation present N_2O emissions.

References

[1]. VALERA-MEDINA, A., XIAO, H., OWEN-JONES, M., DAVID, W. I.F. and BOWEN, P. J. Ammonia for power. *Progress in Energy and Combustion Science*. 2018. Vol. 69, p. 63–102. Available from: DOI 10.1016/j.pecs.2018.07.001.

[2]. VALERA-MEDINA, A., MORRIS, S., RUNYON, J., PUGH, D. G., MARSH, R., BEASLEY, P. and HUGHES, T. Ammonia, Methane and Hydrogen for Gas Turbines. *Energy Procedia*. 2015. Vol. 75, p. 118–123. Available from: DOI 10.1016/j.egypro.2015.07.205.

[3]. KOBAYASHI, H. Ammonia Combustion for Energy System. *Japan-Norway Hydrogen Seminar*. 2017.

[4]. GLARBORG, P., MILLER, J. A., RUSCIC, B. and KLIPPENSTEIN, S. J. Modelling nitrogen chemistry in combustion. *Progress in Energy and Combustion Science*. 2018. Vol. 67, p. 31–68. Available from: DOI 10.1016/j.pecs.2018.01.002.

[5]. DA ROCHA, R. C., COSTA, M. and BAI, X. S. Chemical kinetic modelling of ammonia/hydrogen/air ignition, premixed flame propagation and NO emission. *Fuel*. 2019. Vol. 246, p. 24–33. Available from: DOI 10.1016/j.fuel.2019.02.102.

[6]. XIAO, H., VALERA-MEDINA, A., MARSH, R. and BOWEN, P. J. Numerical study assessing various ammonia/methane reaction models for use under gas turbine conditions. *Fuel*. 2017. Vol. 196, p. 344–351. Available from: DOI 10.1016/j.fuel.2017.01.095.

[7]. OKAFOR, E. C., SOMARATHNE, K. D., KUNKUMA, A., RATTHANAN, R., HAYAKAWA, A., KUDO, T., KURATA, O., IKI, N., TSUJIMURA, T., FURUTANI, H. and KOBAYASHI, H. Control of NOx and other emissions in micro gas turbine combustors fuelled with mixtures of methane and ammonia. *Combustion and Flame*. 2020. Vol. 211, p. 406–416. Available from: DOI 10.1016/j.combustflame.2019.10.012.

[8]. HE, X., SHU, B., NASCIMENTO, D., MOSHAMMER, K., COSTA, M. and FERNANDES, R. X. Auto-ignition kinetics of ammonia and ammonia/hydrogen mixtures at intermediate temperatures and high pressures. *Combustion and Flame*. 2019. Vol. 206, p. 189–200. Available from: DOI 10.1016/j.combustflame.2019.04.050.

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