

NO formation in low-pressure, premixed laminar $\text{H}_2/\text{CH}_4/\text{CO}/\text{O}_2/\text{N}_2$ flames in presence of benzene

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1. Introduction

The minimization of nitrogen oxides (NO_x and N_2O) emissions to comply with current EU directives [1, 2] together with issues related to the rising energy demand and the need of a safer energy supply, are today among the major concerns of combustion-related processes.

A significant amount of research has been devoted to improve the understanding of NO_x formation and to develop environmental friendly and fuel flexible technologies.

The use of a wide palette of novel energy vectors and the exploitation of non-conventional fuel mixtures, as Coke Oven Gas (COG), a valuable by-product of coal carbonization, could potentially fulfill the need of fuel flexibility; however, it introduces new challenges in pollutant control research. For instance, deeper investigations are needed to shed light on NO_x formation during COG combustion. This low calorific value (LCV) fuel is mainly made up of H_2 , CH_4 , CO and small percentages of aromatic compounds [3]. Eddings [4], simulated NO_x formation in combustion of steel industry by-products like COG in a plug-flow reactor, at intermediate temperatures (1200-1400 K), atmospheric pressure and three different equivalence ratios ($\phi = 0.6, 1, 1.4$), by using twelve different kinetic mechanisms. They observed, in all the analysed cases that NO_x emissions were composed of over 99 % of nitric oxide (NO) and that NO formation was controlled by hydrogen attack to $\text{N}=\text{N}$ bond through $\text{H}+\text{N}_2$ reaction to form the NNH intermediate, at the chosen operating conditions, instead of the methyldene attack according to the prompt NO formation mechanism. To our knowledge, not many other studies were later performed to investigate NO_x formation in COG oxidation. Moreover, if the oxidation small aromatic species, such as benzene, has been extensively discussed in literature [5-9] in order to assess the competition between the depletion of such compounds and their growth to PAH and ultimately to soot; no study, until now have tried to determine the role that benzene oxidation chemistry might play in NO_x formation.

The main goal of the present work is to investigate NO_x formation in laminar premixed stoichiometric $\text{H}_2/\text{CH}_4/\text{CO}/\text{O}_2/\text{N}_2$ and $\text{H}_2/\text{CH}_4/\text{CO}/\text{O}_2/\text{N}_2/\text{C}_6\text{H}_6$ flames at low pressure that are representative of a real COG composition. The purpose is highlighting the main NO formation pathways and the role that benzene oxidation chemistry might play on the nitrogen chemistry in such flames through a joint experimental and modelling investigation.

2. Methodology

2.1 Experimental

Experiments were performed in laminar $\text{H}_2/\text{CH}_4/\text{CO}/\text{O}_2/\text{N}_2$ and $\text{H}_2/\text{CH}_4/\text{CO}/\text{O}_2/\text{N}_2/\text{C}_6\text{H}_6$ premixed stoichiometric flames stabilized at low pressure (7.5kPa), on a movable water-cooled Spalding-Botha burner with a diameter of 8 cm, at a fixed dilution ratio, $D=\text{O}_2/(\text{O}_2+\text{N}_2)$ of 0.21. The experimental setup has been described in detail elsewhere [10]. The compositions of the investigated flames are listed in Table 1. They represent industrial COG mixtures with different contents of C_6H_6 (Flame II, Flame III, Flame IV). The flame without benzene (Flame I) was also investigated as reference. The net inlet flow rate of the mixtures was kept constant and equal to 13 l/min.

Table 1- Investigated stoichiometric ($\phi=1$) premixed flame compositions- $P=7.5$ kPa, $D=\text{O}_2/(\text{O}_2+\text{N}_2)=0.21$, $Q=13$ l/min

Flame	XH_2	XCH_4	XCO	XO_2	XN_2	XC_6H_6
Flame I	0.1323	0.0488	0.0115	0.1695	0.6378	-
Flame II	0.1305	0.0482	0.0114	0.1700	0.6396	0.0004
Flame III	0.1256	0.0464	0.0112	0.1713	0.6442	0.0013
Flame IV	0.1225	0.0452	0.0107	0.1721	0.6475	0.0020

Sampling was carried out at different distances from the burner by means of a conical quartz nozzle, with an entrance diameter of 0.2 mm and an angle of 45° . Chemical compounds were detected by gas chromatography (TOGA/Trace GC) equipped with two capillary columns, PoraPLOT Q, and Molsieve 5 Å, in series with RTX1, for the analyzed gas flow rate restriction before the micro-TCD and thermal conductivity and flame ionization detectors. NO concentrations have been measured with a HORIBA PG-250, by chemiluminescence measurements with an accuracy of $\pm 5\%$. Temperature profiles were measured by means of a coated type B (PtRh6% - PtRh30%) thermocouple and the corrections for radiative heat losses were evaluated by the Heat transfer model (HTM) method [11].

2.2 Modelling

In order to interpret the experimental data, two different kinetic mechanisms were used: NOMEcha2.0 sub-mechanism [12] integrated with GDFkin@3.0 [13] and a benzene oxidation sub-mechanism [14] and POLIMI models [15]. NOMEcha2.0 sub-mechanism for N-species formation at high temperature was validated, by Lamoureux et al. [12], on a large experimental database obtained in flames, a jet-stirred reactor (JSR) and a plug-flow reactor under sub-atmospheric and atmospheric conditions; after being implemented in GDFkin@3.0, a robust model dedicated to natural gas oxidation chemistry [13]. Moreover the added sub-mechanism describing benzene oxidation [14] was validated against many data obtained at high and low temperature for n-heptane/benzene and methane/benzene mixtures. The final mechanism consists in 194 species and 1336 reactions.

On the other hand the POLIMI_1810 mechanism was obtained from the related framework, describing the pyrolysis and oxidation of hydrocarbon fuels. Its core C0-C3 mechanism was recently updated by coupling the H_2/O_2 and C1/C2 subsets from Metcalfe et al. [16], C3 from

Burke et al. [17], and heavier fuels from Ranzi et al. [18] Thermodynamic properties were also updated by leveraging the database of Burcat and Ruscic [19]. A full description of the NO_x model is available in the work of Song et al. [20], while the model for the pyrolysis and oxidation of benzene was originally developed by Saggese et al. [21] and included in the general framework. The final size consists in 261 species and 5834 reactions. The investigated premixed laminar flames were simulated using the software OpenSMOKE++ [22].

3. Results

Benzene addition slightly increased the flame temperature in the investigated flames. Indeed the corrected maximum temperatures measured in Flame I and Flame IV, were respectively 1872 K and 1911 K, with an uncertainty estimated at $\pm 5\%$.

The measured NO profiles in the investigated flames showed that also NO formation increased with the fraction of C_6H_6 added to the stoichiometric premixed laminar $\text{H}_2/\text{CH}_4/\text{CO}/\text{air}$ flames. For instance, at 50 mm of distance from the burner, the measured NO on dry basis in Flame IV was $\sim 27\%$ higher than NO measured at the same distance in the reference flame, Flame I, without benzene.

The structures of Flame I and Flame IV were computed by integrating the corrected temperature profiles in the simulations and by using both kinetic mechanisms above described. In particular, the predicted main species mole fraction profiles, in Flame I and Flame IV, were in reasonable agreement with experimental profiles and similar predictions were achieved with POLIMI_1810 and NOMECHA2.0 mechanisms. With regard to the simulated NO profiles both kinetic mechanisms were able to predict the increasing NO trend with increasing concentrations of benzene observed experimentally. However, the comparison between the measured and the simulated NO profiles on dry basis showed that the kinetic models used overestimate the experimental measurements (Fig.1). The highest overestimation was observed in the post-flame zone, as well as in the reaction zone, when C_6H_6 was present in $\text{H}_2/\text{CH}_4/\text{CO}/\text{air}$ flame and NOMECHA2.0 was used.

Very similar NO predictions were achieved with both kinetic mechanisms in the reference flame $\text{H}_2/\text{CH}_4/\text{CO}/\text{O}_2/\text{N}_2$, Flame I (Fig.1.a), where the models underpredicted NO close to the reaction zone while an overprediction of $\sim 50\%$ occurred in post flame zone at 50 mm. However, for Flame IV (Fig 1.b), the NO predictions were moderately overestimated in both the reaction zone and the post-flame zone, with the NOMECHA2.0 mechanism, while the POLIMI_1810 mechanism again slightly underpredicted NO in the reaction zone and overpredicted in the post-flame zone.

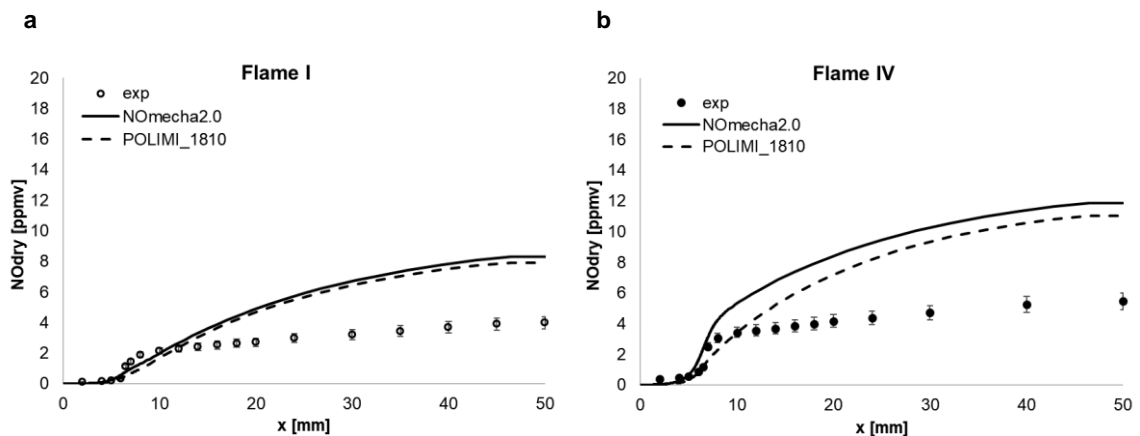


Fig.1- Comparison between experimental (symbols) and simulated NO profiles using NOMECHA2.0 (lines) and POLIMI_1810 (dashed lines), in stoichiometric premixed laminar $\text{H}_2/\text{CH}_4/\text{CO}/\text{N}_2/\text{O}_2$, Flame I, (a) and $\text{H}_2/\text{CH}_4/\text{CO}/\text{N}_2/\text{O}_2/\text{C}_6\text{H}_6(0.2\%)$, Flame IV, (b).

Detailed ROPA and sensitivity analyses allowed to identify the main NO formation pathways in the stoichiometric $\text{H}_2/\text{CH}_4/\text{CO}/\text{N}_2/\text{O}_2$ flames with and without benzene at different distances from the flame front.

It was found that C_6H_6 interacted with the oxidation kinetics of the other fuel components in the stoichiometric $\text{H}_2/\text{CH}_4/\text{CO}/\text{N}_2/\text{O}_2$ flames by increasing the production of intermediate species that play a key role in NO prompt formation route. This NO formation pathway was therefore enhanced by the presence of benzene.

4. Conclusion

NO_x formation in four stoichiometric, low-pressure, premixed laminar $\text{H}_2/\text{CH}_4/\text{CO}/\text{O}_2/\text{N}_2$ and $\text{H}_2/\text{CH}_4/\text{CO}/\text{O}_2/\text{N}_2/\text{C}_6\text{H}_6$ flames was investigated in order to shed light on NO_x formation in COG oxidation. The complete flame structures measurement coupled with a detailed kinetic study performed with two different kinetic mechanisms, NOMECHA2.0 and POLIMI_1810, allowed to clarify the nitrogen chemistry interaction with the fuel oxidation and in particular the role of benzene in the main NO formation routes in such flames.

In the future works, this study will be extended to lean and rich flames, in order to get a deeper understanding on the effect of benzene on NO_x chemistry.

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References

- [1] https://ec.europa.eu/clima/policies/strategies/2020_en
- [2] Directive 2001/80/EC replaced by Directive 2010/75/EU, Annex V, Parts 1 and 2
- [3] Razzaq, R., Li, C., & Zhang, S. (2013). Coke oven gas: availability, properties, purification, and utilization in China. *Fuel*, 113, 287-299.
- [4] Djuricic, Z., & Eddings, E. NO_x Emissions from Intermediate-Temperature Combustion of Steel-Industry By-Product Gases.
- [5] Brezinsky, K. (1986). The high-temperature oxidation of aromatic hydrocarbons. *Progress in Energy and Combustion Science*, 12(1), 1-24.
- [6] Bittner, J. D., & Howard, J. B. (1981, January). Composition profiles and reaction mechanisms in a near-sooting premixed benzene/oxygen/argon flame. In *Symposium (International) on Combustion* (Vol. 18, No. 1, pp. 1105-1116). Elsevier.
- [7] Dupont, L., El Bakali, A., Pauwels, J. F., Da Costa, I., Meunier, P., & Richter, H. (2003). Investigation of stoichiometric methane/air/benzene (1.5%) and methane/air low pressure flames. *Combustion and flame*, 135(1), 171-183.
- [8] Shandross, R. A., Longwell, J. P., & Howard, J. B. (1996, January). Destruction of benzene in high-temperature flames: Chemistry of benzene and phenol. In *Symposium (International) on Combustion* (Vol. 26, No. 1, pp. 711-719). Elsevier.

- [9] Tregrossi, A., Ciajolo, A., & Barbella, R. (1999). The combustion of benzene in rich premixed flames at atmospheric pressure. *Combustion and flame*, 117(3), 553-561.
- [10] Mbuyi Katshiatshia, H., Dias, V., & Jeanmart, H. (2018). Experimental and numerical study of ethyl valerate flat flames at low pressure. *Combustion Science and Technology*, 190(4), 632-662.
- [11] Childs, P. R. N., Greenwood, J. R., & Long, C. A. (2000). Review of temperature measurement. *Review of scientific instruments*, 71(8), 2959-2978.
- [12] Lamoureux, N., El Merhubi, H., Pillier, L., de Persis, S., & Desgroux, P. (2016). Modeling of NO formation in low pressure premixed flames. *Combustion and Flame*, 163, 557-575.
- [13] Pillier, L., Desgroux, P., Lefort, B., Gasnot, L., Pauwels, J. F., & Da Costa, I. (2006). NO prediction in natural gas flames using GDF-Kin® 3.0 mechanism NCN and HCN contribution to prompt-NO formation. *Fuel*, 85(7), 896-909.
- [14] El Bakali, A., Ribaucour, M., Saylam, A., Vanhove, G., Therssen, E., & Pauwels, J. F. (2006). Benzene addition to a fuel-stoichiometric methane/O₂/N₂ flat flame and to n-heptane/air mixtures under rapid compression machine. *Fuel*, 85(7-8), 881-895.
- [15] Ranzi, E., Frassoldati, A., Grana, R., Cuoci, A., Faravelli, T., Kelley, A. P., & Law, C. K. (2012). Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels. *Progress in Energy and Combustion Science*, 38(4), 468-501.
- [16] Metcalfe, W. K., Burke, S. M., Ahmed, S. S., & Curran, H. J. (2013). A hierarchical and comparative kinetic modeling study of C1– C2 hydrocarbon and oxygenated fuels. *International Journal of Chemical Kinetics*, 45(10), 638-675.
- [17] Burke, S. M., Burke, U., Mc Donagh, R., Mathieu, O., Osorio, I., Keese, C., ... & Oehlschlaeger, M. A. (2015). An experimental and modeling study of propene oxidation. Part 2: Ignition delay time and flame speed measurements. *Combustion and Flame*, 162(2), 296-314.
- [18] Ranzi, E., Frassoldati, A., Granata, S., & Faravelli, T. (2005). Wide-range kinetic modeling study of the pyrolysis, partial oxidation, and combustion of heavy n-alkanes. *Industrial & engineering chemistry research*, 44(14), 5170-5183.
- [19] A. Burcat, B. Ruscic, Third millenium ideal gas and condensed phase thermochemical database for combustion with updates from active thermochemical tables, Argonne National Laboratory Argonne, IL, 2005.
- [20] Song, Y., Marrodán, L., Vin, N., Herbinet, O., Assaf, E., Fittschen, C., ... & Battin-Leclerc, F. (2018). The sensitizing effects of NO₂ and NO on methane low temperature oxidation in a jet stirred reactor. *Proceedings of the Combustion Institute*.
- [21] Saggese, C., Frassoldati, A., Cuoci, A., Faravelli, T., & Ranzi, E. (2013). A wide range kinetic modeling study of pyrolysis and oxidation of benzene. *Combustion and Flame*, 160(7), 1168-1190.
- [22] Cuoci, A., Frassoldati, A., Faravelli, T., & Ranzi, E. (2015). OpenSMOKE++: An object-oriented framework for the numerical modeling of reactive systems with detailed kinetic mechanisms. *Computer Physics Communications*, 192, 237-264.