POLITECNICO MILANO 1863

SCUOLA DI INGEGNERIA INDUSTRIALE E DELL'INFORMAZIONE

EXECUTIVE SUMMARY OF THE THESIS

Modellazione Cinetica dei Limiti di Infiammabilità

TESI MAGISTRALE IN SAFETY AND PREVENTION ENGINEERING IN THE PROCESS INDUSTRY – INGEGNERIA DELLA PREVENZIONE E SICUREZZA NEL'INDUSTRIA DI PROCESSO

AUTHOR: BEATRICE MIGNANI

ADVISOR: ALESSIO FRASSOLDATI

ACADEMIC YEAR: 2023-2024

1. Introduction

Nowadays there is an increasing interest in ammonia as energy carrier: thanks to its high hydrogen content (17.8% wt.), and the absence of carbon atoms in its structure, it is an attractive solution both to traditional fuels and to hydrogen for the storage and transportation of energy. For this reason, it is more and more crucial to investigate flammable limits for ammonia mixtures in a wide range of operating and storage conditions of temperature, pressure, and composition, not only for safety reasons, but also to optimize the usage of ammonia as a fuel, that is becoming increasingly widespread in industry. The aim of the thesis is to investigate a predictive model for determining flammability limits.

2. Kinetics Convalidation

Flame speed is a function of φ and its behavior remembers a Gaussian curve with a maximum approximately in φ = 1.1. In lean/rich condition (respectively in the left and right part of the curve) there must be a φ_{lim}, a value in which the propagation of a self-sustaining flame does not occur. This φ_{lim} corresponds to UFL and LFL concentrations. Hence the importance of convalidating the kinetics.

2.1. Methodology

In order to proceed with the kinetics modelling of ammonia flammable limits, it was been necessary to validate the kinetics, proposed by Stagni [1]. For this purpose, 184 simulations related to laminar burning velocity for different ammonia mixtures in different conditions, have been carried out using the software OpenSMOKE++. This tool allows to take in consideration thermodynamics, kinetics, and transport phenomena, and it is able to solve ODE (Ordinary Differential Equations), that describe the combustion process.

10 mixtures have been taking in consideration:

- $NH_3 + AIR$
- $NH_3 + CO + AIR$
- $NH_3 + CO + H_2 + AIR$
- $NH_3 + H_2 + AIR$
- $NH_3 + CH_4 + AIR$
- $NH_3 + C_2H_6 + AIR$

- $NH_3 + C_3H_8 + AIR$
- $NH_3 + CH_3OH + AIR$
- $NH_3 + C_2H_5OH + AIR$
- $NH_3 + O_2 + He + Ar$

In all the simulations, the molar composition of air has been considered 0.21 in oxygen and 0.79 in nitrogen, unless otherwise stated.

2.2. Simulation Results

From simulation results it could be noted a systematic error on the right part of the curve that described the laminar burning velocity behavior, for φ > 1.1: the model overestimates the experimental data, as in the 3 examples reported below. The only exception is the case of $NH_3 + CH_3OH + AIR$ mixtures, for which the results underestimate the experimental data.

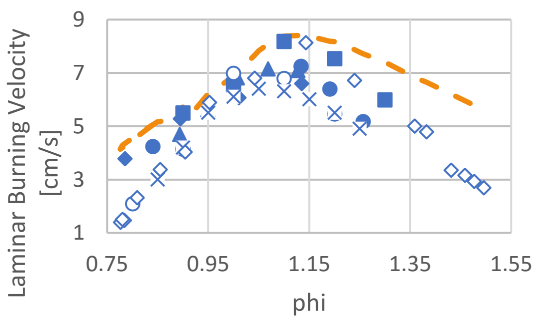

Figure 1: Experimental data related to a mixture of ammonia/air at 298 K and 1 atm: circles [3], squares [4], diamonds [5], triangles [6], empty circles [7], crosses [8], empty diamonds [9]. The orange line represents model result

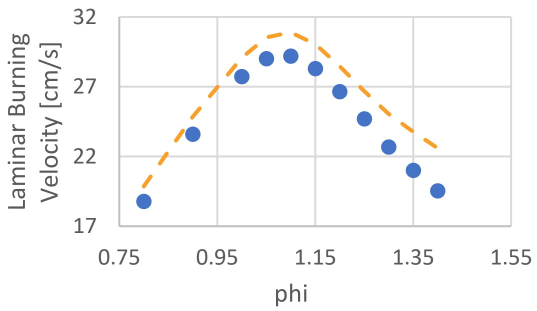

Figure 2: Laminar burning velocity behavior for ammonia/hydrogen/air mixtures, at 298 K, 1 atm and H_2=0.4, taking in consideration experimental data from [10]. The orange line represents model result

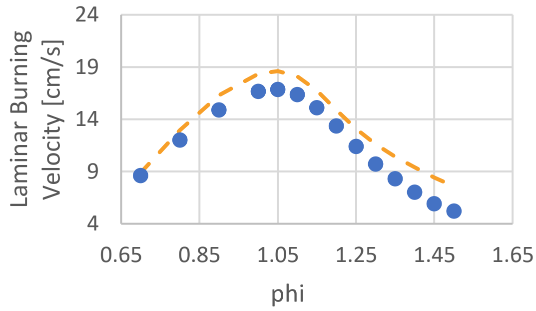

Figure 3: Laminar burning velocity behavior for ammonia/methane/air mixtures, at 298 K, 1 atm and CH_4=0.4, taking in consideration experimental data from [11]. The orange line represents model result

To correct this deviation from experimental data, the contribution of radiation has been considered and in OpenSMOKE++ have been implemented emissive coefficients proposed by Nakamura [2] for nitrogen compounds (NO, N_2O, NH_3). Below are reported the results for the 3 mixtures previously considered.

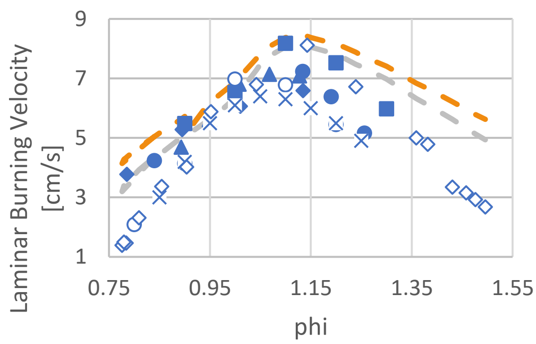

Figure 4: Experimental data related to a mixture of ammonia/air at 298 K, 1 atm: circles [3], squares [4], diamonds [5], triangles [6], empty circles [7], crosses [8], empty diamonds [9]. The two lines represent models results: orange line does not consider radiation contribution and emissive coefficients, that grey line does

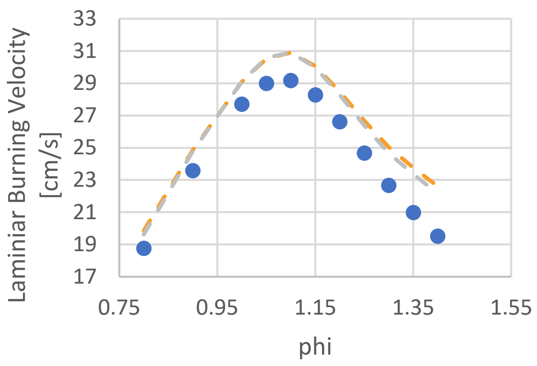

Figure 5: Laminar burning velocity behavior for ammonia/hydrogen/air mixtures, at 298 K, 1 atm and H_2=0.4, taking in consideration experimental results from [10]. The two lines represent models results: orange line does not consider radiation contribution and emissive coefficients, that grey line does

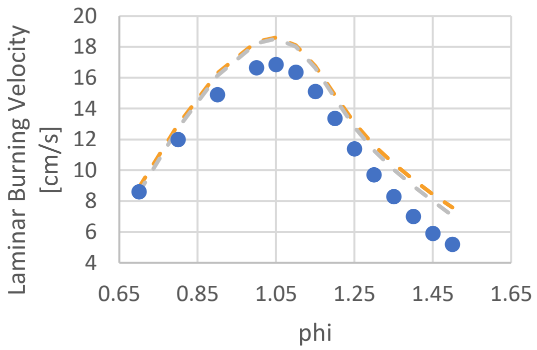

Figure 6: Laminar burning velocity behavior for ammonia/methane/air mixtures, at 298 K, 1 atm and CH_4=0.4, taking in consideration experimental results from [11]. The two lines represent models results: orange line does not consider radiation contribution and emissive coefficients, that grey line does

Although the model better fits experimental data, the error persists. However, the deviation is not significant, and the kinetics shall be considered validated.

3. Flammable Limits

In order to determine the flammable limits for ammonia mixtures, 41 simulations have been carried out in OpenSMOKE++.

10 mixtures have been taken in consideration:

- $NH_3 + AIR$
- $NH_3 + H_2 + AIR$
- $NH_3 + CH_4 + AIR$
- $NH_3 + H_2 + CH_4 + AIR$

3.1. Final Results

Final results are summarized in the following Figures:

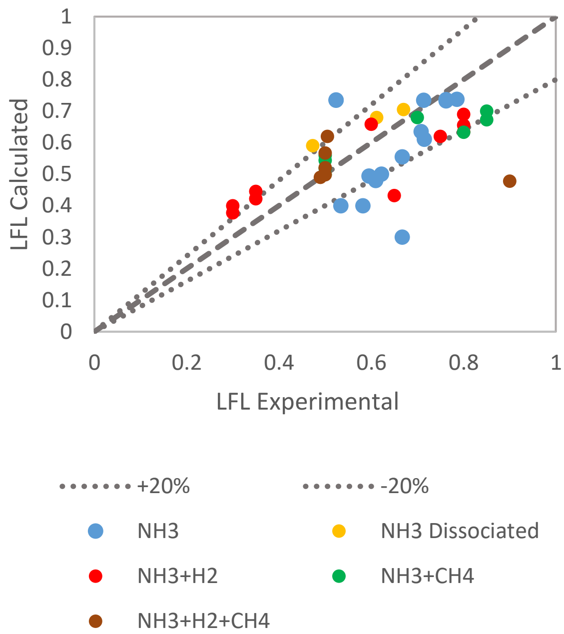

Figure 7: Comparison between experimental data and data obtained by simulations, not considering emissive coefficients proposed by [2]

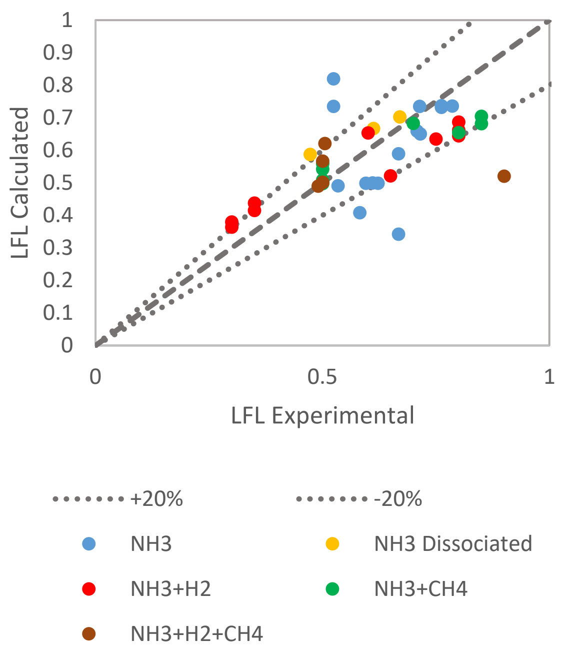

Figure 8: Comparison between experimental data and data obtained by simulations, considering emissive coefficients proposed by [2]

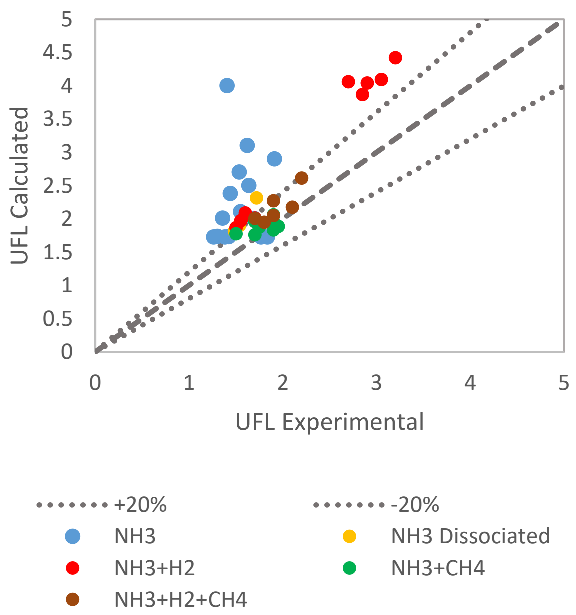

Figure 9: Comparison between experimental data and data obtained by simulations, not considering emissive coefficients proposed by [2]

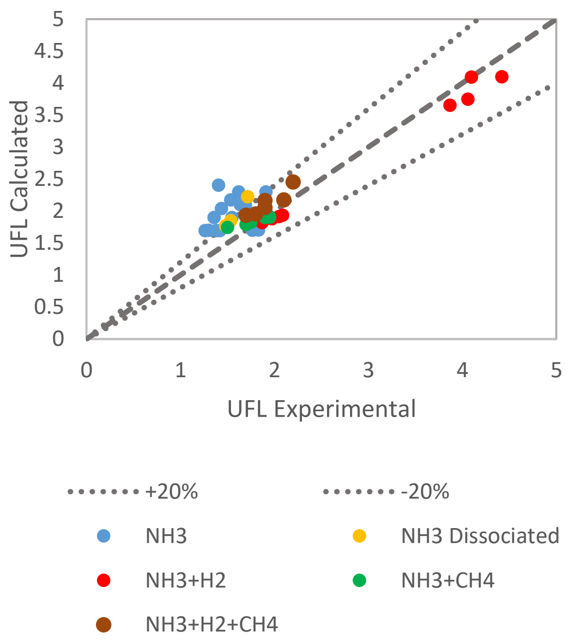

Figure 10: Comparison between experimental data and data obtained by simulations, considering emissive coefficients proposed by [2]

Simulations have been carried out both taking in consideration radiation contribution and emissive coefficients proposed by [2], and ignoring these factors. The difference between the results of these two approaches is not significant for LFL, whilst for UFL there is an improvement in the agreement with experimental data. However, it could be noted a systematic error in overestimating UFL.

4. Conclusions

The interest in ammonia as energy carrier, is becoming more and more relevant. For this reason, it is important to investigate flammable limits of ammonia mixtures in several conditions, not only for safety reasons, but also for industrial applications. In order to predict flammable limits, the flame speed-based method has been considered, and kinetics [1] has been validated after 184 simulations in OpenSMOKE++. Despite the introduction of radiation contribution and emissive coefficients proposed by [2] in the simulations, a systematic error of overestimation in the rich part of the curve persists. However, the deviation from experimental data was not significant and the kinetics has been considered validated. 41 simulations to determine flammable limits in ammonia mixtures, have been carried out and results highlight the overestimation of UFL values. It could be a consequence of a kinetics not consolidated yet, and further investigations are required on this topic. From a safety point of view, an overestimation of UFL can be considered as a conservative approach. All of the experimental data collected for this study have been uploaded in SciExpeM, a valuable tool that will allow different users to use the database I have saved, to develop and convalidate new kinetics.

5. Bibliography

References

[1] A. Stagni *et al.*, «An experimental, theoretical and kinetic-modeling study of the gas-phase oxidation of ammonia», *React Chem Eng*, vol. 5, n. 4, pagg. 696–711, apr. 2020, doi: 10.1039/c9re00429g.

[2] H. Nakamura e M. Shindo, «Effects of radiation heat loss on laminar premixed ammonia/air flames», *Proceedings of the Combustion Institute*, vol. 37, n. 2, pagg. 1741–1748, 2019, doi: 10.1016/j.proci.2018.06.138.

[3] T.; Jabbour e D. F. Clodic, «Burning Velocity and Refrigerant Flammability Classification/DISCUSSION», 2004.

[4] B. Mei *et al.*, «Experimental and kinetic modeling investigation on the laminar flame propagation of ammonia under oxygen enrichment and elevated pressure conditions», *Combust Flame*, vol. 210, pagg. 236–246, dic. 2019, doi: 10.1016/j.combustflame.2019.08.033.

[5] U. J. Pfahl, M. C. Ross, J. E. Shepherd, K. O. Pasamehmetoglu, e C. Unal, «Flammability Limits, Ignition Energy, and Flame Speeds in H 2-CH 4-NH 3-N 2 O-O 2-N 2 Mixtures», 2000.

[6] K. Takizawa, A. Takahashi, K. Tokuhashi, S. Kondo, e A. Sekiya, «Burning velocity measurements of nitrogen-containing compounds», *J Hazard Mater*, vol. 155, n. 1–2, pagg. 144–152, giu. 2008, doi: 10.1016/j.jhazmat.2007.11.089.

[7] Hayakawa, T. Goto, R. Mimoto, Y. Arakawa, T. Kudo, e H. Kobayashi, «Laminar burning velocity and Markstein length of ammonia/air premixed flames at various pressures», *Fuel*, vol. 159, pagg. 98–106, lug. 2015, doi: 10.1016/j.fuel.2015.06.070.

[8] Han, Z. Wang, M. Costa, Z. Sun, Y. He, e K. Cen, «Experimental and kinetic modeling study of laminar burning velocities of NH3/air, NH3/H2/air, NH3/CO/air and NH3/CH4/air premixed flames», *Combust Flame*, vol. 206, pagg. 214–226, ago. 2019, doi: 10.1016/j.combustflame.2019.05.003.

[9] P. D. Rooney, «Mechanism of combustion limits in premixed gas flame at microgravity », NASA-Lewis Grant No. NAG3-965), 1988-1991.

[10] X. Han, Z. Wang, M. Costa, Z. Sun, Y. He, e K. Cen, «Experimental and kinetic modeling study of laminar burning velocities of NH3/air, NH3/H2/air, NH3/CO/air and NH3/CH4/air premixed flames», *Combust Flame*, vol. 206, pagg. 214–226, ago. 2019, doi: 10.1016/j.combustflame.2019.05.003

[11] S. Wang, Z. Wang, C. Chen, A. M. Elbaz, Z. Sun, e W. L. Roberts, «Applying heat flux method to laminar burning velocity measurements of NH3/CH4/air at elevated pressures and kinetic modeling study», *Combust Flame*, vol. 236, feb. 2022, doi: 10.1016/j.combustflame.2021.111788.

6. Acknowledgements

I would like to thank Prof. Frassoldati and CRECK Modeling group for the opportunity to deepen this topic and for the constant support.